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Preface: 69th DAE Solid State Physics Symposium

As the DAE Solid State Physics Symposium 2025 (DAE-SSPS 2025) reaches the 69th glorious year, its aim to reach out and gather the comprehensive set of national researchers working in all branches of condensed matter physics was successfully achieved during its organization at Indian Institute of Technology (IIT) Roorkee, Uttarakhand during December 19-23, 2025. DAE SSPS remains the most prestigious scientific event in this field, which was well reflected by receiving more than 800 manuscripts from researchers desirous to be part of this event. The symposium was organized by the Bhabha Atomic Research Centre (BARC), Mumbai, under the auspices of the Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy, Government of India.

The manuscripts were received under 11 categories covering a wide range of topics of current importance viz., phase transitions under high pressure and temperature, physics of soft matter including biological systems, nano-materials, physics of surfaces, interfaces and thin films, computational condensed matter physics, physics of functional materials including ferroelectrics, piezoelectrics, semiconductors and topological insulators, spintronic materials, materials for energy and environmental applications and quantum materials. Nearly 33 coordinators and around 431 reviewers from across the country were instrumental in completing the peer-review of these manuscripts and finally around 680 manuscripts were accepted for presentation. The best thesis and young achiever categories have also received significant response manifesting the impact of these events among the young scientific community of the country. Over 40 eminent scientists from India and abroad delivered plenary, special evening lectures and invited talks in this symposium. The event also served as an important platform to initiate possible collaborations as various young researchers and PhD students used this opportunity to interact with the experts and learnt the latest scientific advancements in the respective fields.

Among various interesting lectures, the inaugural, keynote and plenary lectures by eminent and accomplished researchers like Dr. S.L. Chaplot, former Director of Physics Group, BARC, Dr. Sakura Pascarelli, from the European XFEL, Prof. Olof Karis, Director of MAX-IV, Prof. Kalobaran Maity, Director Indian Association for Cultivation of Sciences Kolkata and Prof. Christian Bernahard from University of Fribourg, Switzerland, Prof. D. D. Sarma from Indian Institute of Sciences, Bengaluru, Prof. R. Vijayaraghavan from Tata Institute of Fundamental Research, Mumbai and Dr. S. K. Rai from Raja Ramanna Centre for Advanced Technology, Indore kept the participants captivated.

We extend our gratitude to the members of the advisory and organizing committees of DAE SSPS 2025 for their invaluable suggestions and assistance in organizing the symposium. Special acknowledgment is owed to Prof. K.K. Pant, Director, IIT Roorkee, for his enthusiastic support in hosting this event, making it a success. Our heartfelt appreciation also goes to the local organizing committee members spearheaded by the dynamic local convener Prof. Vivek Malik for their dedication, hardwork and support throughout the event. We express gratitude to manuscript reviewers, members of the YAA and Ph.D. thesis evaluation committees, as well as poster reviewers, for their meticulous evaluation and selection process.

Himal Bhatt, Niranjana S. Ramgir and D. Bhattacharyya
Bhabha Atomic Research Centre, Mumbai, India
(Guest Editors)

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Ga Doping Induced Tailoring of Electrical Properties in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Thin Films

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Abstract. The study investigates the current voltage (I-V) characteristics of as-deposited and annealed (160 °C and 260 °C) Ga-doped $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films, with a thickness of 200 nm. In comparison to the undoped GST thin film, Ga doping concentrations up to 10 % increased the current by two orders of magnitude. The current in the as-deposited and annealed (160 °C and 260 °C) Ga-GST thin film ranged from μA to mA , verifying the phase transition from amorphous to crystalline. For 10 % Ga-doped GST thin films, a reduction in electrical resistance by an order of tens was observed, thereby facilitating lower programming current requirements for memory applications. With annealing treatment Ga-doped GST thin films allow controlled tuning of charge transport, leading to reduced power consumption and improved suitability of doped composition for energy-efficient phase-change memories.

INTRODUCTION

Chalcogenide-based thin films have gained significant attention due to their versatile structural, optical, and electrical properties, making them suitable for various applications. Metal doping in chalcogenide thin films, particularly with elements like Bi, Sb, Ag, Sn, and Cu, has been shown to improve the properties, extending their potential in optoelectronic devices such as sensors, waveguides, and optical memories [1, 2]. Particularly in the domain of phase change materials (PCMs), the chalcogenide-based thin films gained immense interest due to their notable potential for data storage applications. The high contrast between the amorphous and the crystalline state, along with the rapid and reversible switching between these two phases, offers them the advantage to store and process data at a single unit, following the neuromorphic architecture. Additionally, the phase change memories hold their properties well at the nanoscale regime, paving a clear path for high-density recording at a compact level [3]. The ongoing quest to find a suitable composition for phase change memories is derived from the necessity of a material with enhanced properties like low writing current and good cyclability, along with longer data retention.

Mainly, Chalcogenide-based PCMs lying on the pseudo-binary tie-line of $\text{GeSb-Sb}_2\text{Te}_3$ exhibit rapid and reversible phase switching between highly stable amorphous and crystalline phases, showing significant phase contrast in electrical and optical properties. Furthermore, among the various existing compositions of GeSbTe , viz., $\text{Ge}_1\text{Sb}_2\text{Te}_4$, $\text{Ge}_1\text{Sb}_4\text{Te}_7$, and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST), the composition with stoichiometry of 2:2:5 exhibits a unique atomic arrangement in the amorphous phase [4, 5]. The presence of even folded ring structure along with wrong bonds like Ge-Ge and GeSb provides stability to the amorphous phase of the GST thin film. To improve the performance and commercial viability of GST thin films, various approaches have been used, including alloying, multilayer deposition along the pseudobinary tie-line, and elemental doping. These methods have been reported to increase the crystallisation speed, data storage density, and optical and electrical contrast between phases. Among the doped elements, Ga as a dopant has shown promise in stabilising the amorphous phase and reducing the writing current [6]. In the present work, undoped and Ga-doped GST thin films are investigated to study the effect of Ga doping on the electrical properties using a suitable characterisation technique.

EXPERIMENTAL DETAILS

The synthesis of Ga-doped GST thin films involved a two-step process: (i) bulk alloy preparation and (ii) thin film deposition. For bulk alloy preparation, the host elements Ge, Sb, and Te were weighed in a ratio of 2:2:5, with Ga as a doping element in concentrations of 3% and 10%. These constituent elements were sealed in quartz ampoules under

vacuum ($\sim 4 \times 10^{-6}$ mbar) and then heated in a rocking furnace for 24 hours, following the increasing order of their melting points. Ga-doped GST bulk alloys were prepared using the melt quenching technique. Thin films were then deposited from the powdered bulk composition using thermal evaporation with a Hind HIVAC system (Model: BC-300) under a vacuum pressure of 10^{-6} mbar. The film thickness was monitored *in-situ* during deposition and maintained at 200 nm. The electrical properties of these deposited $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ga}_x$ ($x = 0, 3, \text{ and } 10$) (Ga-GST) thin films were then measured using a KEYSIGHT B2912A source meter unit.

RESULTS AND DISCUSSION

The current-voltage (I-V) measurements of as-deposited and annealed (160 °C and 260 °C) Ga-GST thin films are shown in Fig. 1. The electrical measurements of these films have been performed at room temperature in planar geometry in the voltage range of -5 to +5 V with a step size of 0.01 V. The linear behaviour of the I-V curve suggests the ohmic nature of the as-deposited Ga-GST thin films, exhibiting current in the order of a few μA . Compared to undoped GST thin films, Ga doping leads to an increase in the value of current in the applied voltage range. The Ga doping of 10% in the GST thin film exhibits an increased current value by an order of tens in reference to the undoped GST thin film. This tailored electric behaviour indicates the generation of new charge carriers with increasing Ga doping concentration in GST thin films. Furthermore, the annealed (160 °C and 260 °C) thin films exhibit current in the range of mA , hence confirming the phase transition from amorphous to crystalline phase, as reported with other characterisation techniques in our previous study [6]. Due to the chaotic arrangement of atoms in the amorphous phase, the charge carriers find hindrance in their path to move freely, causing high resistance and low current. Whereas, in crystalline materials, the periodicity in the atomic arrangement leads to low resistance and high current [7].

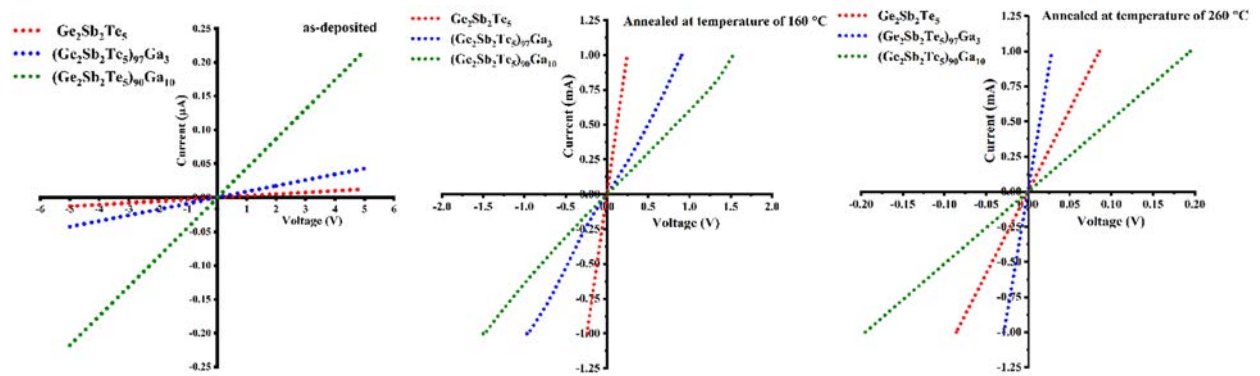


FIGURE 1. I-V measurements of as-deposited and vacuum annealed (160 °C and 260 °C) $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ga}_x$ ($x = 0, 3, \text{ and } 10$) thin films.

Figure 2(a) shows the plot of electrical resistance vs annealing temperatures (160 °C and 260 °C), showing an increase in the resistance value with an increase in Ga doping in GST thin films. This increase is expected due to the strong covalent bonding between newly formed Ga-Te, reducing the atomic diffusivity [6]. Furthermore, the Ga-GST thin films annealed at 260 °C display an irregular trend in the resistance value with a decrease of 3% and an increase of 10% of Ga doping. This unusual behaviour can be explained in terms of structural relaxation during annealing treatment, which will not induce any phase change [8]. For GST thin films with 10% of Ga doping, an increase in the resistance by an order of tens is observed. This increase is supposed to be due to the complete suppression of *hcp* phase along with thermal stabilisation of metastable *fcc* phase in $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{90}\text{Ga}_{10}$ thin film [6]. From Fig. 2(b), it is clear that the electrical resistance contrast of Ga-GST thin films at room temperature (30 °C) and annealing temperatures (160 °C and 260 °C) exhibits a sufficient resistance contrast of the order of 10^6 . Therefore, in reference to the undoped thin film, the 10% Ga doped GST thin film reduces the resistance contrast by a few orders of magnitude, hence helpful in reducing the writing current for memory applications.

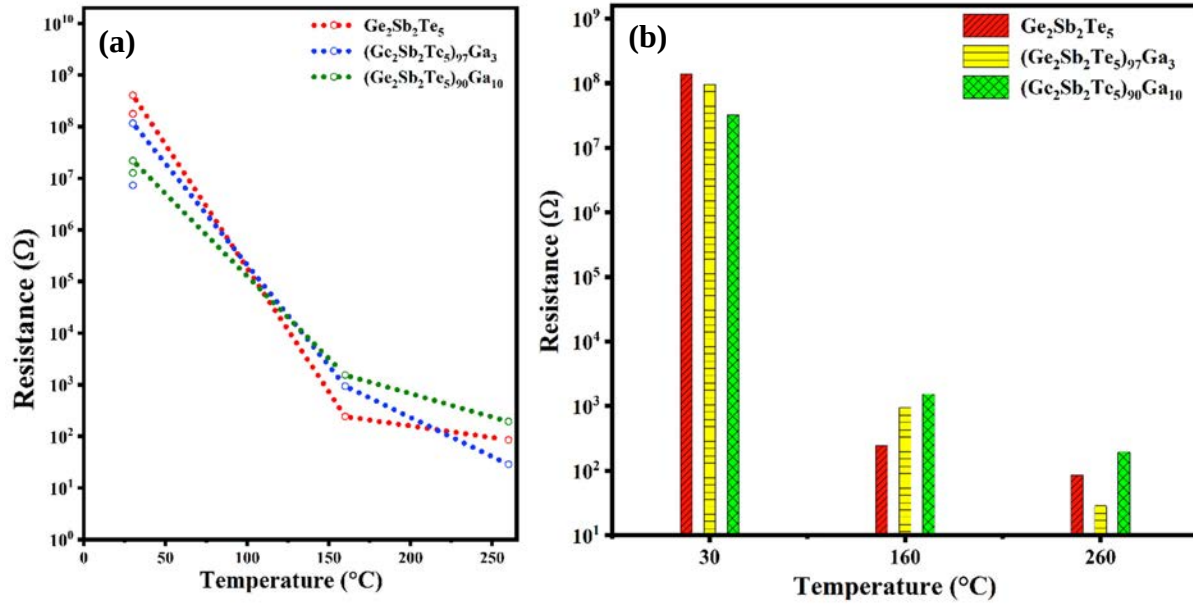


FIGURE 2. (a) Resistance vs annealing temperature (160 °C and 260 °C) study of $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ga}_x$ ($x = 0, 3$, and 10) thin films. (b) R-T measurements of as-deposited and vacuum annealed $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ga}_x$ ($x = 0, 3$, and 10) thin films.

CONCLUSION

In the present study, the as-deposited and vacuum annealed (160 °C and 260 °C) thin films of $(\text{Ge}_2\text{Sb}_2\text{Te}_5)_{100-x}\text{Ga}_x$ ($x = 0, 3$, and 10) (Ga-GST) have been investigated in terms of electrical properties. The study involves a comparative investigation of current-voltage (I-V) and resistance-temperature (R-T) characteristics of as-deposited and annealed (160 °C and 260 °C) Ga-GST thin films. Notably, the Ga doping of 10% in GST thin films reduced the electrical resistance contrast by the order of tens, hence helpful in reducing the switching time and power consumption during phase transition. In conclusion, Ga-GST thin films position themselves as promising contenders for phase change memories with enhanced properties like low power consumption, rapid switching speed, and better data retention.

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Theoretical Insights Into Phase Behavior of Surfactant-DNA Complexes Based On Lattice Electrostatics

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Abstract. We present a theoretical model to analyze phase stability in DNA-surfactant complexes via electrostatic energy calculations. By evaluating micelle-DNA and micelle- micelle interactions within square, hexagonal, and super-hexagonal lattices using linearized Poisson-Boltzmann theory, we predict stable structures under varying micelle sizes and ionic strengths. Our results explain experimental phase transitions observed in DTAB and MTAB systems, establishing a framework for rational design of polyelectrolyte-surfactant assemblies.

INTRODUCTION

The self-assembly of cationic surfactants and DNA results in ordered mesophases governed by electrostatics (1,2). Understanding these arrangements is vital for gene delivery and nanostructure fabrication. While SAXS and other techniques offer structural insights, a robust theoretical model is essential for explaining and predicting phase behavior (3,4).

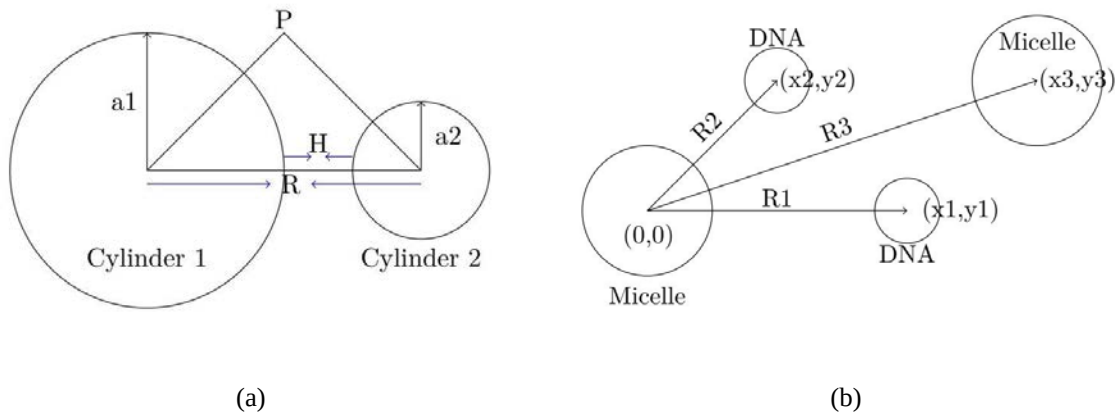


FIGURE 1. A system of two parallel dissimilar hard cylinders 1 and 2 of radii a_1 and a_2 . R is the center-to-center distance between two cylinders. $H (= R - a_1 - a_2)$ is the closest separation between two surfaces of two cylinders. (a), Center to center distances of micelle and DNA molecules from a micelle whose center is at the origin (b).

THEORETICAL MODEL

Lattice Framework: DNA is modeled as rigid negatively charged rods and surfactant micelles as cylindrical (**FIGURE 1.**) charged entities forming periodic 2D lattices (**FIGURE 2 (a)**). Three configurations are considered (1,2):

- **Square lattice:** alternating DNA and micelle columns.
- **Hexagonal lattice (Type I):** DNA at micelle interstitials.
- **Super-hexagonal (Type II):** intercalated DNA increasing repulsion.

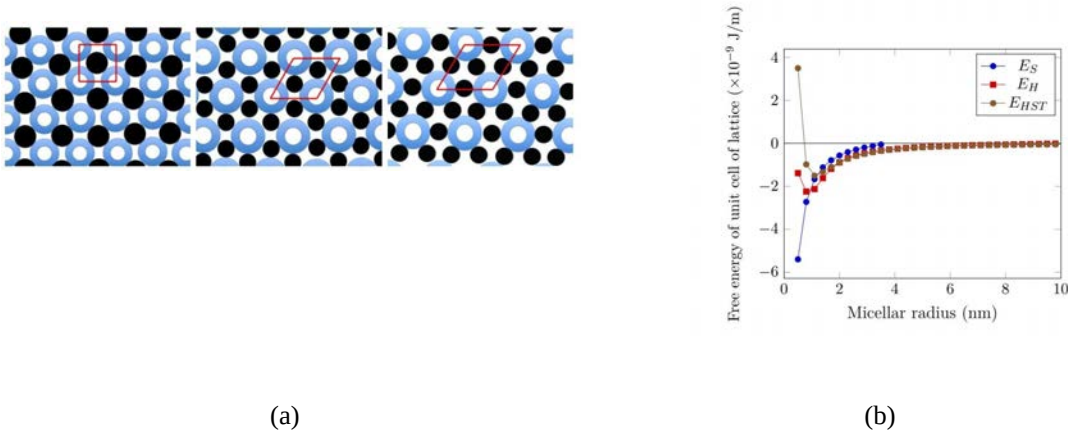


FIGURE 2. 2D lattice structures (a), Energy profiles of different lattice structures for $\kappa = 2 \text{ nm}^{-1}$ (b).

Electrostatic Interaction Energy: Electrostatic potentials between particles are derived under the Debye-Hu"ckel approximation (3):

$$V(r) = \frac{Z_1 Z_2 e^2}{\epsilon r} \exp(-\kappa r)$$

with Z_1, Z_2 as charge valencies, ϵ the dielectric constant, and κ^{-1} the Debye screening length. The energy contributions include (4): E_M : micelle with all other micelles and DNA molecules interaction (**FIGURE 1 (b)**) and E_D : DNA with all other micelles and DNA molecules interaction. Total lattice energies are:

$$E_{\text{square}} = E_M + E_D$$

$$E_{\text{hexagonal}} = E_M + 2E_D$$

$$E_{\text{super-hexagonal}} = E_M + 3E_D$$

RESULTS AND DISCUSSION

Micelle Radius Dependence: Energy profiles as a function of micelle radius (R) show (**FIGURE 2 (b)**):

- For **small micelles** (e.g., DTAB, $R \sim 0.9 \text{ nm}$): square lattice is most stable due to minimized repulsion.
- For **large micelles** (e.g., MTAB, $R \sim 1.3 \text{ nm}$): hexagonal lattice is energetically favored.
- At **intermediate radii** ($R \sim 1.1 \text{ nm}$): phase coexistence is likely.

Salt Concentration Effects: High salt concentrations reduce screening length, altering stability:

- At $\rho = 1$ with 300 mM NaCl: super-hexagonal lattice becomes favorable.
- At $\rho = 5$: square lattice is stabilized due to higher micelle population and reduced repulsion.

Hexagonal Lattice Subtypes: **Type I** hexagonal structure is stable over a wide radius range. **Type II** becomes unstable for small micelles due to strong DNA-DNA repulsion, restricting its occurrence to low screening regimes and large micelles (**FIGURE 2(a)**).

CONCLUSION

Electrostatic energy modeling successfully explains observed phase transitions in surfactant- DNA assemblies:

- Square lattice dominates for small micelles like DTAB.
- Hexagonal lattice is favorable for larger micelles like MTAB.
- Ionic strength modulates repulsion and lattice stability.
- A critical micelle radius around 1.1 nm marks a transition region.

These insights align with SAXS data and provide predictive power for designing DNA- based nanostructures.

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Finite-temperature STLS Study of Dynamical Dielectric Response of Warm-dense Electron Gas

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Abstract We present a comprehensive study of the dynamic dielectric function and plasmonic excitations in the warm-dense three-dimensional homogeneous electron gas (3DHEG) at the Fermi temperature, employing the finite-temperature extension of the Singwi-Tosi-Land-Sjölander (STLS) theory. Specifically, we compute the frequency and wavenumber dependent dielectric function $\epsilon(q, \omega)$ and the imaginary part of inverse dielectric function $\text{Im}[\epsilon^{-1}(q, \omega)]$, quantities directly relevant to X-ray Thomson scattering experiments. Particular emphasis is placed on analyzing the zeros of $\text{Re}[\epsilon(q, \omega)]$, which determine the plasmon dispersion and damping of electron gas. By comparison with the recent path-integral Monte Carlo (PIMC) simulations due to Dornheim *et al.*, we illustrate that in the weak coupling regime, the STLS quantitatively captures exchange-correlation effects via regenerating position and broadening of the PIMC plasmon peak, which are otherwise significantly overestimated by mean field approach Random Phase Approximation (RPA). With increasing coupling strength, the STLS continues to follow the plasmon flattening and enhanced damping, although its quantitative accuracy gradually diminishes. Our results establish the STLS approach as a reliable theoretical framework for modeling screening effects and collective excitations in 3DHEG, providing notable improvements over RPA.

INTRODUCTION

Over the past decade, warm dense matter (WDM) has attracted significant theoretical as well as experimental interest due to the coexistence of temperature, quantum, and correlation effects along with recent advances in laser fusion experiments. The WDM can be physically realized in astrophysical environments such as planetary interiors [1], and in laser fusion experiments [2]. A prerequisite model for studying the dynamic response of WDM is the finite-temperature 3DHEG, which captures essential many-body correlations without complications from ionic structure [3]. This model serves not only a starting point for exploring electron correlations, thermal effects, and excitations, but also act as a benchmark for first-principles simulations. The thermodynamic state of the warm dense uniform electron gas is characterized by two key dimensionless parameters: the density parameter $r_s = a_0^{-1}(3/4\pi n)^{1/3}$, which quantifies the average inter-electron spacing and the effective coulomb coupling, and the reduced temperature $\tau = k_B T / \epsilon_F$. Here, $\epsilon_F = \hbar^2 q_F^2 / 2m$ is the Fermi energy, and q_F is the Fermi wavenumber and a_0 is Bohr atomic radius.

A key quantity characterizing the density response of 3DHEG is the dynamic dielectric function $\epsilon(q, \omega)$, which provides direct access to density fluctuations and plays a crucial role in understanding dynamic screening and plasmons present in system. Recent developments in the PIMC techniques have provided benchmark simulation data for static and dynamic properties of the WDM [4,5]. In particular, Hamann *et al.* [6] have reported *ab initio* PIMC-based results for the dielectric function and plasmon dispersion of the warm-dense electron gas, revealing significant deviations from the RPA predictions and highlighting the importance of correlation effects in plasmon dispersion and damping. In this work, we employ the finite-temperature STLS [7] formalism to study the dynamic dielectric function $\epsilon(q, \omega)$ and plasmon excitations in the warm-dense 3DHEG at the Fermi temperature. By systematically comparing our results with the PIMC benchmarks [6] across weak-to-intermediate coupling regimes, we assess the accuracy of STLS in capturing the correlation-induced modifications to screening and collective excitations spectra.

THEORETICAL FORMALISM

To determine the dynamic dielectric function $\epsilon(q, \omega)$, we study the response of electron number density to an external space-time dependent electric potential $V_{ext}(r, t)$. In the linear response regime, the resulting change in electron density is characterized by the (linear) density-density response function, expressed as

$$\chi(q, \omega, T) = \frac{\chi_0(q, \omega, T)}{1 - V(q)[1 - G(q, T)]\chi_0(q, \omega, T)}, \quad (1)$$

where $\chi_0(q, \omega, T)$ represents the density response of non-interacting electrons, and $G(q, T)$ is the static local-field correction (LFC) factor, which incorporates exchange-correlation effects beyond the RPA. In STLS approach, the LFC is given by:

$$G(q, T) = -\frac{1}{n} \int \frac{dq'}{(2\pi)^3} \frac{q \cdot q' v(q')}{q^2 v(q)} [S(|\mathbf{q} - \mathbf{q}'|; T) - 1]. \quad (2)$$

The static structure factor $S(q; T)$ in Eq. (2) can be obtained using the fluctuation-dissipation theorem as

$$S(q; T) = -\frac{\hbar}{2\pi n} \int_{-\infty}^{\infty} d\omega \coth\left(\frac{\hbar\omega}{2k_B T}\right) \times \text{Im}\chi(q, \omega; T, \mu). \quad (3)$$

The set of equations (1), (2), and (3) constitute a self-contained system that can only be solved numerically in an iterative way. The iteration process continues until the static structure factor $S(q; T)$ achieves convergence within a tolerance of 10^{-6} for different r_s and τ at each wavenumber q . Further, the dynamic dielectric function $\varepsilon(q, \omega)$ can be obtained [8] from $\chi(q, \omega)$ as:

$$\varepsilon(q, \omega, T) = 1 - \frac{V(q)\chi_0(q, \omega, T)}{1 + V(q)G(q, T)\chi_0(q, \omega, T)}$$

The zeros of the dielectric function $\varepsilon(q, \omega)$ directly yield the plasmon dispersion relation.

RESULTS AND DISCUSSION

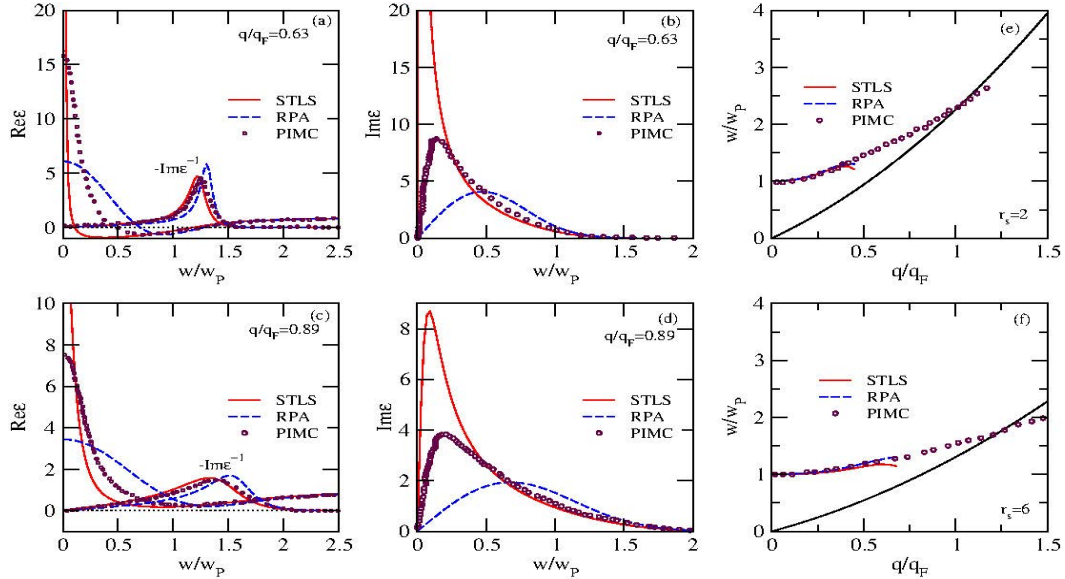


Figure 1. Frequency-dependence of the real (in panels (a) and (c)) and imaginary (in panels (b) and (d)) parts of dielectric function $\text{Re}\varepsilon(q, \omega)$ and $\text{Im}\varepsilon(q, \omega)$ at indicated wavenumbers for $r_s = 6$ and $\tau = 1$. Panels (e) and (f) show the plasmon dispersion for $r_s = 2, 6$ and $\tau = 1$. ω_p is the usual plasmon frequency. Symbols: PIMC simulation data, solid line: STLS, and dashed line: RPA.

The self-consistent results for the dielectric function and plasmon dispersion are plotted in Figure 1. Left (middle) panels show the real (imaginary) part of $\varepsilon(q, \omega)$ at two representative wavenumbers ($q = 0.63q_F$ and $0.89q_F$) for $r_s = 6$ (intermediate coupling regime) and $\tau = 1$. Here, the STLS approach qualitatively reproduces the PIMC dielectric function for both wavenumbers, while significant deviations can be seen in the RPA. Though not reported here, in the weak coupling regime (e.g. $r_s = 2$), the STLS accounts quite well both the peak location and width in close agreement with the PIMC data, where the RPA provides only a qualitative description. We have also shown in Figure 1 the results for the imaginary part of inverse dielectric function $\text{Im}[\varepsilon^{-1}(q, \omega)]$, a quantity which is a direct measure of the dynamic structure factor $S(q, \omega)$. It is important to note that for $q = 0.63q_F$ the peak in $\text{Im}[\varepsilon^{-1}(q, \omega)]$ coincides exactly with the zero-crossing of real and imaginary parts of $\varepsilon(q, \omega)$, indicating the existence of well-defined plasmons in this regime. Subsequently, with increasing q ($= 0.89q_F$), the peak broadens, indicating a damping of plasmonic excitation.

The corresponding dispersion of plasmons is plotted in panels (e) and (f) of Figure 1 for $r_s = 2$ and 6, respectively. It can be seen that at $r_s = 2$, the STLS results match closely with the PIMC data, whereas the RPA somewhat overestimates the plasmon energy at higher q due to the neglect of exchange-correlation effects. Further, at $r_s = 6$, the STLS still follow the qualitative trend in the PIMC study, showing the redshift and flattening of the plasmon dispersion due to stronger correlation effects, while the RPA continues to overestimate it. Beyond a critical wavenumber (say q_c), the equation $\text{Re}[\epsilon(q, \omega)] = 0$ no longer supports a numerical solution, which signifies the absence of well-defined plasmon. As the coupling parameter r_s increases from 2 to 6, the value of q_c increases, indicating that the plasmon mode remains undamped over a broader q -range at moderate coupling. This behaviour reflects that the enhanced correlation effects at larger r_s tend to stabilize the plasmon modes. However, both STLS and RPA approaches predict a smaller critical wavenumber q_c as compared to PIMC simulations, meaning that plasmons damp out earlier in these mean-field theories. This underestimation may stem from the static nature of local-field correction in the STLS approach, which is less accurate at capturing the correlation-induced stabilization compared to PIMC simulations.

SUMMARY AND CONCLUSIONS

In this work, we have investigated the dynamic dielectric function and plasmon excitations of the warm-dense 3DHEG at the Fermi temperature using the finite-temperature STLS approach. By comparing with an accurate benchmark provided by the recent PIMC data across coupling strengths $r_s = 2 - 6$, we find that the STLS qualitatively captures key correlation-driven features, including plasmon peak position, broadening, and damping, which are significantly misrepresented by the (lower-order) RPA. At weak coupling, STLS shows excellent agreement with the PIMC for both the dielectric function and plasmon dispersion. As the coupling increases, it captures the flattening of the plasmon dispersion curve quantitatively, except at large wavenumbers.

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Strength Properties of Tungsten Carbide (WC) Under Dynamic Loading

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Abstract: Planar dynamic loading experiments have been carried out on polycrystalline tungsten carbide in 63 mm bore Gas Gun facility to measure the Hugoniot data, Hugoniot Elastic Limit (HEL), dynamic yield strength and spall strength under high strain rates employing time resolved interferometry. The yield strength has been found to vary in the range 2.97-3.44 GPa for the peak shock pressure range of ~ 16 -18 GPa. However, the spall strength observed to lie between 1.47 to 1.62 GPa, indicating sensitivity towards the applied peak shock pressure. Both the yield strength and spall strength are found to be significantly higher than their quasi-static loading counterparts.

INTRODUCTION

Tungsten Carbide (WC) is a brittle ceramic material possessing high compressive strength (approximately three times stiffer than steel) and low tensile strength. WC comes in gray powder form which can be sintered to form solid metal piece with the help of cobalt binder. It finds wide use in metal cutting tools, ammunitions, drill bits, nuclear industries (good neutron reflector), and surgical instruments to name a few. Due to its exceptionally high hardness, resistance to wear properties as well as its thermal stability at elevated temperature, it is used in high-temperature high-pressure presses for synthesis of diamond and cubic boron nitride. Considering these wide range of applications involving quasi-static to high strain rate phenomena, it is worth to have knowledge of all aspects of strength properties of this ceramic under high pressures. In past Grady [1], through shock compression experiments on two types of liquid-phase sintered WC samples, derived equation of state (EOS) under shock loading, i.e., shock Hugoniot up to ~ 80 GPa and compared the data with that reported by McQueen et al. [2]. Subsequently, Dandekar and Grady [3] and McQueen *et al.* [2] have conducted shock study on hot pressed pure WC and with $\sim 5\%$ Co doped WC and found that the Hugoniot elastic limit (HEL) shows significant reduction from ~ 6 GPa for pure WC to ~ 4 GPa for Co doped WC. Recently, Wang *et al.* [4] carried out shock experiments on two different grades of WC with varied percentage of cobalt binder and reported that the HEL is lower for the sample with high Co concentration. Savinykh *et al.* [5] reported that the spark plasma sintered (SPS) WC samples display a strong attenuation in elastic precursor with the propagation distance. Additionally, they found that the HEL and spall strength (σ_s) of SPS WC is more than two-fold as compared to that of hot-pressed WC.

The present work focuses, to determine the HEL and spall strength for commercially available WC in low shock pressure regime (≤ 25 GPa) where data on the elastic-plastic response are limited.

EXPERIMENTAL METHODS

In each plate impact experiment conducted using 63 mm bore size single stage gas gun [6], a cemented WC disk was subjected to planar shock loading using symmetric planar impact conditions. The cemented WC circular disk procured from M/S Tungs Carbs India Pvt. Ltd., had density 14.92 ± 0.06 g/cm³ as compared to 15.66 g/cm³ of pure WC. The composition of WC samples was measured as 94.66% WC, 5.25% cobalt as binder and remaining other impurities. Prior to subjecting shock compression, the quasi-static measurements have been carried out in the sample,

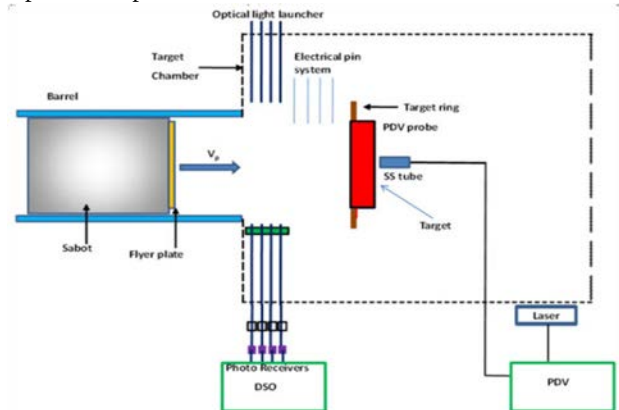


FIG 1: Schematic (not to scale) of target assembly of gas gun facility.

which include sound velocity measurements using pulse-echo ultrasonic method. The longitudinal and shear sound velocity (C_L and C_S) determined in the sample at ambient conditions was 6.89 km/s and 4.08 km/s, respectively and the bulk sound velocity and Poisson ratio derived from this were 5.03 km/s and 0.23, respectively. Figure 1 shows a schematic of the experimental setup along with diagnostics used to measure impact velocity and free surface velocity (FSV) history. The impactor and sample plate dimension used in symmetric and asymmetric impact experiments are displayed in Table 1.

RESULTS AND DISCUSSION

The FSV history of the WC target plate derived from time resolved Doppler shift measured using PDV interferometry [7] is displayed in Fig. 2 for all the three experiments. Profiles show steady structured shock comprising elastic rise followed by large post-yield hardening and sharp rise to final equilibrium Hugoniot state. After attaining HEL, a large ramp like inelastic region found which could be due to pressure hardening, increase of shear stress, deformation hardening or due to an increase of mean stress above that calculated by the compressibility of fully dense solid [3]. No elastic precursor decay observed after reaching the elastic limit. Under shock compressive stress brittle shear failure may occur in WC ceramics. Plasticity as well as shear fracture mechanism contribute to the inelastic shock deformation region in compression. Either all of these possible factors may be contributing significantly or any of these three may be dominant over others in present case. The shock pressures calculated from particle velocity (u_p) and shock velocity (U_s) derived from measured FSV, in conjunction with shock jump condition are plotted in Fig. 3 along with data from other sources [3-4]. It may be noted that the presence of elastic and plastic wave features on the FSV history utilized to derive the U_s in the material [8]. The present data are in line with those reported in literature in the low-pressure regime [1]. The FSV profiles have been utilized to derive the strength properties like HEL, yield strength and spall strength under high strain rate shock employing the recipe discussed elsewhere [9]. The HEL along with corresponding yield strength and the spall strength so obtained are plotted in Fig. 4 and listed in Table 2. The HEL with average value of 4.48 GPa remains more or less fixed in the strain rates of present study and lies reasonably close with other data [3-4]. The spall strength ranging from 1.47 GPa to 1.62 GPa is more than fourfold as compared to quasi-static UTS of 0.344 GPa [10]. It shows that the spall strength of WC ceramic is much less than its dynamic yield strength, which is expected [1,3,5].

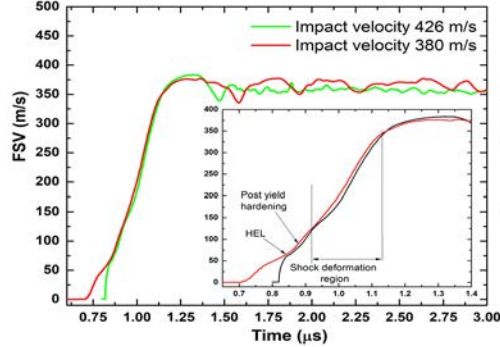


FIGURE 2: Free surface velocity history of three shock experiments.

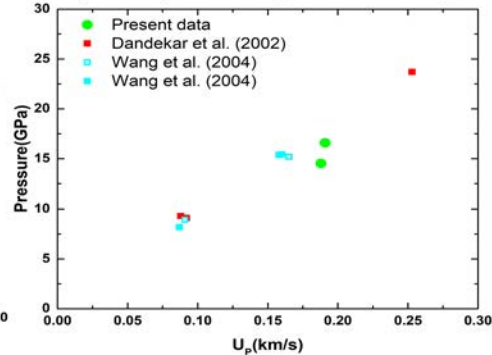


FIGURE 3: Hugoniot equation of state of WC in P - u_p plane.

TABLE 1: Shock wave experimental parameters for present experiments.

Shot no.	Flyer thickness (mm)	Sample thickness (mm)	Impact velocity V_i (km/s)	Peak FSV (km/s)	Particle velocity U_p (km/s)	Shock velocity U_s (km/s)	Stress P (GPa)
1	WC (2.01)	WC (2.00)	0.380	0.376	0.188	5.17	14.52
2	WC (2.49)	WC (2.66) +WC (5.16)	0.416	0.383	0.191	5.82	16.58

TABLE 2: Strength properties of WC measured from FSV profile of shock experiments. For shot no. 2 results of two PDV observations are kept.

Shot no.	Peak shock stress (GPa)	HEL (GPa)	Yield strength (GPa)	Strain rate at HEL $10^4(s^{-1})$	Spall strength (GPa)	Strain rate at spall $10^4(s^{-1})$
1	14.52	4.244	2.97	1.69	1.47	3.14
2	16.58	4.82	3.23	9.08	1.62	4.43

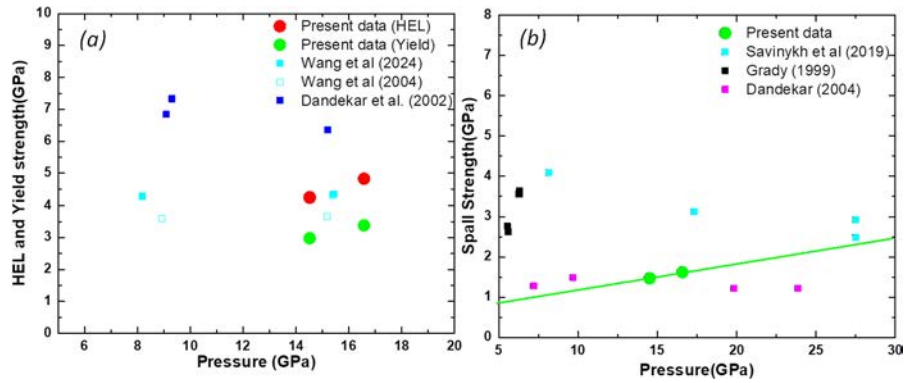


FIGURE 4: Variation of (a) HEL, dynamic yield strength (left graph) and (b) spall strength (right graph) in the elastic-plastic regime of Hugoniot as a function of pressure.

The ratio between HEL and spall strength sometimes related to brittleness of the material under shock loading [11]. So, to examine possible fracture mode of the WC samples in present experiments, we have plotted the ratio of spall strength to the HEL in Fig. 5 along with data for different alloys/compounds available in literature [11].

As may be noticed from figure, the ratio is more than 0.1 but smaller than 1 indicating, that the fracture behaviour of WC lies between brittle ceramics and pure metals.

To summarize, the HEL, yield strength and spall strength of WC has been determined from FSV profile recorded in planar shock loading experiment. The Yield strength has been found to increase manifold as compared to static value, however, it is found more or less fixed with pressure for present range of pressure. The spall strength which, is about four times the corresponding static loading counterpart; exhibits sensitivity towards peak shock pressure, unlike the yield strength.

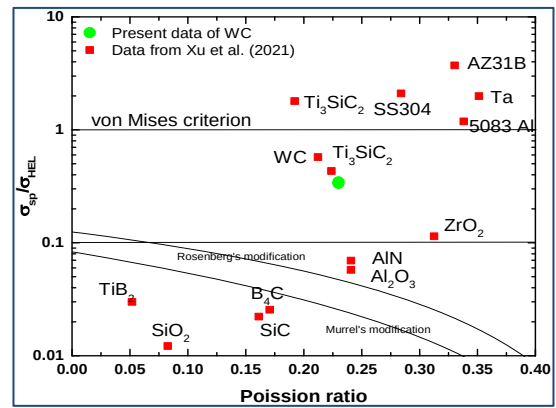


FIGURE 5: Comparison of ratio of spall strength to HEL for WC with other materials from available literature

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Cu at high pressure and high temperature: *Ab-initio* study

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Abstract. The structural stability of copper has been analyzed under high pressure and high temperature, employing density functional theory and density functional perturbation theory based calculations. Enthalpy calculations as a function of pressure at 0 K, do not show any possibility of the face-centered cubic (FCC) to body-centered cubic (BCC) phase transition up to 400 GPa, consistent with previous theoretical studies. However, introduction of thermal effects within quasi harmonic approximations, suggest that upon heating above 2500 K at ~ 200 GPa, the FCC phase will transform to BCC phase. Further, lattice dynamical study revealed that the dynamical stability of FCC Cu persists from 0 GPa to 200 GPa, whereas the BCC phase emerges as dynamically stable structure from 20 GPa to 400 GPa. The shock Hugoniot derived from theoretical calculations in conjunction with Rankine Hugoniot relation agrees well with the experimental data. Further, the P-T Hugoniot, indicates that the shock induced temperature rise could be one of the possible factors causing the experimentally observed FCC to BCC transition at ~ 180 GPa, under shock loading.

INTRODUCTION

The distinctive response of copper to high-pressure environments renders it a key material for exploring fundamental physical phenomena and advancing high-performance industrial technologies. At ambient temperature and pressure, copper adopts a face centred cubic (FCC) structure. In high-pressure research, copper serves as a widely accepted pressure calibration standard, primarily because of its simple electronic structure with a fully filled 3d shell and its remarkable stability in the FCC phase under extreme compression. The availability of accurate shock wave data makes copper an important material for pressure standards in the high-pressure community. Previous theoretical studies reported that copper remains stable in FCC phase up to ultrahigh pressures of ~ 100 TPa [1]. However, molecular dynamic (MD) simulations by Neogi and Mitra [2] predict FCC to body-centred tetragonal (BCT) transition at ~ 120 GPa, when Cu single crystal is shocked along $\langle 100 \rangle$ direction. Further, around the same pressure the FCC structure transforms to body centred orthorhombic phase when shocked along $\langle 110 \rangle$ direction [3]. A ramp compression experimental work, published in recent past, reported the FCC phase to exist even up to 1.15 TPa [3], in line with the predictions of Greeff *et al.* [1]. However, more recent shock compression experiments report that FCC structure transforms to BCC phase at approximately 180 GPa [4].

The differing outcomes of various theoretical and experimental studies prompt us to re-visit the problem of structural stability of copper under high pressure-high temperature conditions. In this context, it may be noted that most of the previous theoretical investigations have been conducted at 0 K, leaving possibility open for the thermodynamic stability of BCC phase in copper at elevated pressures and temperatures. Present work, therefore, examines the structural and lattice dynamic stability of copper under high pressure and high temperature, employing density functional theory (DFT) and density functional perturbation theory (DFPT) based calculations. The DFPT calculations have been carried out within quasi harmonic approximation (QHA).

THEORETICAL METHOD

All calculations have been performed using the plane-wave pseudopotential method as implemented in the Quantum ESPRESSO package [5]. The structural stability analysis has been performed through static lattice calculations within the framework of the generalized gradient approximation. The electronic wave functions have been expanded in a plane-wave basis set with an energy cutoff of 100 Ry, while the charge density has been represented using plane waves with an energy cutoff of 500 Ry. The Brillouin zone sampling has been carried out using a $16 \times 16 \times 16$ k-point mesh. The dynamic stability of the FCC and BCC phases at a given pressure has been investigated by analyzing the phonon spectra obtained from lattice dynamical calculations. These calculations have

been performed within DFPT framework, employing a $4 \times 4 \times 4$ q-point grid for FCC and a $2 \times 2 \times 2$ q-point grid for BCC, for Brillouin zone integrations. Further, the finite-temperature effects at a given pressure have been incorporated using phonon spectra derived from DFPT calculations within QHA [6]. The mechanical stability of FCC and BCC phases at a given pressure has been investigated by analyzing the elastic constants. Elastic constants calculations have been performed using ElaStic Tool [7].

RESULT AND DISCUSSION

The structural stability of the FCC and BCC phase of Cu under hydrostatic compression has been analyzed by calculating the total energy (E) as a function of unit cell volume (V). The pressure-volume (P - V) data, derived from E - V relation, has been subsequently used to compute the enthalpies of the FCC and BCC phases at various pressures and a comparison of the same for both the phases has been made (Fig. 1(a)). As evident from the figure, FCC remains stable upto 400 GPa, in line with previous theoretical results [1]. The equation of state (EOS) derived from E - V data (Fig. 1(b)) exhibits good agreement with the available experimental data [8]. The zero-pressure equilibrium volume, bulk modulus and its pressure derivative, calculated from EOS are presented in Table 1.

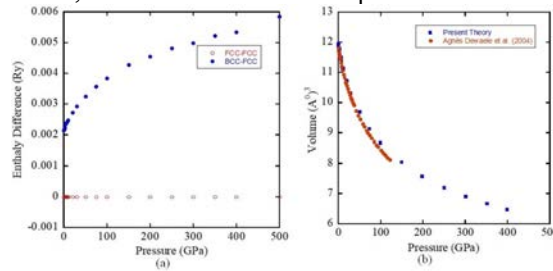


FIGURE 1 (a) Enthalpy difference of BCC phase with respect to FCC phase as a function of pressure. (b) The equation of state of copper at 0 K along with experimental data [8].

To investigate the dynamical stability of the FCC and BCC phases, phonon calculations have been performed using DFPT. As displayed in Fig. 2(a), at 0 GPa, the phonon frequencies of FCC phase exhibit excellent agreement with experimental data [9], confirming its dynamical stability at ambient condition. Also, it may be noted (Fig. 2(a)) that it remains dynamically stable even at 200 GPa. The phonon spectra for the BCC phase at different pressures up to 30 GPa are shown in Fig. 2(b), while those at still higher pressures of 200 and 400 GPa are shown in Fig. 2(c). In contrast, the BCC phase at 0 GPa shows imaginary phonon frequencies, indicating dynamical instability of this phase at ambient condition. But above 20 GPa, all phonon frequencies of the BCC phase become positive, signifying the onset of dynamical stability and this stability persists upto 400 GPa. The elastic constants calculated for both the FCC and BCC phases are listed in Table 1 along with available experimental data [10] and their pressure variation for BCC phase is plotted in Fig. 2 (d). The theoretically derived zero pressure elastic constants for FCC phase agree reasonably with experimental data [10]. For BCC phase, the $C_{11} < C_{12}$ up to 15 GPa (Fig. 2(d)), resulting into negative shear modulus $(C_{11}-C_{12})/2$ and thus, mechanical instability up to this pressure.

TABLE 1. Properties of FCC and BCC phase calculated in this work along with the experimental data at zero pressure

Properties	$V_0 (\text{\AA}^3)$	B_0 (GPa)	B_0'	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
FCC-Theory	11.95	144.11	4.82	183.2	131.0	81.5
Experiment	11.81[8]	135.1[8]	4.91[8]	176.2 [10]	124.9 [10]	81.8 [10]
BCC-Theory	11.99	151.26	4.56	143.0	147.9	116.3

Further, to understand the effect of temperature on structural stability under pressure, we have calculated the Gibbs free energy as a function of temperature at a fixed pressure of 200 GPa for both the FCC and BCC phase. The Gibbs free energy of the two phases as a function of temperature at 200 GPa is shown in Fig. 3(a). As may be observed, the Gibbs free energy of BCC phase becomes lower than that of FCC phase beyond ~ 2500 K, indicating the possibility of FCC to BCC transition at ≥ 200 GPa upon heating up to ≥ 2500 K.

In order to explore, whether the shock induced FCC to BCC transition reported experimentally [4] is driven by temperature, we have calculated the shock Hugoniot using the thermodynamic data obtained from QHA calculations, combined with the Rankine–Hugoniot energy conservation relation. The shock Hugoniot in P - U_p plane (U_p being material speed behind the shock) shown in fig. 3(b) display a good agreement with the experimental data [11, 12].

Fig. 3(c), displays shock induced temperature rise as a function of Hugoniot pressure, i.e., in P-T plane, along with the experimental data available from Ref 4.

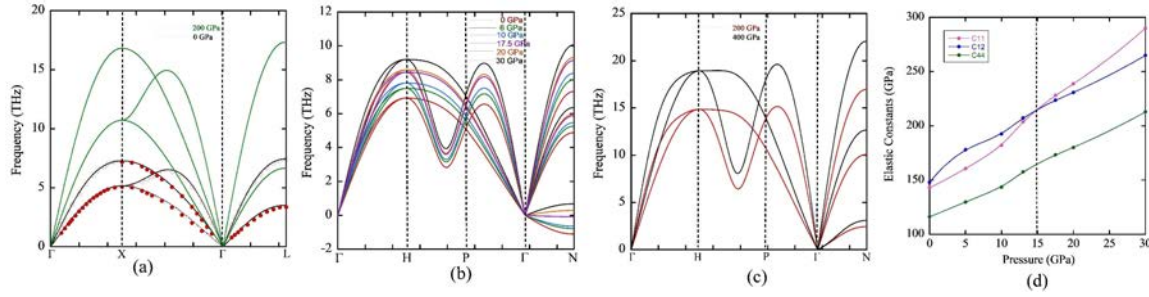


FIGURE 2. The phonon dispersions (a) for FCC phase at 0 GPa and 200 GPa along with experimental data [9], (b) and (c) for BCC phase up to 30 GPa and at 200 and 400 GPa, (d) Elastic constants of BCC phase as a function of pressure up to 30 GPa.

The theoretical P-T curve displays good agreement with the experimental data at least up to ~ 140 GPa, while it deviates systematically from experimental data beyond this pressure. This deviation could be due to the overestimation of thermal component within QHA. It may be noticed that at ~ 200 GPa, the material is heated to ~ 4800 K by shock, which is well beyond 2500 K, indicating that the temperature could be one of the possible factors inducing the experimentally observed FCC to BCC transition under shock compression [4].

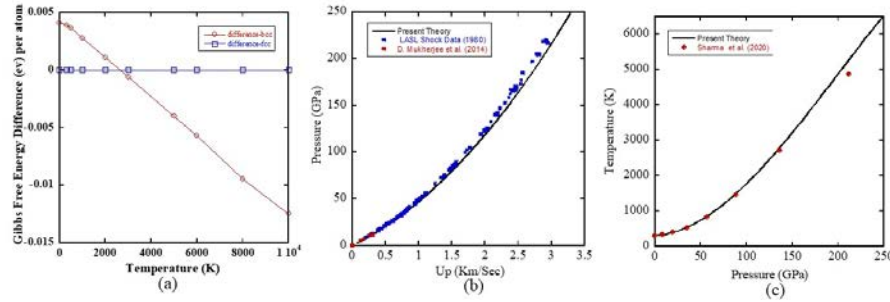


FIGURE 3. (a) Gibbs free energy difference of BCC phase with respect to FCC phase at 200 GPa as a function of temperature.

(b) The Hugoniot curve of Cu along with experimental data [11, 12]. (c) P-T plane of shock Hugoniot with experimental data [4].

To summarize, our theoretical calculations do not suggest FCC to BCC phase transition up to 400 GPa at 0 K, in line with previous works [1]. However, upon adding thermal effects at 200 GPa, the FCC $\rightarrow$ BCC transition occurs for temperatures ≥ 2500 K. The ground state properties and EOS compare well with the existing experimental data [8, 10]. The theoretically derived Hugoniot agrees well with the experimental data [4, 11, 12]. The P-T Hugoniot, indicates that the shock induced temperature rise could be one of the possible factors causing the experimentally observed FCC to BCC transition at ~ 180 GPa, under shock loading.

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Structural Stability of α -WP₂ at High Pressure

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Abstract. The high-pressure behavior of α -WP₂ has been investigated up to 39 GPa, revealing that it remains structurally stable and is significantly less compressible than WP and β -WP₂. The compound exhibits anisotropic lattice compressibility, with the highest compressibility observed along the *b*-axis, and comparable compressibility along the *a*- and *c*-axis. This anisotropy is likely linked to the presence of covalent P–P bonds along the *a*-axis and metallic W–W interactions along the *b*-axis. The bulk modulus of α -WP₂ is estimated to be 278(20) GPa. Further investigation into the bonding nature within and between the WP₅ polyhedra is essential to fully understand the mechanical response of this material under pressure.

INTRODUCTION:

The binary phase diagram of tungsten-phosphorus (W–P) hosts two stable stoichiometries—WP and WP₂. WP crystallizes in an orthorhombic structure (space group *Pnma*) under ambient conditions and exhibits superconductivity with a transition temperature (*T_c*) of 0.8 K [1]. WP₂, on the other hand, exists in two polymorphic forms at ambient pressure—designated as α -WP₂ (monoclinic, *C2/m*) and β -WP₂ (orthorhombic, *Cmc2₁*) [2]. Recent studies exploring the physical and chemical properties of these compounds have revealed several intriguing phenomena and potential applications, thereby intensifying research interest in this system [3–5]. The β -phase of WP₂ has been experimentally confirmed to be a Weyl semimetal due to the absence of inversion symmetry, whereas the α -phase, possessing both time-reversal and inversion symmetry, is topologically trivial [5]. Notably, both phases exhibit extremely large magnetoresistance (XMR) despite being non-magnetic, placing them among a rare class of XMR materials [4–6]. Furthermore, tungsten phosphides have shown promise as efficient, non-noble metal based electro-catalysts for the hydrogen evolution reaction, with α -WP₂ demonstrating the highest catalytic performance [2, 7]. Given these multifaceted properties, there is a growing interest in understanding the behavior of these materials under extreme conditions [8]. For topological WP₂ i.e., β phase, anisotropic resistivity below 100 K [8], and strain-induced modulation of carrier density [10] have been reported. β -WP₂ remains structurally stable up to 50 GPa with a bulk modulus of 230(4) GPa with indication of Lifshitz transition above 20 GPa [3]. Mechanical properties of WP is reported to improve with high pressure and shows high incompressibility with bulk modulus in range of 230–238 GPa [9]. In this manuscript, we explore the behaviour of α -WP₂ phase under high pressure up to 39 GPa.

MATERIALS AND METHOD

For synthesis of WP₂, 3 g of WO₃ (sigma Aldrich, 99.995%) and 1.8 g of stabilized red P (Spectrochem, 99%) powders were mixed thoroughly with grinding. Four pellets were prepared from the mixed powder. The pellets were vacuum sealed inside a quartz tube. The temperature was ramped up from 28 to 300 °C in 15 minutes, followed by further ramping to reaction temperatures of 750, 800, 850 and 950 °C for the individual pellets in 90 minutes. The reaction temperature was maintained for 8 hours and then they were cooled naturally to room temperature. The synthesized samples were characterized using powder X-ray diffraction.

High pressure X-ray diffraction (HP XRD) experiments were carried out at BL-11, Indus-2, RRCAT, Indore, India using a Mao-Bell type diamond anvil cell (DAC) with $\lambda = 0.7388$ Å. The Debye-scherrer rings were collected on a mar-345 image plate detector and converted to intensity vs. 2θ pattern using fit2D software [11]. Rietveld

refinement was carried out using FullProf Suite [12]. The structures were visualized using VESTA[13]. Preliminary phase identification was done using PCW [14].

RESULTS AND DISCUSSION

The ambient XRD results revealed that reaction temperature of 800 and 850 °C led to mixed phases whereas 750 and 950 °C yielded monoclinic and orthorhombic phases, respectively. As we focus on exploring the behaviour of the monoclinic phase i.e., α -WP₂, its Rietveld refined ambient XRD pattern (0.732 Å) is presented in Fig.1. Crystal structure was determined to be monoclinic with $a=8.5039(7)$ Å, $b=3.1712(2)$ Å, $c=7.4570(6)$ Å, $\beta = 119.338(6)^\circ$, and $V = 175.321(27)$ Å³ which is in good agreement with ICDD PDF no. 04-004-6770. In the unit cell, longer W-W bonds are present along b -axis (Fig.2a) and the P-P covalent bond are predominantly oriented along a with a small angle with the axis (Fig.2b). The WP₅ polyhedra as shown in Fig. 2c, run as chain along b axis and are packed by edge-sharing along c axis.

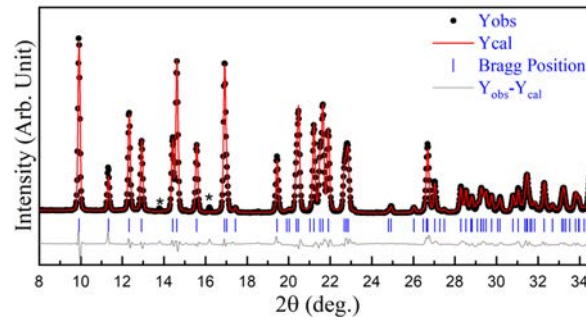


FIGURE 1: Ambient XRD pattern of α -WP₂ adopting monoclinic phase

HP XRD patterns are presented in Fig. 3a, indicating no structural transition up to 39 GPa. The pressure evolution of normalized volume and lattice parameters are presented in Fig. 3b and 3c respectively. The bulk modulus (B_0) and its pressure derivative (B'_0) were estimated to be 278(20) GPa and 4.4(1.6) respectively by fitting the P-V data to third order Birch-Murnaghan equation [15]. This suggests that α -WP₂ is less compressible as compared to β -WP₂ and WP [3, 9]. Both WP and β -WP₂ are known to show good refractory properties [16]. In this line, α -WP₂ may exhibit superior refractory properties.

The lattice compressibility was observed to be anisotropic as presented in Fig. 3c. The unit cell shows highest compressibility along b axis and comparable compressibility along a and c axes. This is in contrast to the behaviour β -WP₂ wherein the b axis is least compressible, signifying the distinct structural behaviour of the two polymorphs. Low compressibility along a could be because of the presence of P-P covalent bond along the a -axis. Despite the presence of polyhedra chain along b , the presence of metallic W-W chain could result in higher compressibility along b -axis. However, understanding this anisotropic compressibility requires further analysis of bond strength and bond nature using density functional theory.

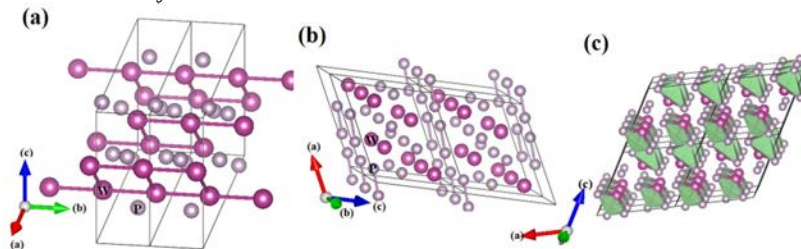


FIGURE 2: Alignment of (a) W-W bonds, (b) P-P covalent bonds, (c) polyhedra chain along b axis and edge shared packing along c axis

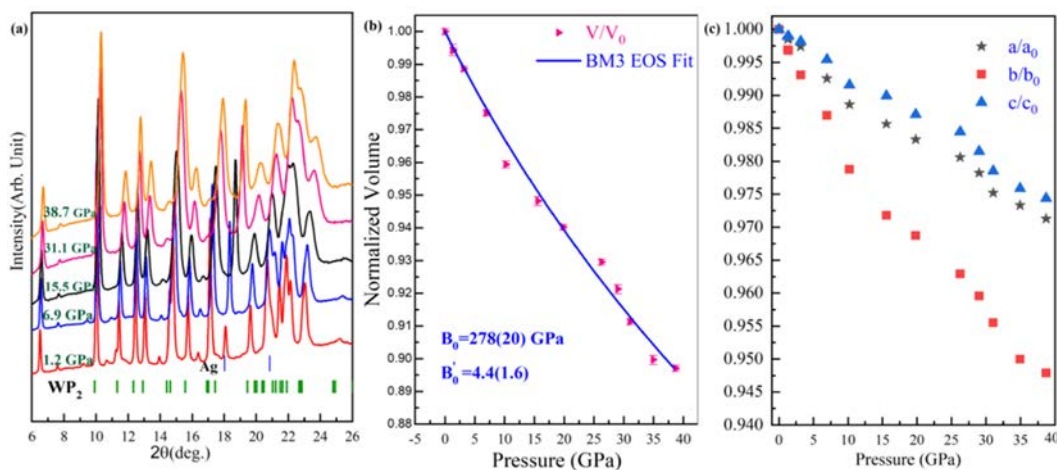


FIGURE 3: (a) HP XRD patterns of α -WP₂ showing structural stability, (b) pressure evolution of volume, (c) lattice evolution with pressure

SUMMARY

α -WP₂ is structurally stable up to 39 GPa and less compressible than WP and β -WP₂. The lattice compressibility is anisotropic with highest compressibility along b and comparable compressibility along a and c axes. This could be because of presence of covalent P-P and metallic W-W bonds along a and b respectively. Understanding the nature of bonds within and between the WP₅ polyhedra is required to further understand this pressure response.

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Implications of Short-Range Structural Correlations Of Pb^{2+} In Network-Forming Properties Of Lead-Borate Glasses: An EXAFS study

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Abstract. Borate glasses exhibit unique behaviour known as borate anomaly where there is an inflation of properties around some intermediate composition of added network modifier. This is due to change in local co-ordination of the boron atom from BO_3 to BO_4 , when the modifier is added to the system. In the present system of lead-borate glasses, PbO is the modifier oxide. As the local coordination and structure around the network forming cation, boron, is already well-reported, the atomic scale structure around the modifier cation, Pb, has been studied using x-ray absorption spectroscopy in this work. Herein, we report the Pb L₃-edge extended x-ray absorption fine structure (EXAFS) results to determine the local coordination environment of Pb ions in three $x\text{PbO}:(1-x)\text{B}_2\text{O}_3$ glasses with x being 20, 40 and 80 mol%. A single shell fitting of EXAFS spectra of the glasses showed that lead is octahedrally co-ordinated to oxygen when PbO concentration is 20% while it is tetrahedrally co-ordinated when the concentration of PbO was 80%. The co-ordination number varied from 6.2 to 4.0 when PbO concentration varied from 20-80%. EXAFS studies helped in delineating the optimum concentration at which the local co-ordination change occurs and lead oxide manifests as a network former.

INTRODUCTION

Lead-borate glasses have found adequate use as transparent shielding materials for gamma and neutrons in nuclear industry. Undoped borate glass has a layered structure of boroxol (B_3O_6) rings where each boron atom is three-coordinated (BO_3). However, when modifier oxides are included in the glass system, an inflation of properties is known to occur around some intermediate composition of modifier used for doping. This unique behaviour known as borate anomaly takes place due to the changes in local co-ordination of boron when the modifier is added to the system. Some boron atoms change from BO_3 to BO_4 configuration which converts the otherwise planar structured glass to three-dimensional, thereby manifesting as the borate anomaly. Such rich dynamics and structure of borate glasses has invoked great interest owing to the variety of structural changes in these systems with the type and composition of modifier cations [1,2].

Lead is known for its various structural roles in glasses depending upon the glass-forming systems and their compositions. Structural roles of Pb in $\text{PbO}:\text{B}_2\text{O}_3$ glasses are particularly interesting since Pb is not considered to be a conventional glass-former. Previous studies suggest that Pb is a network former, a charge compensator and also a network modifier [3]. Network-forming properties of lead are through the formation of PbO_3 and (or) PbO_4 polyhedra. Polarizability of Pb^{2+} also contributes to network formation by allowing changes in the polyhedral angles.

Structural studies of glasses predominantly intend to establish relations between their observed properties corresponding to their short (1.5-3 Å) range orders. X-ray absorption fine structure (XAFS) spectroscopy is atomic-species selective and does not require the existence of long range order. It is therefore, widely used to characterize the short-range structural order of glassy materials [4,5]. The technique has become increasingly popular owing to the availability of intense synchrotron beamline facilities. For the present lead-borate glass systems, the local structure

around the network-forming cation, boron, has been extensively studied in the literature [1]. However, the structure around the modifier cation and its effect on the glass network structure has not been studied in detail. In this work, we explore the effect of lead-modification on the local structure and glass network formation in a set of lead-borate glasses using x-ray absorption spectroscopy of the Pb edge.

EXPERIMENTAL

Extended X-ray Absorption Fine Structure (EXAFS) technique has been used to investigate the local structure of Pb ions in three $x\text{PbO}:(1-x)\text{B}_2\text{O}_3$ glasses [3] with x being 20, 40 and 80 mol%. The experiments were performed at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. Energy-scanning EXAFS beamline (BL-9) was used in 4–25 keV energy range. Indus-2 Synchrotron Source (2.5 GeV, 100 mA) was used in the transmission mode. The data collection was performed using ionization chambers which measure the incident flux (I_0), transmitted flux (I_T) and the x-ray absorption spectrum of a reference metal foil for energy calibration.

The absorption coefficient (μ) is calculated using, $I_T = I_0 e^{-\mu x}$ where, x denotes absorber thickness. Oscillations $[\mu(E)]$ in the absorption spectra were converted to absorption function $[\chi(E)]$ using $\chi(E) = [\mu(E) - \mu_0(E)] / \Delta\mu_0(E_0)$, where, E_0 is the absorption edge energy, $\mu_0(E)$ is the background due to the bare atom and $\Delta\mu_0(E_0)$ is the change in $\mu(E)$ value at the absorption edge. The above relation is known to yield a qualitative information regarding the local structure of the system.

The conversion of energy dependent absorption coefficient $\chi(E)$ to the wave number dependent absorption coefficient $\chi(k)$ is performed by the equation, $K = \sqrt{2m(E - E_0)/(h/2\pi)^2}$, where, m denotes electron mass. $\chi(k)$ multiplied by k^2 enhances the oscillations at high k and the $\chi(k)k^2$ functions are Fourier transformed in R space to create the $\chi(R)$ versus R spectra in real space distances from the centre of the absorbing atom. Demeter software package with set of EXAFS data analysis program comprising background reduction and Fourier transform have been used to obtain the $\chi(R)$ versus R spectra from the absorption spectra (using ATHENA software). Production of theoretical EXAFS spectra starting from an assumed crystallographic structure and final fitting of experimental data with the theoretical spectra using ARTEMIS software were used for the analysis.

RESULTS AND DISCUSSION

The normalised Pb L_{3} -edge extended x-ray absorption fine structure (EXAFS) spectroscopy has been used to determine the coordination environment of Pb ions in three $x\text{PbO}:(1-x)\text{B}_2\text{O}_3$ glasses with x being 20, 40 and 80 mol% as depicted in Fig. 1 (a). The reference compounds are tetragonal litharge (α -PbO), where Pb is in tetrahedral environment and red lead Pb_3O_4 where Pb is in octahedral environment, respectively. $\chi(R)$ versus R plots at Pb L_{3} -edge are generated by Fourier transform of $k^2\chi(K)$ vs. k spectra following the methodology described in the experimental section and the corresponding plots are shown in Fig. 1 (b). The EXAFS data of all samples have been fitted in the range of 0–3.0 Å in R space. The scattering paths have been generated from the lead oxide crystal structure. The EXAFS fitting show decrease in average coordination number around Pb corresponding to the Pb-O coordination shell when there is an increase in Pb concentration from 20 to 80 mol %. The average coordination number was estimated and was found to be varying between 6.26 to 4.0 for the PbO increase from 20 mol% upto 80 mol%. We suggest that such reduction in coordination number indicates lead in these high-PbO glasses mainly acts as a network-former. At lower concentrations, Pb introduces more non-bridging oxygens in the structure and makes the glass polymerised. However, when molar concentration of PbO increases upto 80 mol%, it is a predominantly lead glass rather than a borate glass. This change in composition modifies the lead polyhedral structure and hence the network of Pb-O-Pb in the matrix. As coordination number reduces, the role of lead changes to a network former and helps maintain the glassy state. Hence, Pb changes its role from being a network modifier at lower concentrations from being a network former at higher concentrations. In short, we report the significant role played by Pb in determining the network structure as the composition of PbO is varied in the glass matrix.

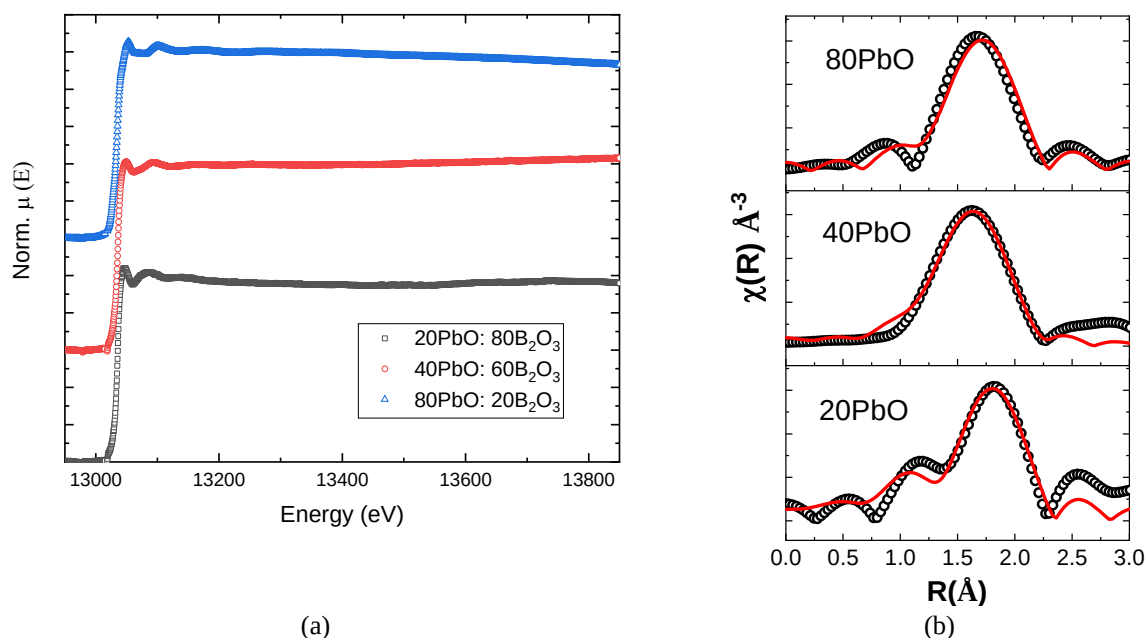


FIGURE 1. (a) Normalised XAFS spectra and (b) Fourier transformed XAFS spectra of lead-borate glasses studied in the present work. In (b), the experimental spectra are represented by scatter points and the theoretical fits are represented by solid lines.

CONCLUSIONS

The coordination number of the Pb-O correlations were investigated by XAFS measurements to study the modification of the short-range structure in lead borate glasses. It is found that composition dependence of the short-range structure was varied due to PbO modification in the lead borate glass system. A single-shell fitting on Pb L₃-edge EXAFS spectra of these three PbO:B₂O₃ glasses show that the average oxygen coordination numbers around lead vary in the range of 6.26 to 4.0. This marked change in local environment is responsible for transforming modifier properties of Pb to that of a network-former for the high lead glasses.

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Atomistic study of shock induced phase transformations and Hugoniot elastic limit (HEL) in single crystal copper

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Abstract. Large-scale nonequilibrium molecular dynamics (NEMD) simulations, employing a realistic embedded-atom-method (EAM) potential, are used to investigate the response of bulk single-crystal Cu subjected to shock loading in different crystal orientation with piston velocities ranging from 250 m/s to 3000 m/s. Our NEMD simulation reports the FCC–BCC phase transition in Cu single crystal to occur at pressures ≥ 126 GPa, when loaded along $\langle 100 \rangle$ direction and at pressures ≥ 185 GPa upon loading along $\langle 110 \rangle$ direction. The same transition is reported experimentally to happen at 180 GPa in polycrystalline sample. The Hugoniot elastic limit (HEL) and its dependence on relevant physical parameters (length and time scale) are also determined.

INTRODUCTION

Because of the vast applications and importance, copper and its alloys have attracted numerous experimental and theoretical investigations [1-5]. According to a high-pressure investigation carried out through electronic structure calculations, Cu is reported to remain stable in face-centered-cubic (FCC) phase upto ultrahigh pressures of 100 TPa [5], which, latter is substantiated by experimental work conducted in diamond-anvil-cell up to 150 GPa [6]. However, *ab-initio* and classical MD based simulations published in recent past [7] predict FCC to body-centred tetragonal and body centred orthorhombic transition upon shock loading along $\langle 100 \rangle$ direction and $\langle 110 \rangle$ direction, respectively. Subsequently, ramp compression experiments using OMEGA laser facilities claimed to have observed the FCC phase to exist even up to 1.15 TPa [8], further strengthening the predictions of Greeff *et al.* [5]. In contrast to previous studies, in a recent, in-situ x-ray diffraction measurements carried out in shock loaded samples of polycrystalline Cu, a FCC–BCC phase transition is reported to have been observed at ~ 180 GPa [9], prompting to revisit the high pressure investigations resorting both the, experimental and theoretical tools. Though, more recently, sound speed measurements under shock loading in Cu have been reported up to 190 GPa but no mention of any phase transition has been given [10]. As far as strength properties of copper under high strain rates are concerned, many experimental studies have been reported in past with strain rates varying from $10^3/s$ to $10^8/s$ [11-15]. The strain rates up to $10^7/s$ have been achieved in samples of bulk thickness (a few mm) using gas guns or explosive methods [11-14] with measured spall strengths in the range 1-3 GPa, whereas, these in thin samples of $\sim 10 \mu\text{m}$ thickness have been reached to ultra-high values $\sim 10^8/s$ with spall strength of ~ 15 GPa [15]. In view of above-mentioned studies, we have revisited the problem on structural stability of single crystal Cu under shock loading employing the molecular dynamics (MD) simulations as a tool. In order to understand the mechanism of elastic precursor decay, the influence of various physical parameters—such as sample length and lateral dimensions is systematically investigated as a function of increasing shock strength. The present study successfully bridges the gap across length scales ranging from submicron to millimeter and strain rates spanning from 10^4 to 10^{10} s^{-1} .

THEORETICAL METHOD

The embedded-atom method (EAM) potential for copper, as developed by Mishin *et al.*, [16] is employed for the molecular dynamics (MD) simulations. All simulations are carried out using the LAMMPS framework [17]. For nonequilibrium molecular dynamics (NEMD) simulation of shock propagation in Cu single-crystal, atomic system (simulation box) containing ~ 1.6 billion atoms and having approximate dimension of $36.1 \text{ nm} \times 36.1 \text{ nm} \times 722 \text{ nm}$ in the x, y and z directions, respectively, has been constructed. While periodic boundary conditions are applied in the transverse directions, a free boundary condition is imposed along the shock propagation direction (z-axis). Prior to the shock simulations, the system is equilibrated at 300 K and zero pressure for 30 ps using the NPT ensemble. A time

step of 1 fs is employed throughout the simulations. Starting few-unit cells spanning up to length of ~ 10 Å have been used as infinitely massive piston moving inward along z-direction by a fixed velocity to introduce a planar shock in the sample. The planar shock so induced led to the rapid changes in thermophysical parameters, e.g. temperature, stress, material velocity and density. In all MD simulations, shock loading is applied to single-crystal FCC copper along the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ crystallographic orientations. Structural evolution is analyzed using adaptive common neighbor analysis (a-CNA), which identifies local atomic environments corresponding to FCC, BCC, and HCP structures [18,19]. The a-CNA analysis is performed using OVITO [19], based on a short-range structural characterization of atomic coordination.

RESULTS AND DISCUSSIONS

The Pressure –Particle Velocity ($P-u_p$) Hugoniot of single crystal Cu derived from present simulations is plotted in Fig.1 (left) for shock propagation along the three different orientations. Also, plotted are the experimental data [10, 11] for polycrystalline Cu for comparison. It may be observed that theoretical Hugoniot is quite close to the experimental data at lower pressures; however, it is somewhat overestimated at higher pressures. Further, in Fig. 1 (three right figures), the evolution of different plausible phases in terms of volume fraction of different lattice configuration at different shock intensities for shock loading in different directions is displayed. As is obvious from Fig. 1, BCC phase has been observed for shock loading along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions but not along $\langle 111 \rangle$ direction. The FCC to BCC phase transition in single crystal copper shock loaded along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions has been identified through a-CAN pattern analysis as shown in Fig. 2 (left). Fig. 2 (right) shows the kinetic energy when the shock is applied in along $[001]$ direction.

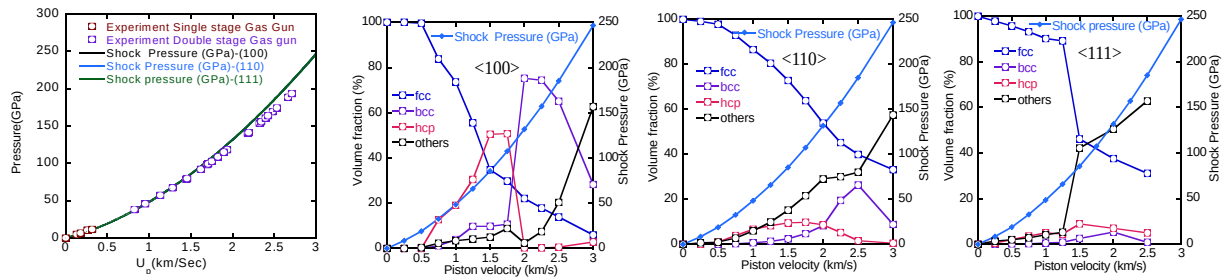


FIGURE 1. Shock Hugoniot of single crystal Cu in different crystallographic directions along with experimental shock data [10,11] (left) and Evolution of different phases from initial undeformed FCC copper at different velocity along different directions (right).

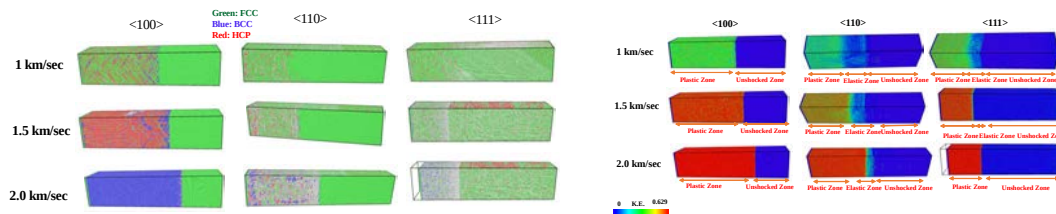


FIGURE 2. a-CNA of Cu where, color green, blue, red and white represent FCC, BCC, HCP and other phase respectively (left) and atoms colored according to their kinetic energies, with red being maximum and blue corresponding to zero velocity (undisturbed) (right).

Fig 3 (left), displays snapshots of pressure pulse at different post impact times for various impact velocities along different crystallographic directions. Interesting features observed in these profiles in Cu are similar to those have been reported in bcc system Ta by Singla and Ray [20]. As can be seen for shock propagation along $\langle 100 \rangle$ direction the elastic precursor gets overdriven for all impact speeds. However, the same is visible even up to impact speed of 2 km/s for $\langle 110 \rangle$ and $\langle 111 \rangle$ propagation. The reason for overdriving of elastic precursor at relatively lower velocity for $\langle 100 \rangle$ propagation as compared to that for other two directions could be due to lower longitudinal sound speed along this direction. It may also be noticed that the elastic precursor height decreases with increasing travel time, which is associated with the decay of the elastic wave as it propagates through the material. A sharp spiking feature in stress (Fig. 3) at elastic-plastic transition could be associated to the complex nature of dislocation mobility and resulting stress relaxations [20, 21]. The Hugoniot elastic limit (HEL) is estimated from the spatiotemporal evolution of the stress wave in NEMD simulations by analyzing the decay of the elastic stress amplitude as the shock propagates through the sample. The elastic to plastic (EP) transition stress (σ_{HEL}) after travel through a given thickness in sample,

can be related to the thickness (Z_0) at which first EP transition wave splitting occurs and corresponding stress σ_0 using the empirical relation [22, 20] as: $\sigma_{HEL} = \sigma_0 \left(\frac{z}{z_0}\right)^{-n}$. In Fig 3 (right) and table 1, we list σ_0 and n derived from above relation for loading along $\langle 110 \rangle$ and $\langle 111 \rangle$ directions with different impact velocities and available experimental data [12,13]. The decay in elastic precursor amplitude with thickness compares reasonably with experimental data.

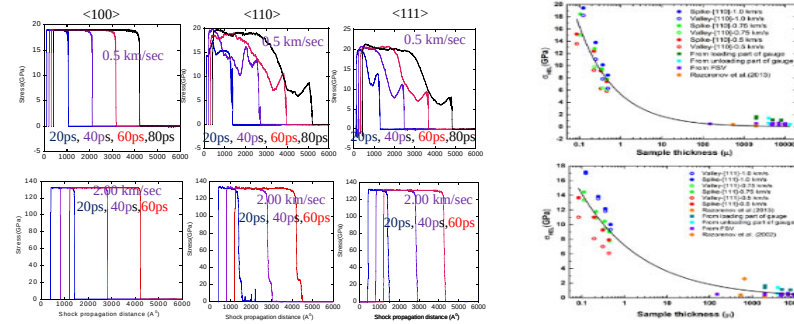


FIGURE 3. Snapshots displaying the spatial distribution of pressure profile in 722-nm-thin Cu sample impacted by different velocities (left). The HEL variation with sample thickness (right) from our model and available experimental data [12-13].

To summarize, detailed NEMD calculations combined with a-CNA on single crystal copper shocked along different crystallographic direction produces FCC-BCC phase transitions at ≥ 126 GPa along $\langle 100 \rangle$ and at ≥ 185 GPa along $\langle 110 \rangle$. The shock Hugoniot of single crystal agrees with experimental data on polycrystalline sample. The HEL of single crystal shows anisotropy such that at 300 K $\sigma_{HEL}^{111} > \sigma_{HEL}^{110}$ for all impact velocities for 722 nm length of single crystal Cu. The decay rate (n) from our study has values between ~ 0.3 to 0.4 along $\langle 111 \rangle$ whereas its value lies from 0.3 to ~ 0.64 along $\langle 110 \rangle$ which is close to the experimental value of ~ 0.4 - 0.6 of the polycrystalline sample [23].

TABLE 1. Coefficients σ_0 and n

U_0 (km/s)	location	σ_0 $\langle 110 \rangle$	n $\langle 110 \rangle$
0.5	Spike	6.228	0.374
0.75	Spike	5.416	0.551
1.0	Spike	6.228	0.374
0.5	Valley	3.969	0.507
0.75	Valley	3.648	0.634
1.0	Valley	3.969	0.507
		σ_0 $\langle 111 \rangle$	n $\langle 111 \rangle$
0.5	Spike	6.335	0.313
0.75	Spike	7.128	0.325
1.0	Spike	8.018	0.367
0.5	Valley	4.548	0.354
0.75	Valley	6.142	0.360
1.0	Valley	7.468	0.397

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Electronic, Magnetic and Thermodynamic Properties of High Spin Metallic $\text{Ce}_4\text{Ni}_3\text{O}_8$: A First Principles Study

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Abstract We report a first-principles investigation of the structural, electronic, magnetic properties of layered nickelate $\text{Ce}_4\text{Ni}_3\text{O}_8$. Density functional theory (DFT) calculations were carried out within GGA and the modified Becke Johnson potential to treat strong electronic correlations. $\text{Ce}_4\text{Ni}_3\text{O}_8$ stabilizes in a ferromagnetic metallic ground state. The electronic structure reveals dominant Ni-3d and O-2p states near the Fermi level, while Ce-4f orbitals contribute to localized magnetism. Thermodynamic results indicate stable phonon behaviour and favourable heat capacity trends.

INTRODUCTION

Rare-earth layered nickelates have gained attention due to their resemblance to high-temperature cuprates [1–3] and diverse physical properties. We present a first-principles study of $\text{Ce}_4\text{Ni}_3\text{O}_8$ using DFT in WIEN2k [4]. The compound crystallizes in tetragonal I4/mmm (139) structure [5], confirmed dynamically stable. Magnetic analysis shows the ferromagnetic metallic state is energetically favored. Band structure and DOS reveal strong Ni-3d and O-2p contributions at the Fermi level, with localized Ce-4f enhancing exchange splitting. Projected moments confirm Ni-3d and Ce-4f stabilize ferromagnetism. Thermodynamic analysis indicates stable vibrational contributions and smooth heat capacity variation, establishing $\text{Ce}_4\text{Ni}_3\text{O}_8$ as a correlated metallic nickelate.

COMPUTATIONAL METHODOLOGY

Spin-polarized DFT calculations were performed using WIEN2k [6] with FP-LAPW [7]. Muffin-tin radii were set as 2.22 a.u. (Ce/Pr), 1.81 a.u. (Ni), and 1.56 a.u. (O). Exchange–correlation effects were treated using GGA-PBE [8,9] with mBJ. Magnetic states (FM, AFM) were examined and thermodynamics via GIBBS2 [10].

RESULTS AND DISCUSSION

Structural properties

The layered rare-earth nickelate $\text{Ce}_4\text{Ni}_3\text{O}_8$ crystallizes in a tetragonal structure, composed of alternating Ce-O and NiO_2 layers inf Fig.1(a). Ni atoms occupy 2a and 4e Wyckoff positions, reflecting a mixed coordination environment, while oxygen resides at 4c, 8g and 4d sites, forming a robust three-dimensional network. This arrangement enables strong electronic correlations within the NiO_2 planes, comparable to cuprates. To evaluate structural stability, the Birch–Murnaghan equation of state [11,12] was employed across FM, AFM and NM configurations which show in Fig 1(b). Results confirm the FM phase as the energetically most stable, with optimized lattice parameters consistent with related nickelates.

Electronic properties

The electronic structure of $\text{Ce}_4\text{Ni}_3\text{O}_8$ was investigated using spin-polarized DFT within GGA and the modified Becke Johnson (mBJ) potential to account for strong correlations. The band structure reveals several bands crossing the Fermi level in both spin channels, confirming its metallic nature. Within GGA, the states near the Fermi level are primarily derived from Ni-3d orbitals hybridized with O-2p, while Ce-4f states lie slightly above E_F . The use of mBJ improves the description of exchange correlation effects, sharpening the metallic bands and increasing the density of states (DOS) at E_F , which reflects enhanced exchange splitting of Ni-3d states. The total and partial DOS clearly show finite states at E_F , the strong Ni-3d-O-2p hybridization, coupled with localized Ce-4f contributions, stabilizes the

ferromagnetic metallic ground state. This electronic configuration provides a high density of mobile carriers, favourable for charge transport and spin polarization. These results not only resolve discrepancies with earlier reports but also highlight $\text{Ce}_4\text{Ni}_3\text{O}_8$ as a correlated metallic oxide, whose robust electronic structure makes it a promising candidate for future functional applications in spintronics and energy-related technologies.

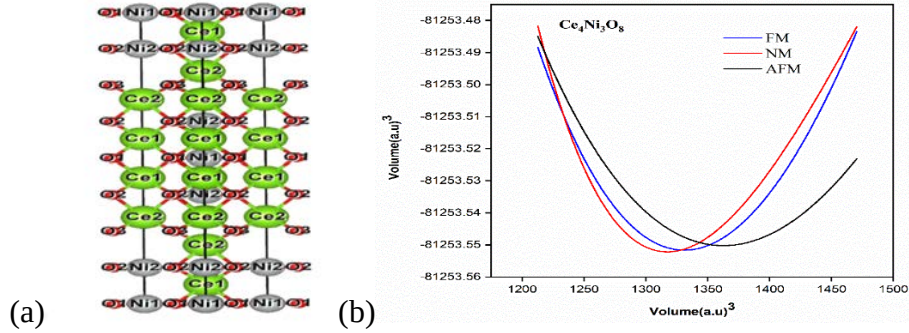


FIGURE.1 (a) Crystal structures of $\text{Ce}_4\text{Ni}_3\text{O}_8$ and (b) Optimization curve in Ferromagnetic (FM), Nonmagnetic (NM) and Antiferromagnetic (AFM) phases for the layered nickelates $\text{Ce}_4\text{Ni}_3\text{O}_8$.

TABLE 1: The extracted parameters for $\text{Ce}_4\text{Ni}_3\text{O}_8$ include the equilibrium lattice constant ($a = b$ and c in $\text{\AA}$), the Bulk modulus B_0 (GPa), the first derivative of Bulk modulus B_0' (GPa), the ground-state energy E_0 (Ry), Cohesive energy E_{coh} (eV/atom), Formation energy E_{for} (eV/atom)

Compound	Phase	Lattice Constant ($\text{\AA}$)			B_0	B_0'	E_0	V	E_{coh}	E_{for}	Ref.
		a	b	c							
$\text{Ce}_4\text{Ni}_3\text{O}_8$	FM	3.808	3.808	25.239	156.86	2.92	-81253.55	1331.02	6.55	-	[2,3]
	NM	3.808	3.808	25.239	148.46	5.0	-81253.52	1317.34		98.47	
	AFM	3.808	3.808	25.239	156.46	3.51	-81253.54	1330.47			
$\text{La}_4\text{Ni}_3\text{O}_8$	-	3.967	3.967	26.108	-	-	-	-	-	-	

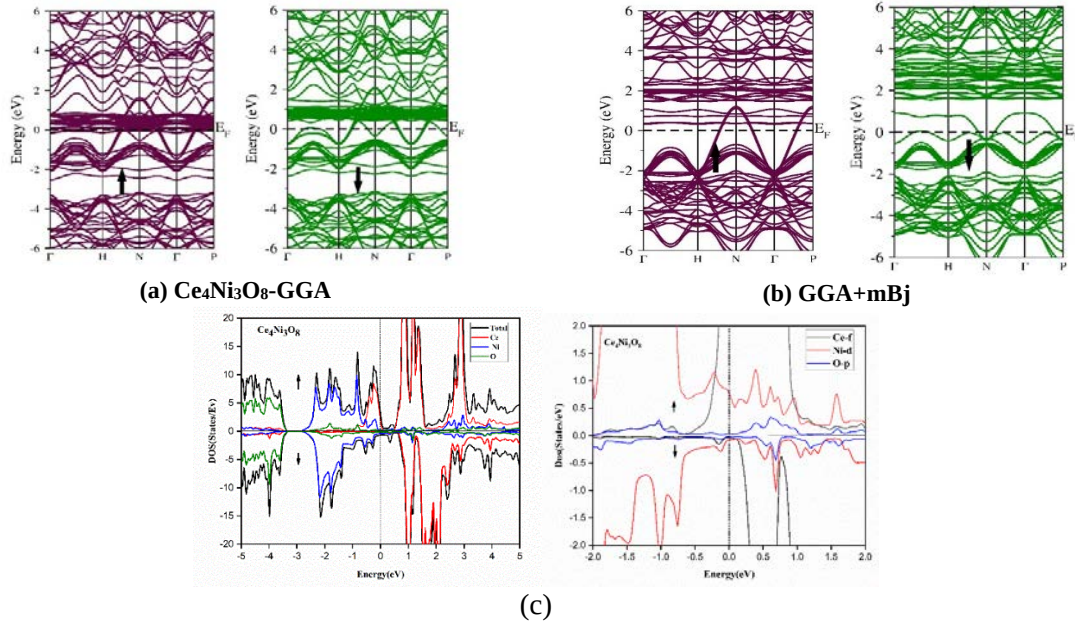


FIGURE. 2 (a,b) the band structures of $\text{Ce}_4\text{Ni}_3\text{O}_8$ calculated using the GGA and GGA + mBJ approaches. (c) PDOS for $\text{Ce}_4\text{Ni}_3\text{O}_8$ compound by mBJ calculation in both spins.

Magnetic properties

Spin-polarized DFT with GGA and mBJ shows enhanced Ni-3d and Ce-4f localized moments due to improved correlation treatment. The ferromagnetic phase is energetically favoured, while AFM suppression arises from sublattice compensation. Effective magnetic moments follow Curie–Weiss behaviour, confirming localized Ce³⁺ 4f contributions and stabilizing metallic ferromagnetism suitable for spintronics.

Heat capacities

The temperature-dependent heat capacities of Ce₄Ni₃O₈ were evaluated under varying pressures in Fig.3. At low temperatures, C_v and C_p rise sharply, consistent with the Debye T^3 law, while at higher temperatures both approach the Dulong Petit limit (375–400 J/mol·K) [13], confirming full phonon excitation. Increasing pressure slightly reduces C_v and C_p at elevated temperatures due to lattice stiffening, which suppresses atomic vibrations and phonon contributions. The convergence of C_v and C_p at high temperatures indicates diminishing anharmonic effects and confirms thermodynamic stability. These results highlight the strong correlation between lattice dynamics, pressure, and thermal stability in Ce₄Ni₃O₈.

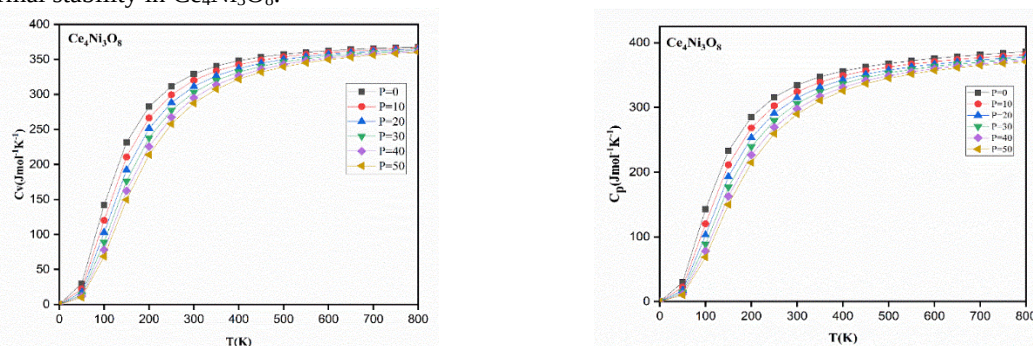


FIGURE.3 The Variation of Heat Capacities at constant-volume C_v and C_p with temperature (K) at different pressure (0–50Gpa) of Ce₄Ni₃O₈.

CONCLUSION

The compound Ce₄Ni₃O₈ shows stable structural, electronic, magnetic, and thermodynamic properties, with heat capacities following the Debye model and saturating at the Dulong Petit limit. Its pressure-dependent lattice behaviour and strong electron electron correlations in Ni-3d and Ce-4f orbitals highlight its potential for spintronic devices, thermoelectric performance, and unconventional superconductivity research.

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Pacman Particles at Play: Hybrid Colloidal Systems for Reconfigurable Microstructured Materials

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Abstract. We investigate the field-directed assembly of patchy colloidal particles composed of magnetic hematite cubes encapsulated in TPM shells. These “Pacman-like” particles exhibit specific interactions via their magnetic patch, enabling tunable structures under external fields. A magnetic field drives patch-to-patch interactions, while an AC electric field induces stacking and spreading. By using this multi-field combination and by varying field parameters, such as frequency and amplitude we achieve programmable transitions between distinct assembly modes. Our work offers a versatile platform for designing reconfigurable colloidal architectures with potential applications in micro-robotics and smart materials.

INTRODUCTION

Field-directed self-assembly of colloidal particles offers a powerful platform for designing dynamic and reconfigurable materials. The ability to tune interparticle interactions by using external electric or magnetic fields allows for precise control over structure formation at the microscale. While spherical and anisotropic colloids have been extensively studied in this context [1-3], introducing asymmetry in both shape and functionality, for example by using ‘patchy’ particles, opens new avenues for directional binding and structural programmability.

In this work, we investigate a system of hybrid patchy particles composed of magnetic hematite microcubes encapsulated in TPM spheres. We explore the collective behavior of these particles in aqueous suspension under varied electric (AC) and magnetic fields. Our results demonstrate a broad spectrum of assemblies, from small clusters to extended chains and lattices, which depend sensitively on field orientation, frequency, and amplitude. Notably, when both electric and magnetic fields are applied simultaneously, the system exhibits complex, reconfigurable structures. Through particle tracking and analysis of the system dynamics, we highlight regimes where magnetic and electric forces achieve a delicate balance, enabling reversible dimer formation. These findings suggest new strategies for constructing smart, externally tunable materials using simple colloidal building blocks.

MATERIALS AND METHODS

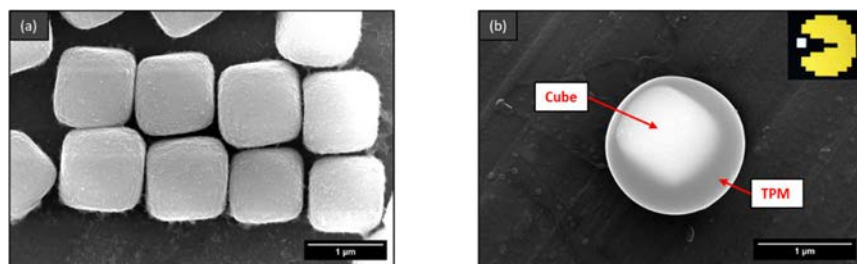


FIGURE 1. (a) SEM images of hematite cubes synthesized by a sol-gel method. (b) The hematite cube encapsulated in a TPM sphere making the cube + TPM conjugate: a ‘Pacman’ particle. Inset: Pacman schematic.

Hematite cubes of size $1.0 \pm 0.1 \mu\text{m}$ were synthesised by a sol-gel method (Fig. 1a) as outlined by Sugimoto *et al.* [4]. The particles exhibit canted antiferromagnetism, so there is a residual magnetic moment. For encapsulation of hematite cubes by TPM shells, 60 μL of aqueous ammonia (28 wt%) was added to 60 mL of an aqueous suspension

of cubes (0.5 wt%). After thorough mixing, 400 μL of the oil precursor, 3-(methacryloxypropyl)trimethoxysilane (TPM), was introduced into the suspension under continuous stirring. The nucleation and subsequent growth of TPM shells around the hematite particles were monitored at regular intervals using optical microscopy, and controlled by introducing additional volumes of TPM (200 μL at a time) [5]. The composite particles created had the hematite cube as the magnetic 'patch' and the non-magnetic TPM sphere as a functionalizable non-interacting part (Fig. 1b).

RESULTS AND DISCUSSION

When suspended in water, the TPM-hematite composites interact primarily through their magnetic cube region, while the rest of the surface remains inert. Like the arcade character Pacman, only the "mouth"- here, the magnetic patch- is active, leading to assemblies that resemble Pacman-like units clustering via their functional sites.

Structures from Purely Electric and Purely Magnetic Fields

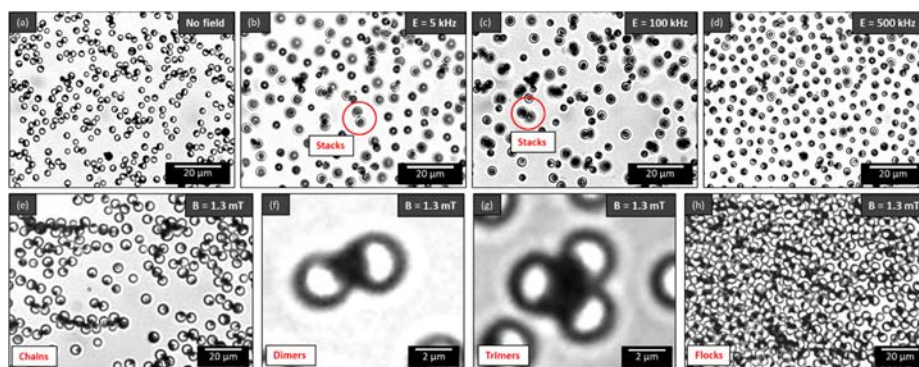


FIGURE 2. (a) In no field condition particles form small clusters. When an out of plane AC electric field of 20 V pp is applied, columnar stacks form under a frequency of (b) 5 kHz and (c) 100 kHz. (d) The particles form a non-close packed lattice under a frequency of 500 kHz. Structures from an in-plane magnetic field of 1.3mT (zero electric field): (e) staggered chains, (f) dimers, (g) trimers and (h) flocks.

In water and without external fields, the Pacman particles tend to interact via their magnetic patches, typically forming small clusters of 2-3 particles (Fig. 2a). When subject to an out-of-plane AC electric field (20 V peak-to-peak (Vpp)), they exhibit frequency-dependent assemblies. At ~ 5 kHz, the particles align into columnar stacks along the field due to dipole-dipole interactions (Fig. 2b), and this persists up to ~ 100 kHz. At 500 kHz the particles start to spread on the substrate forming well-separated, non-close packed lattice configurations, driven by inter-particle repulsion similar to the structures observed in isotropic systems by Wu *et al.* [1]

Although the Pacman particles exhibit short range interactions even in the absence of an external field, applying an in-plane uniform magnetic field of 1.3 mT leads to the formation of various configurations, including staggered chains (Fig. 2e), dimers (Fig. 2f), trimers (Fig. 2g), and flock-like clusters (Fig. 2h) which often incorporate smaller chain fragments within them.

Reconfigurable Structures from Combined Electric and Magnetic Fields

We built reconfigurable colloidal architectures by using a combination of electric field (applied along z) and magnetic field ($B = 1.3$ mT applied along x direction). As before, under only B field chains and clusters were observed (Fig. 3a). Under an applied AC electric field $E = 20$ Vpp with frequency 5 kHz, smaller and sparser stacks ((Fig. 3b) were formed in comparison to the purely electric case (Fig. 2b). At lower voltages (8 Vpp), the stack size was even smaller (Fig. 3d). At higher frequencies (1 MHz), the particles still spread out, though less uniformly than before, and often retained dimers due to residual magnetic attraction (Fig. 3e). An increase in the voltage at 1 MHz leads to a more ordered non-close packed lattice (Fig. 3c).

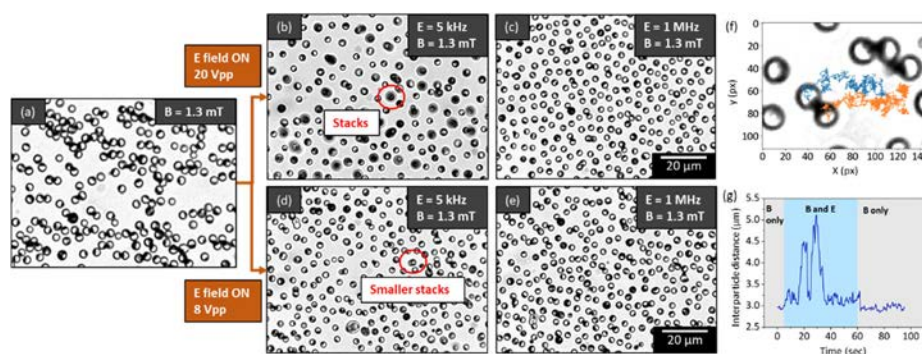


FIGURE 3. (a) Linear chains and small clusters formed under B field only. Structures formed under an AC E field of 20 Vpp, at 5 kHz (Fig. 3b) and 1 MHz (Fig. 3c), and at 8 Vpp for the same frequencies (Fig. 3d-e). A spontaneously reconfiguring dimer with particle trajectories shown (Fig. 3f). An interparticle distance vs time plot showing repeated attachment and detachment.

In a multi-field system, there is a competition between E and B based ordering, as seen in the previous structures (Fig. 3b-e) where B field induced linear chaining prevents formation of E field induced columnar stacks. Sometimes this leads to a delicate balance where a spontaneously reconfiguring structure is observed. Under a constant B field of 1.3 mT and an E field of 10 kHz and 8 Vpp, we observed that dimers formed via magnetic interactions (Fig. 3f) repeatedly broke and reassembled due to a balance between the magnetic attraction and the electric field based repulsion. By tracking the particle trajectories (Fig. 3f) and quantifying the inter-particle distance with time, we explored this spontaneous reconfiguration (Fig. 3g). The peaks in the blue region in Fig. 3f show the repeated forming and breaking of the dimer while the grey region shows the stable dimer configuration without the E field. This resulting interplay between fields gives rise to rich, complex structures with potential for use in reconfigurable soft materials.

CONCLUSION

The assembly behaviour of Pacman particles- hematite and TPM conjugates were studied under crossed electric and magnetic fields. By tuning the delicate balance between the electric and magnetic fields, and harnessing the selectivity of the magnetic patch, a variety of structures were obtained like chains, stacks, dimers, trimers, non-close packed lattice, flocks and even a combination of these structures like chains in flocks, stacks in lattices and even dimers in stacks or lattices. This paves the way to a rich composition of structures for the design of reconfigurable or switchable smart materials controlled externally by electric or magnetic fields.

ACKNOWLEDGMENTS

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Chiral Active Gyrotator: Diffusive Dynamics

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Abstract. We theoretically explore the diffusive dynamics of an inertial chiral active Ornstein-Uhlenbeck particle in a two-dimensional anisotropic harmonic potential, immersed in a viscous medium. The system is driven by two different thermal baths along the two orthogonal directions of the potential. The motion is governed by underdamped Langevin equations with inertia and constant active torque. In the steady state, the anisotropy in diffusion in the x and y directions arises even in the absence of a temperature gradient, purely due to chirality. For a fixed temperature gradient, the anisotropy in both x and y directions exhibits a non-monotonic dependence on chirality: it first increases, shows a maximum, and then decreases. Moreover, for a very high chirality strength, the system recovers the isotropy in diffusion in both x and y directions even in the absence of a temperature gradient.

INTRODUCTION

For the past few decades, active matter research has revealed a wide range of phenomena that arise when self-propelled particles interact with their environment in a nonequilibrium setting¹. Active systems are inherently out of equilibrium and composed of particles that consume energy to generate motion. Examples range from biological systems like bacteria, spermatozoa, and flocking birds to artificial systems like synthetic microswimmers² and Janus particles. While most theoretical models focus on overdamped dynamics, recent studies highlight the significant role of inertia in active particle behaviour³. In particular, chiral active particles have drawn attention due to their ability to perform circular motion in the absence of external torques, and are relevant for understanding the motion of microorganisms, synthetic spinners, and driven colloidal systems⁴. The dynamics become more complex when these particles are subject to anisotropic noise or asymmetric confinement⁵. In this work, we investigate the dynamics of an inertial chiral active particle moving in a two-dimensional anisotropic harmonic potential, and coupled to two orthogonal heat baths. The motion is governed by coupled underdamped Langevin equations. We explore how chirality and temperature asymmetry lead to anisotropic spatial distributions in the system. The model is introduced in the following sections, and the results are presented and discussed thereafter.

MODEL

We consider the dynamics of an inertial chiral active particle confined in a two-dimensional anisotropic harmonic potential. The particle's motion is described by the Langevin equation⁶

$$m\ddot{\mathbf{r}}(t) = -\gamma\dot{\mathbf{r}}(t) - \nabla V(\mathbf{r}) + \boldsymbol{\xi}(t) + \boldsymbol{\eta}(t), \quad (1)$$

where $\mathbf{r}(t) = x(t)\hat{i} + y(t)\hat{j}$ is the particle position, m is the mass, and γ is the viscous drag coefficient. The inertial force is $m\ddot{\mathbf{r}}(t)$. The anisotropic harmonic potential is $V(x, y) = \frac{1}{2}k(x^2 + y^2) + \alpha xy$, with k as the harmonic constant and α controlling confinement anisotropy. The term $\boldsymbol{\eta}(t) = \eta_x\hat{i} + \eta_y\hat{j}$ represents thermal noise from the two independent heat baths along the x and y directions, with $\langle \eta_i(t) \rangle = 0$ and $\langle \eta_i(t)\eta_j(t') \rangle = 2T_i\delta_{ij}\delta(t - t')$, where T_i is the effective temperature in direction i , with $i, j \in \{x, y\}$. The self-propulsion force $\boldsymbol{\xi}(t)$ is modelled by an Ornstein-Uhlenbeck process with chirality as

$$t_c \dot{\boldsymbol{\xi}}(t) = -\boldsymbol{\xi}(t) + \sqrt{2t_c} \boldsymbol{\zeta}(t) + \Omega \boldsymbol{\xi}(t) \times \hat{z}, \quad (2)$$

where t_c is the activity timescale, Ω represents the chirality strength, and $\boldsymbol{\zeta}(t)$ is Gaussian white noise with zero mean and unit variance. The cross-product term introduces active rotation. The steady-state autocorrelation of the active

force components is given by $\langle \xi_i(t) \xi_j(t') \rangle = \xi_0^2 \delta_{ij} \exp\left(-\frac{|t-t'|}{t_c}\right) \cos(\Omega(t-t'))$, which captures both self-propulsion and circular motion arising from chirality.

RESULTS AND DISCUSSION

To characterize the anisotropic spreading of the particle in the steady state, we compute the variances $\langle x^2 \rangle$ and $\langle y^2 \rangle$. In the long-time limit, the system reaches a stationary nonequilibrium state where the mean square displacement (MSD) becomes time-independent. In this regime, the variances of the position can be obtained by solving the steady-state Lyapunov equation, which governs the evolution of the covariance matrix $C_{ij} = \langle X_i X_j \rangle$, where $X_i \in \{x, y, \dot{x}, \dot{y}\}$. For a linear system, the Lyapunov equation is $\mathbf{A}\mathbf{C} + \mathbf{C}\mathbf{A}^T = 2\mathbf{D}$, with $\mathbf{A}$ as the drift matrix encoding the deterministic dynamics, and $\mathbf{D}$ the noise covariance matrix. The quantities of interest, $\langle x^2 \rangle$ and $\langle y^2 \rangle$, are directly extracted from the diagonal elements of $\mathbf{C}$. We have exactly calculated the MSD of the particle as

$$\begin{aligned} \langle x^2 \rangle + \langle y^2 \rangle = & \frac{k(T_x + T_y)}{k^2 - \alpha^2} \\ & + \frac{t_c \xi_0^2}{\gamma} \left(\frac{(m + t_c \gamma)(m + t_c(t_c(k + \alpha) + \gamma)) + m^2 t_c^2 \Omega^2}{(k + \alpha)((m + t_c(t_c(k + \alpha) + \gamma))^2 + t_c^2(2m(m - t_c^2(k + \alpha)) + 2mt_c \gamma + t_c^2 \gamma^2)\Omega^2 + m^2 t_c^4 \Omega^4)} \right. \\ & \left. + \frac{(m + t_c \gamma)(m + t_c(kt_c - t_c \alpha + \gamma)) + m^2 t_c^2 \Omega^2}{(k - \alpha)((m + t_c(kt_c - t_c \alpha + \gamma))^2 + t_c^2(2m^2 + t_c^2 \gamma^2 + 2mt_c(-kt_c + t_c \alpha + \gamma))\Omega^2 + m^2 t_c^4 \Omega^4)} \right) \quad (3) \end{aligned}$$

This expression separates the contribution from thermal noise (first term) and active noise (second term), modulated by the damping coefficient γ , chirality strength Ω , and the activity timescale t_c . The degree of anisotropy in the spatial diffusion is determined using the ratio $\langle x^2 \rangle / \langle y^2 \rangle$.

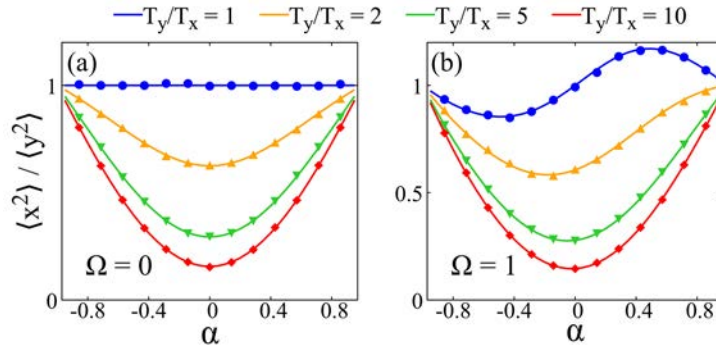


FIGURE 1. $\langle x^2 \rangle / \langle y^2 \rangle$ as a function of α , for different values of T_y/T_x , corresponds to $\Omega = 0$ in (a), and corresponding to $\Omega = 1$ in (b). The other parameters used are fixed at $m = 1$, $k = 1$, $t_c = 1$ and $T_x = 1$.

In **Fig. 1**, we plot $\langle x^2 \rangle / \langle y^2 \rangle$ as a function of α for an achiral particle ($\Omega = 0$) in (a) and a chiral particle ($\Omega = 1$) in (b), for different values of T_y/T_x . When $\Omega = 0$, the ratio $\langle x^2 \rangle / \langle y^2 \rangle$ remains unity and independent of α in the absence of a temperature gradient ($T_x = T_y$), reflecting the isotropic spreading. With increase in the thermal asymmetry T_y/T_x , the directional bias strengthens, resulting in the suppression of $\langle x^2 \rangle / \langle y^2 \rangle$, where the particle becomes less displaced in the x direction [Fig. 1(a)]. For $\Omega = 1$ [Fig. 1(b)], even without a temperature gradient, the ratio $\langle x^2 \rangle / \langle y^2 \rangle$ deviates from unity due to the intrinsic rotational bias in the dynamics. The chirality-induced coupling between the x and y components causes the particle to explore the space asymmetrically, which is further amplified at higher T_y/T_x .

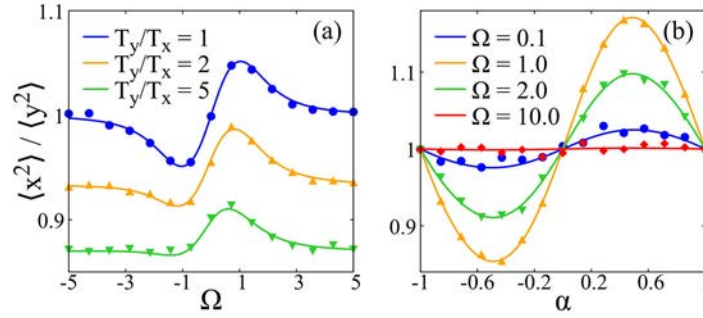


FIGURE 2. $\langle x^2 \rangle / \langle y^2 \rangle$ as a function of Ω , for different values T_y/T_x and for a fixed $\alpha = 0.9$ in (a), and as a function of α , for different values of Ω , and for a fixed $T_y/T_x = 1$ in (b). Other common parameters are fixed at $m = 1$, $k = 1$, $\gamma = 1$ and $t_c = 1$.

In **Fig. 2**, we have plotted $\langle x^2 \rangle / \langle y^2 \rangle$ as a function of Ω for different values of T_y/T_x in (a), and as a function of α for different values of Ω in (b). For a fixed T_x/T_y , the ratio $\langle x^2 \rangle / \langle y^2 \rangle$ varies non-monotonically with Ω , initially increasing, reaching a maximum, and then decreasing [Fig. 2(a)]. For a fixed Ω [Fig. 2(b)], the ratio $\langle x^2 \rangle / \langle y^2 \rangle$ is non-monotonic with α . At high values of Ω , the effects of α is minimal, and the ratio $\langle x^2 \rangle / \langle y^2 \rangle$ approaches unity, reflecting the isotropic spreading in both x and y directions of the potential.

SUMMARY

In summary, we investigated the dynamics of an inertial chiral active Ornstein-Uhlenbeck particle confined in an asymmetric harmonic trap and coupled to two orthogonal heat baths. We analyzed its diffusive behaviour by evaluating the anisotropy in diffusion of the particle as a ratio of variances of position in the two orthogonal directions using the covariance matrix formalism. Our results reveal that this ratio is sensitive to the difference in bath temperatures and can be tuned by adjusting the temperature gradient. Notably, the anisotropy persists even when the two thermal baths are at the same temperature. Unlike the passive case, finite chirality and persistent self-propulsion break spatial symmetry. We find that the steady-state diffusion of the particle becomes anisotropic only at finite values of chirality, returning to isotropy again at the very strong chirality limit. This study highlights how chirality and directional temperature gradients can give rise to novel transport phenomena in active systems.

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Coarse-Grained Dean's Equation for Active Brownian Particles with Position-Dependent Dissipation

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Abstract. Starting with the microscopic Langevin equation for a single active Brownian particle, which contains an active noise term, a macroscopic equation for mass density is obtained. The overdamped limit is taken, and the time dependence of momentum is ignored. Frictional drag is taken to be position-dependent. Active noise in the microscopic equation drives the system in a non-equilibrium state. An exact balance equation for the microscopic mass density is obtained. The microscopic equation, having position coordinates only, is averaged over the local equilibrium ensemble. This obtains the stochastic time evolution equation for macroscopic mass density. This equation contains multiplicative noise and additional terms that are absent in the Dean's equation for passive Brownian particles.

Keywords: Active matter, Local equilibrium distribution, Mass density field, Active noise, Stochastic density dynamics

INTRODUCTION

In recent years, the study of active matter physics has rapidly evolved into a vibrant and compelling area of interdisciplinary research [1, 2]. Active matter systems inherently possess the ability to extract energy from their environment and drive themselves out of equilibrium. Both active and passive particle systems can exist in non-equilibrium states. In a passive particle system, the non-equilibrium condition is sustained by an external force, whereas in an active system (for both natural and engineered entities), the non-equilibrium arises from the internal energy of each constituent particle. These systems exhibit a range of striking behaviors, including swarming and the emergence of collective properties, which are impossible within systems that remain in thermal equilibrium. Active or self-propelled particles demonstrate dynamics that are not constrained by time-reversal invariance and do not adhere to time-reversal symmetry. In active matter systems, the relationships between noise, activity, and dissipation typically deviate from the usual dependences that are fully developed in equilibrium statistical physics, thereby disrupting the detailed balance at the microscopic scale [3]. The system considered here is driven by the active noise term in the Langevin equation and has short-range interactions. We follow the same method proposed by Dean [4] to obtain the exact microscopic equation for mass density, which is averaged over the local equilibrium ensemble to obtain the fluctuating hydrodynamic equation for the mass density.

MICROSCOPIC DYNAMICS

We consider here a system of N particles whose microscopic dynamics is described in terms of position and momentum coordinates $\{\mathbf{x}_\alpha, \mathbf{p}_\alpha\}$ for $\alpha = 1 \dots N$. The generalized Langevin equation for the α -th particle is given as

$$\frac{dx_\alpha^i}{dt} = p_\alpha^i, \quad \frac{dp_\alpha^i}{dt} = -f_\alpha^i - \sum_\beta \zeta_{\alpha\beta}^{ij}(x_\beta, p_\beta) p_\beta^j + \sqrt{A_0} \xi_\alpha^i. \quad (1)$$

In the above expression, the Greek indices α, β denote the particle index, and the Roman indices i, j denote the Cartesian component. For simplicity, we have assumed a unit mass for the particles. The quantity force f_α^i denotes the interaction term given as $f_\alpha^i = \nabla_\alpha \sum_\beta U(\mathbf{x}_\alpha(t) - \mathbf{x}_\beta(t))$, where nabla operator ∇_α denotes a derivative operator for the i -th component of position $\mathbf{x}_\alpha$. The quantity U is the interaction potential on the system. We will consider here the Einstein summation convention for the repeated Roman indices. The general form of frictional drag, $\zeta_{\alpha\beta}^{ij}$ on the α -th particle depends on both the space and momentum variables. But, we take here the overdamped limit and only the

position dependence of the coefficients is taken into account [5, 6]. The quantity ξ_α is the active random noise term, and $\tilde{A}_0$ is the noise strength. The noise-noise correlation is given as

$$\langle \xi_\alpha^i(t) \xi_\beta^j(t') \rangle_F = \delta_{ij} \delta_{\alpha\beta} \delta(t - t'), \quad (2)$$

where the subscript F on the angular brackets symbolizes the averaging over the fast degree of freedom. Eq. (2) does not follow the fluctuation-dissipation relation. The overdamped Langevin equation in terms of position coordinates corresponding to Eq. (1) is given by

$$\zeta(x_\alpha) \frac{dx_\alpha^i}{dt} = -f_\alpha^i + \sqrt{2\tilde{A}_0} \xi_\alpha^i. \quad (3)$$

Next, we define microscopic mass density and momentum density as

$$\hat{\rho}(\mathbf{x}, t) = \sum_\alpha m \delta(\mathbf{x} - \mathbf{x}_\alpha(t)), \quad (4)$$

$$\hat{\mathbf{g}}(\mathbf{x}, t) = \sum_\alpha \mathbf{p}_\alpha \delta(\mathbf{x} - \mathbf{x}_\alpha(t)). \quad (5)$$

Here we will not discuss the time evolution equation for momentum density, but its definition is required to understand the averaging process. Now applying the chain rule of the Itô calculus for Eq. (4) and using Eq. (3), we obtain the exact balance equation for microscopic mass density as [4, 7]

$$\frac{\partial \hat{\rho}}{\partial t} = \tilde{A}_0 \nabla^2 \hat{\rho} + \nabla \cdot [\zeta^{-1}(\mathbf{x}) \hat{\rho}(\mathbf{x}, t) \nabla \int d\mathbf{x}' U(\mathbf{x} - \mathbf{x}') \hat{\rho}(\mathbf{x}', t) + \hat{\eta}(\mathbf{x})], \quad (6)$$

where $\hat{\eta}(\mathbf{x}) = -\nabla^i [\zeta^{-1}(\mathbf{x}) \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_\alpha(t)) \xi_\alpha^i(t)]$ and $\tilde{A}_0 = A_0/\zeta^2$. The hats on the quantities denote the phase-space dependence.

FIELD-THEORETIC DESCRIPTION

In order to obtain the macroscopic time evolution equation for the mass density field, we average Eq. (6) over a suitable ensemble. In the averaging process, the phase-space dependence of the microscopic variables of Eq. (6) are integrated out. We take the analogy from the thermal equilibrium system and extend the idea to the active Brownian particle system, which is not a thermal system [7, 8]. To average Eq. (6), we consider the fluid from a co-moving frame with local velocity $\mathbf{v}(\mathbf{x}, t)$ so that the fluid appears at rest in the vicinity of point $\mathbf{x}$ at time t . We will denote quantities in the moving frame by a prime on them. The momentum and position coordinates in the moving frame are related to the rest frame by the following transformation rule

$$\mathbf{p}_\alpha = \mathbf{p}'_\alpha + m\mathbf{v}(\mathbf{x}'_\alpha) \quad \text{and} \quad \mathbf{x}_\alpha = \mathbf{x}'_\alpha. \quad (7)$$

The mass density and momentum density fields in the two frames are related by $\hat{\rho} = \rho'$ and $\hat{\mathbf{g}} = \mathbf{g}' + \hat{\rho}\mathbf{v}$. Next, we define a local equilibrium distribution function $f_{le}(\Gamma'_N, t)$ in the primed frame as [6, 7]

$$f_{le}(\Gamma'_N, t) = Q_l^{-1} \exp\{-\tilde{\beta}[H' - \mu(\mathbf{x}, t)\hat{\rho}'(\mathbf{x})]\}, \quad (8)$$

where Q_l symbolizes the normalization constant and Γ_N is the phase-space coordinates. The temperature analogue factor $\tilde{\beta}$ is related to the average kinetic energy of the particles as $\epsilon_0 = d/2\tilde{\beta}$ in d dimensions. H' denotes the Hamiltonian in the local rest frame, and $\mu(\mathbf{x}, t)$ denotes the local chemical potential. We denote the Local equilibrium average (LEA) of the phase-space dependent quantities for the distribution function defined in Eq. (8) by angular brackets $\langle \dots \rangle$. The LEA of $\hat{\rho}$ will be denoted by ρ . Applying the notion discussed above, the LEA of Eq. (6) is obtained as

$$\frac{\partial \rho}{\partial t} = \tilde{A}_0 \nabla^2 \rho + \nabla \cdot [\zeta^{-1}(\mathbf{x}) \nabla \int d\mathbf{x}' U(\mathbf{x} - \mathbf{x}') \langle \hat{\rho}(\mathbf{x}, t) \hat{\rho}(\mathbf{x}', t) \rangle + \eta(\mathbf{x})]. \quad (9)$$

Eq. (9) is the generalized Dean's equation. Deducing the average of the second term on the right-hand side of the above equation, we write Eq. (9) as

$$\frac{\partial \rho}{\partial t} = \left[\tilde{A}_0 - \frac{\gamma_0}{\zeta} \right] \nabla^2 \rho + \zeta^{-2} [\gamma_0 \nabla \rho - \rho \nabla \mu] \cdot \nabla \zeta + \zeta^{-1} \nabla \cdot (\rho \nabla \mu) + \eta. \quad (10)$$

The coefficient γ_0 is the average momentum correlation. The noise term in the above equation is multiplicative. The noise-noise correlation is obtained as [7]

$$\langle \eta(\mathbf{x}, t) \eta(\mathbf{x}', t') \rangle = [\nabla_{\mathbf{x}} \cdot \{\zeta^{-1}(\mathbf{x}) \rho(\mathbf{x}) \nabla_{\mathbf{x}'} \{\zeta^{-1}(\mathbf{x}') \delta(\mathbf{x} - \mathbf{x}')\}\}] \delta(t - t'). \quad (11)$$

Eq. (10) reduces to the conventional Dean's equation for passive particles if we replace the active noise contribution to the thermal noise.

DISCUSSION

We have obtained the coarse-grained version of the time evolution of the mass density field equation, which contains a multiplicative noise term. This equation has additional terms than the conventional passive particle Brownian equation. These terms arise due to the active noise in the microscopic equation. The space-dependent dissipative coefficient can be taken as a polynomial function of the position coordinate. The diffusion coefficient is space-dependent due to the position-dependent frictional drag. For a specific model of active motion, the diffusion coefficient can be obtained as a function of density and self-propulsion speed. This kind of relation is responsible for the motility-induced phase transition [9]. The chemical potential can be expressed in terms of Taylor's expansion of density fluctuations [6]. In the above calculation, we have not considered the thermal noise contribution.

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Effect of Ti Doping on Bioactivity of Borate Bioglasses

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Abstract. Numerous bioactive glass compositions have been proposed for cutting-edge biomedical applications, such as soft tissue engineering, drug delivery, bone and dental repair. In this study, the effect of Ti doping on bioactivity of the biodegradable borate bioglass (1393-B3) is investigated, obtained by conventional melt-quenching process. Ti modified glasses including the parent 1393-B3 glass have shown in-vitro bioactivity in simulated body fluid (SBF). The glasses confirmed the formation of the hydroxyapatite (HA) phase over the glass surface. The bioactivity mechanism is attributed to the sequence of dissolution and precipitation similar to those observed in 45S5 silicate bioglass. Melt-derived bioactive glasses with the borate 1393-B3 configurations degraded rapidly and converted to a calcium phosphate product when immersed in SBF. The PO_4^{3-} groups from the solution respond to Ca^{2+} situated on the glass surface, prompting the nucleation of Hydroxyapatite. Where, the incorporation of Ti into the borate network enhanced the bioactivity due to its intrinsic bioactive characteristics.

INTRODUCTION

Restoration of damaged body parts and their physical functionality has been a driving force for the development of new biomaterials. The definition of "biocompatibility" has been broadened to include all those compounds that can aid a living system in responding favorably by forming a strong tissue-implant link (second-generation materials) or through genetically activating specific cell pathways which leads to the third-generation smart materials [1]. In between 1969 and 1971 Hench and his associates investigated different glass compositions based on the $\text{SiO}_2\text{-Na}_2\text{O-CaO-P}_2\text{O}_5$ oxide system and invented the composition $45\text{SiO}_2\text{-}24.5\text{Na}_2\text{O-}24.5\text{CaO-}6\text{P}_2\text{O}_5$ (in wt%), characterized by high amounts of Na_2O and CaO , as well as a relatively high $\text{CaO/P}_2\text{O}_5$ ratio which makes the surface of the material very reactive, resulting in the nucleation and growth of hydroxyapatite phase in the body fluids [2]. This glass composition has been referred as 45S5 bioglass (BG). Over the past 50 years, a large number of unique compositions of BG have been investigated for the enhancement of the bioactive behavior for various applications. In addition to silica based BG, phosphate and borate based BG have been studied due to their other advantages. Moreover, borate glasses have gained interest due to potential to create apatite without the subsequent formation of a silica-rich layer and the ability to dissolve swiftly. The present study reports the borate-based 1393-B3 bioactive glasses doped with Titanium and their bioactive behavior. Titanium based biomaterials have been known for their high biocompatibility, self-healing ability and superior osseointegration [3]. So, the effect of Ti on the 1393-B3 bioglass are studied in this work

EXPERIMENTAL METHODS

For preparing SBF, KCl, K_2HPO_4 , NaCl, NaHCO_3 , MgCl_2 , CaCl_2 , and Na_2SO_4 were dissolved in deionized water in the preparation of SBF by taking appropriate weight fractions. In 500 ml deionized (DI) water, constituents were added one by one after each constituent dissolves completely as reported elsewhere [4]. The glass batch containing the following composition $(54.6 - x)$ wt% B_2O_3 , 18.5 wt% CaO , 5.5 wt% Na_2O , 11.1 wt% K_2O , 4.6 wt% MgO , 3.7 wt% P_2O_5 and $x=1, 3, 5, 8$ and 10 wt% TiO_2 were prepared, with starting material as Magnesium Oxide (99% MgO), Calcium Carbonate (99% CaCO_3), Sodium Carbonate (99% Na_2CO_3), Potassium Carbonate (98% K_2CO_3) and Boric acid (99% H_3BO_3). The materials were mixed for 30 minutes in a mortar and pestle. These reagents were then melted in a platinum crucible for 4 h in an electric furnace at 1200 °C. Additionally, the glass melt was water quenched to form glass frits for further characterization. Prepared Ti- modified 1393-B3 bioglass samples were characterized for structural and microstructural features using X-ray diffraction (XRD, PANalytical Multifunctional X'PERT³ Diffractometer) and scanning electron microscope (SEM, JSN-IT300 InTouchScopeTM). The bioactivity studies were

carried out by immersing the samples in SBF at 37 °C in an incubator and characterization of the SBF treated samples after washing in Milli-Q water.

RESULT AND DISCUSSION

XRD patterns of different Ti-containing borate glasses are presented in Fig.1 after treating in SBF for different time durations to affirm the bioactive nature. No HA peaks are identifiable on the first day of SBF treatment (Fig. 1(a)). After seven days of dousing in SBF, detectable HA peaks are observed in XRD Fig. 1(b). The HA Bragg peak was found to be prominent for the T10 borate glass sample. This indicates that, the substitution of Ti into the borate matrix is favoring the bioactivity and HA formation kinetics. Ti-modified borate glasses could facilitate the ion interchange process which helps in nucleating and forming HA due to network modification.

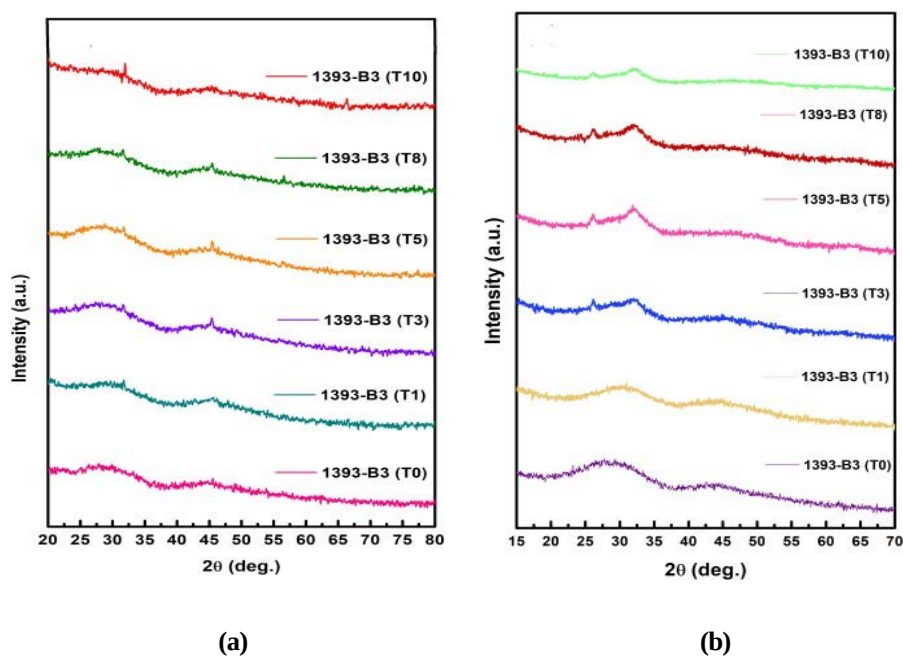


FIGURE 1: XRD Pattern of samples treated in SBF for a) 1 day, and b) 7 days

SEM pictures for the Ti-modified borate bioglasses after treatment in SBF for 1 day and 7 days are shown in Fig.2(a-d) and Fig.2(e-h) respectively. Particle-like microstructural growth can be seen on the surface of the glass frits. Enhanced formation of typical HA is noticed on the surface of the Ti- containing borate glasses. At higher Titanium doping (T10), the amount of apatite like microstructures on the surface is more pronounced [5]. The growth of the particles is observed to be higher for glasses containing higher contents of Titanium. The degree of bioactivity of the glass depends directly upon the ability of the glass to form a hydroxyapatite layer.

Melt-derived bioactive glasses with the borate 1393-B3 configurations degraded rapidly and converted to a calcium phosphate product when immersed in SBF. During the change of borate glasses to HA must have followed set of dissolution and precipitation reactions similar to that observed in 45S5 bioactive glass system excluding development of a SiO₂ enrich layer. From the glass surface, ions are dissolve in the SBF solution, and parallelly, the phosphate ions tend to attack the B-O network structure of the glass. The PO₄³⁻ ions from the solution react with Ca²⁺ ions located on the glass surface leading to the nucleation of HA. The continuation of the dissolution-precipitation reactions leads to the thickening of the HA layer on the inward surface of the glass particle. In different borate glass compositions that we have studied, for the one with the highest Ti doping, until the complete conversion of glass to HA the process is continued.

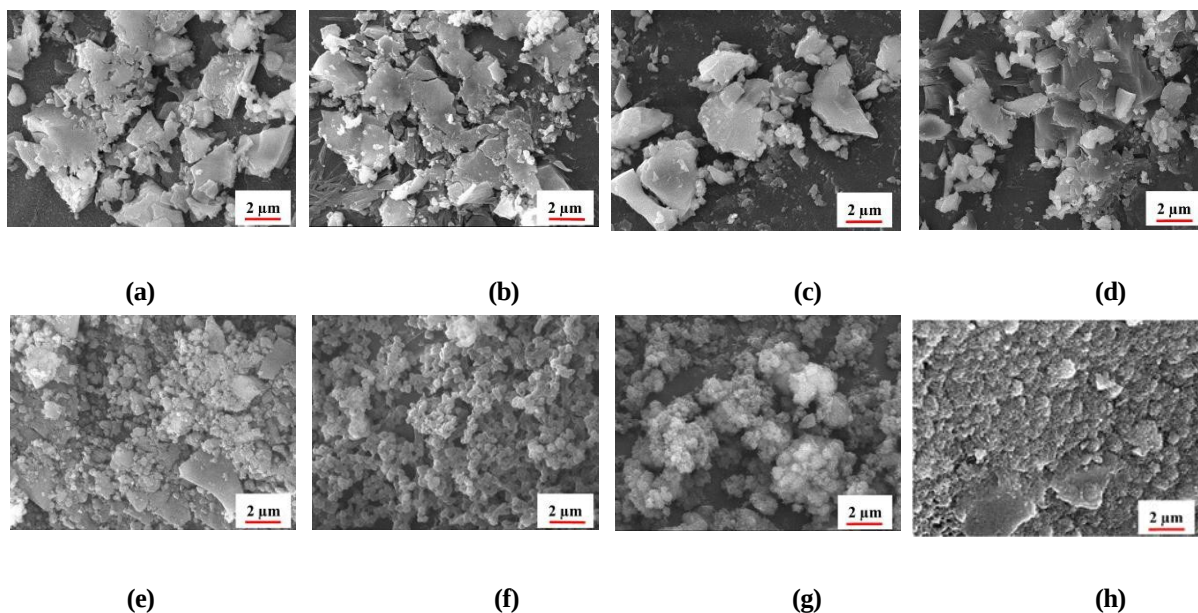


FIGURE 2: SEM images of (a) 1393-B3-T1, (b) 1393-B3-T3, (c) 1393-B3-T5, (d) 1393-B3-T10 treated in SBF for one day and (e) 1393-B3-T1, (f) 1393-B3-T3, (g) 1393-B3-T5, (h) 1393-B3-T10 after treating in SBF for 7 days.

CONCLUSIONS

The 1393-B3 borate-based bio-active glasses are studied by modifying them with different Ti contents. Glasses are prepared by the melt quenching method and characterized by XRD, and SEM. The borate bio-active glasses have reacted and enabled to form hydroxyapatite (HA) on their surfaces upon immersing in simulated body fluid at 37 °C. It is found that, a higher Titanium doping results in faster and heavy growth of HA. The crystallization of HA phase is enhanced at high Titanium doping in glasses as analyzed from XRD and SEM studies. The bioactivity is unique to the glassy systems and can be enhanced by modifying with suitable elements like Ti as investigated in this work. Enhanced HA generation ability of Ti-modified borate glasses in simulated body fluids can be considered as one of the important bioglass candidate for biomedical applications.

ACKNOWLEDGMENTS

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Non-Markovian Gyrator

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Abstract. We investigate the two-dimensional motion of a Brownian particle confined in an asymmetric harmonic potential and coupled to two thermal baths maintained at different temperatures. Such a system exhibits gyration due to the combined effects of temperature gradient and potential asymmetry. We examine how the gyrating behavior is affected when the system is immersed in a non-Markovian environment characterized by a finite memory timescale. We have exactly calculated the angular velocity and observe that memory introduces a non-monotonic dependence of angular velocity on the potential asymmetry. Moreover, the peak in angular velocity shifts toward lower asymmetry values as the memory timescale increases, indicating that the optimal asymmetry required for maximum rotation can be tuned by varying the persistent duration of memory. Further, we observe a self-inversion in the rotational motion by tuning the temperature gradient.

INTRODUCTION

A Brownian gyrator is a minimal stochastic model that consists of a Brownian particle confined in an asymmetric harmonic potential and coupled to two thermal baths kept at different temperatures. The imposed temperature gradient facilitates the heat transfer from the hot to the cold reservoir, consequently making the system out of equilibrium, allowing the particle to exhibit gyrating motion across the potential minimum¹⁻³. Such a model is integral to the study of non-equilibrium statistical mechanics and stochastic energetics⁴. However, these systems are typically studied in Markovian environments where memory effects are ignored. In realistic scenarios, it is more appropriate to consider a non-Markovian system with finite memory effects⁵. Memory plays a crucial role in a wide range of stochastic systems including biological processes^{2,6,7}. In this work, we investigate the effective gyration of the Brownian particle in a non-Markovian environment with finite memory, when confined by an asymmetric harmonic potential and coupled to two heat baths. We find that rotation occurs only when both potential asymmetry and a temperature gradient are present. Moreover, the maximum angular velocity can be controlled by tuning the memory timescale and can reverse its sign by tuning the temperature gradient. In the next following sections, we address the model under consideration in detail. The results are presented in the subsequent section and finally, we conclude.

MODEL

We consider the motion of a Brownian particle of mass m confined in an asymmetric potential of the form $V(x, y) = \frac{1}{2}k(x^2 + y^2) + \alpha xy$, coupled to two heat baths and suspended in a non-Markovian environment. The dynamics of such a system can be described using the generalized Langevin equation of motion^{7,8}

$$m\ddot{\mathbf{r}}(t) = - \int_0^t g(t-t')\dot{\mathbf{r}}(t')dt' - \nabla V + \boldsymbol{\eta}(t). \quad (1)$$

Here, ' m ' is the mass of the particle and the position vector of the particle is given by $\mathbf{r}(t) = x(t)\hat{i} + y(t)\hat{j}$. The time dependent memory kernel $g(t-t')$ based on the Jeffrey fluid model², is given by

$$g(t-t') = \frac{\gamma}{2} \left[\delta(t-t') + \frac{1}{t'_c} e^{-(t-t')/t'_c} \right], \quad (2)$$

with t'_c as the memory time scale of the medium and $\boldsymbol{\eta}(t) = \boldsymbol{\eta}^T(t) + \boldsymbol{\eta}^A(t)$. Here, $\boldsymbol{\eta}^T(t)$ is the Gaussian thermal noise with properties, $\langle \eta_i^T(t) \rangle = 0$ and $\langle \eta_i^T(t) \eta_j^T(t') \rangle = \delta_{ij} k_B T_i g(t-t')$. The $\boldsymbol{\eta}^A(t)$ is the force that follows the Ornstein-Uhlenbeck process

$$t'_c \dot{\eta}^A(t) = -\eta^A(t) + \begin{pmatrix} \sqrt{\gamma k_B T_x} & 0 \\ 0 & \sqrt{\gamma k_B T_y} \end{pmatrix} \cdot \zeta'(t).$$

The temperature T_i corresponds to the thermal bath influencing motion along the i -direction, where $i, j \in \{x, y\}$ and $\zeta'(t)$ is a delta correlated white noise with zero mean. Throughout the rest of this paper, the Boltzmann constant k_B is set to unity. To preserve the generality of the model [Eq. (1)], all physical quantities are expressed in dimensionless form. We define the parameters, $\omega_0 = \sqrt{k/m}$, $\Gamma = \frac{\gamma}{m}$, and the temperature gradient $\Delta T = T_x - T_y$. The steady state angular velocity can be calculated using the formulation, $\langle \omega \rangle = \lim_{t \rightarrow \infty} (\mathbf{r} \times \mathbf{v})$.

RESULTS AND DISCUSSION

In order to quantify the rotational motion, we have exactly calculated the steady state angular velocity. We introduce the correlation matrix Ξ , whose elements are defined as $\Xi_{ij} = \langle \chi_i \chi_j \rangle - \langle \chi_i \rangle \langle \chi_j \rangle$, with the matrix $\chi = (x, y, v_x, v_y, u_x, u_y, \eta_x^A, \eta_y^A)^T$. According to the correlation matrix formalism, Ξ satisfies the matrix equation $A \cdot \Xi + \Xi \cdot A^T + B = 0$, where A is the drift matrix and B is the noise correlation matrix. Once the above equation is solved, the magnitude of the average $\langle \omega \rangle$ can be calculated as

$$\begin{aligned} \langle \omega \rangle &= \langle x v_y \rangle - \langle y v_x \rangle = (\Xi_{4,1} - \Xi_{2,3}) \\ &= \frac{-2k_B(T_x - T_y)\alpha\Gamma[2t_c'^4\alpha^2 - m^2(2 + t_c'(\Gamma + t_c'\omega_0^2))(2 + t_c'(\Gamma + 2t_c'\omega_0^2))]}{S - 8m^2\alpha^2 - 8m^4\Gamma^2\omega_0^2}, \end{aligned} \quad (3)$$

$$\text{where, } S = t_c'[2m^2t_c'\alpha^2(\Gamma^2 - 8\omega_0^2) - 2m^4t_c'\Gamma^2\omega_0^2(\Gamma^2 + 4\omega_0^2) - 4m^2\Gamma(\alpha^2 + 2m^2\Gamma^2\omega_0^2) + 2t_c'^3(4\alpha^2 + m^2\Gamma^2\omega_0^2)(\alpha^2 - m^2\omega_0^4) + m^2t_c'^2\Gamma(-4m^2\Gamma^2\omega_0^4 + \alpha^2(\Gamma^2 - 12\omega_0^2))].$$

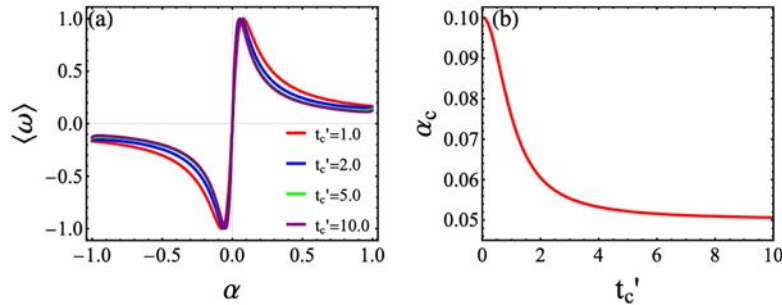


FIGURE 1. $\langle \omega \rangle$ as a function of α for different values of t_c' in (a) and α_c as a function of t_c' in (b). The other common parameters are $\Delta T = -2.0$, $\Gamma = 0.1$, and $m = \omega_0 = 1$.

In Fig. 1 (a), we have shown the plot of $\langle \omega \rangle$ as a function α for different values of t_c' . We observe that $\langle \omega \rangle$ shows a non-monotonic dependence on α . It increases with α , shows a maximum and then decreases. It is observed that as t_c' increases, the peak of $\langle \omega \rangle$ shifts progressively towards the left. This indicates that the critical $\alpha(\alpha_c)$, for which the system achieves maximum angular velocity, decreases with increase in t_c' . This behavior is reflected from Fig. 1(b), where α_c shows a decreasing function of t_c' . This monotonic decay suggests that, as the memory of the medium becomes stronger, a smaller asymmetry is sufficient to initiate maximum angular rotation of the particle.

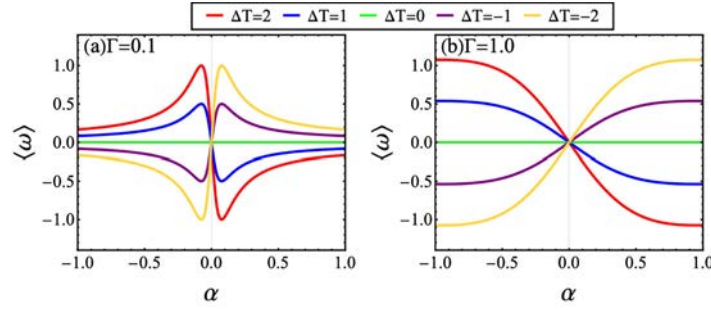


FIGURE 2. $\langle \omega \rangle$ as a function of α for different values of ΔT in (a), for $\Gamma = 0.1$ and (b), for $\Gamma = 1.0$. The other common parameters are $t'_c = m = \omega_0 = 1$.

In Fig. 2(a) and 2(b), we have plotted $\langle \omega \rangle$ as a function of α for the inertial regime ($\Gamma = 0.1$) and for overdamped regime ($\Gamma = 1.0$), respectively. It is evident that in the absence of a temperature gradient or potential asymmetry, the angular velocity $\langle \omega \rangle$ remains zero, indicating no rotational motion. Moreover, the introduction of a temperature gradient leads to a self-inversion of the particle rotation, depending on the sign of the product $\alpha \Delta T$. In particular, $\langle \omega \rangle$ is positive when $\alpha \Delta T < 0$ and it is negative for $\alpha \Delta T > 0$.

CONCLUSION

In summary, we have investigated the two-dimensional motion of a Brownian particle confined in an asymmetric harmonic potential and coupled to two thermal baths maintained at different temperatures. The system is immersed in a non-Markovian environment characterized by a finite memory timescale. From the exact calculation of angular velocity, we observe a non-monotonic dependence of angular rotation on the potential asymmetry. Further, the peak in angular velocity shifts toward the lower asymmetry values as the memory timescale increases, indicating that the asymmetry required for maximum rotation can be tuned by varying the persistence of memory. With increasing duration of persistence of memory, a lower asymmetry value is sufficient for attaining maximum angular velocity. Additionally, we observe a self-inversion in the rotational motion as the temperature gradient is varied. This suggests that tuning the asymmetry or temperature gradient, one can modulate the rotation in either the clockwise or counterclockwise direction.

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Impact of Roughness on the Transport Coherence of an Overdamped Rocking Ratchet

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Abstract: In this work, we investigate the transport coherence of an overdamped Brownian particle in a periodic rough potential driven by a time-dependent force in the presence of a thermal bath. We delve into the impact of roughness on the transport by analysing several transport properties such as, the current, effective diffusion coefficient, and Peclet number as a function of the amplitude of the rough potential. We find that roughness improves particle current and coherence at low temperatures and optimal values of the amplitude and spatial frequency of the rough potential.

INTRODUCTION

Brownian motion has been at the center of discussion and extensively studied since its discovery by the Scottish botanist Robert Brown in 1827. It is known that Brownian motion can be converted to directed motion by rectifying the random fluctuations. Such systems have their symmetry broken and are not in thermal equilibrium. This is the basic principle behind the Brownian motor [1]. Based on how the symmetry is broken, Brownian motors are classified as: Flashing ratchets [1], Rocking ratchets [1,2], Büttiker-Landauer ratchets [3], etc. While most previous studies on Brownian ratchets consider a smooth potential, in reality, most of the microscopic particles encounter a rough energy landscape [4, 5]. Therefore, it is necessary to understand how roughness in a potential will impact the transport behavior of the Brownian ratchet. Roughness is often believed to create a hindrance to the particle motion. Previous studies had shown the suppression of diffusion [6] as well as particle current [7] in the presence of a rough potential. However, in recent years, it has been reported that roughness in the potential promotes the particle transport in the presence of a time-dependent force [8] or a non-Gaussian noise [9]. Even though current and diffusion have been investigated in the presence of various rough potentials, the transport coherence of the Brownian ratchet has not been explored. The quantity that characterizes the coherence in the transport is known as the Peclet number. In this work, we have investigated the impact of roughness on the transport coherence of an overdamped rocking ratchet by analyzing the variation of Peclet number with parameters controlling the roughness in the potential. Our results show that roughness can enhance the transport coherence of the ratchet at optimal values of the amplitude and spatial frequency of the rough potential.

In the next section, we introduce the model and numerical methods employed in this work. Then we present our results and end with a conclusion.

METHODS

We have considered an overdamped Brownian particle in a periodic potential in the presence of thermal noise $\xi(t)$ and driving force $F(t)$. The following Langevin equation describes the dynamic behavior of the overdamped rocking ratchet:

$$\gamma \dot{x} = -V'(x) + F(t) + \xi(t) \quad (1)$$

Here, γ is the friction coefficient, and the time-dependent force takes the form $F(t) = a \sin \omega t$, where a and ω are the amplitude and frequency, respectively. The thermal fluctuations are modeled by a Gaussian white noise obeying the fluctuation-dissipation relation, $\langle \xi(t) \xi(t') \rangle = 2\gamma k_B T \delta(t - t')$, and whose mean is zero ($\langle \xi(t) \rangle = 0$). k_B is the Boltzmann constant, and T , the temperature of the system. The potential $V(x)$ is generated by superimposing a

fast-fluctuating function $V_1(x)$ (rough potential) on the asymmetric smooth potential, $V_0(x)$. Both $V_0(x)$ and $V_1(x)$ are spatially periodic with period $L = 1$, where,

$$V_0(x) = -\frac{1}{2\pi} (\sin 2\pi x + \frac{1}{4} \sin 4\pi x) \quad (2)$$

$$V_1(x) = -\varepsilon (c_1 \sin(2\pi\lambda_1 x) + c_2 \sin(2\pi\lambda_2 x)) \quad (3)$$

and,

$$V(x) = V_0(x) + V_1(x) \quad (4)$$

Here, ε is the amplitude of the rough potential, $V_1(x)$. λ_1 and λ_2 are the spatial frequencies such that $\lambda_2 = 2\lambda_1$. c_1 and c_2 are the amplitudes of the two sine functions. We note that $V_1(x)$ is also spatially asymmetric. The particle executes drift and diffusive motion. The transport parameter associated with the drift motion is the particle current, which is defined as,

$$\langle v \rangle = \lim_{t \rightarrow \infty} \frac{\langle x(t) \rangle}{t}. \quad (5)$$

The diffusion of the system is measured by the effective diffusion coefficient given by,

$$D_{eff} = \lim_{t \rightarrow \infty} \frac{(\langle x^2(t) \rangle - \langle x(t) \rangle^2)}{2t}. \quad (6)$$

In Eqs. (5) and (6), the angular brackets denote ensemble averaging over independent realizations of the thermal noise and initial positions of the Brownian particle. The diffusion is said to be enhanced when $D_{eff} > D_0$, where $D_0 = k_B T / \gamma$ is the free diffusion coefficient. In this work, we take $k_B = 1$ and $\gamma = 1$. The Peclet number quantifies the coherence of the particle transport, and it is expressed as,

$$Pe = \frac{L|\langle v \rangle|}{D_{eff}}, \quad (7)$$

where L is the characteristic length of the system, taken here to be the spatial period of the potential. When the drift motion overpowers the diffusion, the particle transport will be more coherent, resulting in a larger Pe ($Pe \geq 2$). For $Pe < 2$, randomness dominates, and the transport is incoherent. We numerically solve the Langevin equation using the stochastic Runge-Kutta 4th order algorithm, with a time step $dt \leq 10^{-2}$, and average over 3750 independent trajectories to calculate the various transport quantities. The initial position is randomly taken from the uniform distribution in the interval $(0, 1)$, respectively.

RESULTS AND DISCUSSION

In our model, the symmetry of the system is broken by choosing an asymmetric smooth potential [$V_0(x)$], driven out of equilibrium by a symmetric time-dependent sinusoidal force. Furthermore, the rough potential, $V_1(x)$, is also asymmetric. We have considered the adiabatic limit of the system by choosing a low driving frequency ($\omega = 0.25$). The amplitude of the time-dependent force is fixed at $a = 1.5$. Earlier, it was shown that the transport coherence is enhanced in this regime in the presence of only the asymmetric smooth potential, $V_0(x)$ [10], the model we have adopted in this work. Now, we check the impact on the transport by the addition of the asymmetric rough potential, $V_1(x)$. In this work, we fix $c_1 = 1$, $c_2 = 0.25$, vary λ_1 from 1 to 5 ($\lambda_2 = 2\lambda_1$), and study the transport properties as a function of the amplitude of roughness, ε , at a low temperature, $T = 0.01$ [Fig. 1]. We observe that there is an optimum value of ε at which the current reaches a peak. In our system, the roughness in the potential acts as a ladder for low to moderate amplitudes of roughness. In this regime, the tiny wells of the rough potential suppress the backwards motion of the particle and aid in overcoming the barrier. This results in the enhancement of the current. Large values of the

amplitude of roughness deepen the tiny wells, trapping the particle for a long time, reducing the particle current. There is also an optimum value of λ_1 (λ_2) at which the current is maximized.

To illustrate the impact on coherence, we also plot D_{eff}/D_0 and Pe . We observe that the effective diffusion coefficient decreases with the increase in the amplitude of roughness, and there is an optimal value of λ_1 (λ_2) at which D_{eff}/D_0 attains a minimum. At larger values of λ_1 (λ_2), we observe a marginal increase in the diffusion coefficient at larger values of ϵ , but it is always lower than D_{eff}/D_0 in the presence of only $V_0(x)$. The Peclet number is enhanced at an optimal value of the roughness amplitude when D_{eff}/D_0 has a minimum. This suggests that the drift motion is enhanced in the presence of roughness, resulting in coherent transport. We observe that adding a rough potential of optimal amplitude and spatial frequency boosts the transport coherence by almost a factor of 3 [see curve $\lambda_1=3$, in Fig. 1 (c)].

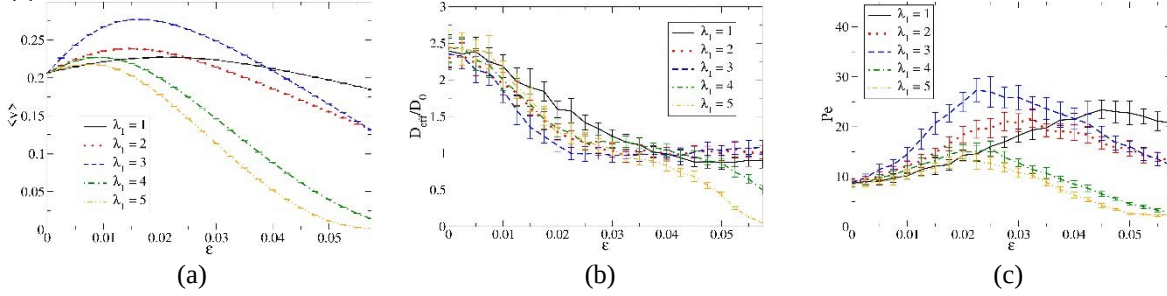


FIGURE 1. (a) Particle current, (b) Scaled effective diffusion coefficient, and (c) Peclet number as a function of ϵ . Here $\omega = 0.25$, $a = 1.5$, $c_1 = 1$, and $c_2 = 0.25$.

CONCLUSION

In this work, we studied how the roughness in the potential influences the transport of an overdamped rocking ratchet. We report that at low temperatures, roughness prevents the backwards motion of the particle by acting like a ladder, thus helping to overcome the potential barrier. As a result, the particle current is enhanced at optimal values of the amplitude and spatial frequency of the rough potential. In the considered operating regime, the diffusion also gets suppressed by the roughness, leading to an enhancement of transport coherence. When the roughness parameters are optimally chosen, the Peclet number is boosted by almost a factor of 3, generating highly regular transport.

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Transport Coherence of a Fluctuating force Brownian ratchet

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Abstract. The transport coherence of a Brownian particle driven by dichotomous perturbations, also known as the Fluctuating force ratchet or the run and tumble ratchet, is studied via numerical simulations of the overdamped Langevin equation. We analyze the particle current, effective diffusion coefficient, and the Peclet number (Pe), which characterizes the transport coherence, by carrying out simulations to explore the effects of the magnitude of the fluctuating force (v_0), the temperature and the switching rate τ of the fluctuating force, in achieving regular transport. The average current shows a non-monotonic dependence on the fluctuating force, while the diffusivity rises monotonically with increasing v_0 , suppressing the transport coherence. The effective diffusion coefficient increases, and the Peclet number, in general, decreases with increasing temperature. However, at low values of v_0 , there exists an optimal temperature at which Pe is maximized, though the transport coherence is poor. In the non-adiabatic regime and at low temperatures, Pe is just above the threshold at which transport is considered to be coherent.

INTRODUCTION

The random motion of pollen grains in water, reported by Robert Brown (1828) as a physical property of the microscopic particles and Einstein's theoretical description (1905), facilitates the study of non-equilibrium statistical mechanics in the subsequent centuries with Brownian motion as a foundation. The source of the random motion is thermal fluctuations, for a long time considered as noise, hindering the transport, later discovered as an indispensable phenomenon for microscopic transport. The systems achieving noise-induced directional transport by symmetry breaking (temporal or spatial) when driven out of equilibrium are called Brownian motors because these motors have been developed from passive Brownian particles, where we need to supply constant energy to overcome thermal fluctuations to extract work from the particles [1]. In this paper, we are considering a Brownian particle in a fluctuating force ratchet [2]. The model is similar to run-and-tumble particles in an asymmetric sawtooth potential, where our fluctuating force acts as a kind of self-propelled force of the active particle [3]. The fluctuating force can be generated by dichotomous noise with a magnitude v_0 which can take two values $\{+v_0, -v_0\}$ randomly. We are considering a medium with a high Reynolds' number, and hence the inertial effects are neglected. Our study is carried out to understand the effect of increasing v_0 , D_T and switching rate τ on the transport coherence of the system. We observe, in general, poor transport coherence across the parameter space. However, in the non-adiabatic regime and at low temperatures, marginally enhanced transport coherence is obtained.

THE MODEL

We consider a one-dimensional overdamped Brownian particle suspended in a thermal bath and subjected to an asymmetric saw-tooth potential $U(x)$ of spatial period L . The dynamics of the system can be described using the following Langevin equation:

$$\gamma \dot{x} = v_0 \sigma(t) - U'(x) + \sqrt{2D_T} \xi_x(t) \quad (1)$$

where, v_0 is the magnitude of the fluctuating force, D_T is the translational diffusion coefficient having a magnitude $k_B T / \gamma$, where k_B is the Boltzmann constant, T is the temperature and γ is the friction coefficient. $\sigma(t)$ is the dichotomous noise with a magnitude v_0 , which can take values either $+1$ or -1 randomly. The rate of flip from one

state to another is denoted by τ and the flip time is exponentially distributed. $\xi_x(t)$ is the unbiased ($\langle \xi_x(t) \rangle = 0$) and uncorrelated $\langle \xi_x(t) \xi_x(t') \rangle = \delta(t - t')$ Gaussian white noise. The piece-wise linear potential $U(x)$ is given by,

$$U(x) = \begin{cases} u_0 \frac{x}{\alpha}, & 0 \leq x \leq \alpha \\ u_0 \frac{L-x}{L-\alpha}, & \alpha \leq x \leq L \end{cases} \quad (2)$$

where, u_0 is the barrier height, L is the length of the potential with periodic boundary conditions [$U(x + L) = U(L)$] and α is the asymmetry parameter of the potential. To numerically solve Eq. (1), we carry out Brownian dynamics simulations using the stochastic Euler-Maruyama algorithm. We have taken the equation in dimensionless form, and hence the values of u_0 , L , γ and k_B are taken as 1. Hence, $D_T = T$, the temperature of the heat bath. The asymmetric parameter is kept constant ($\alpha = 0.8$) in our simulations, and we choose a time step $\Delta t = 0.0005$ in our simulations, and average over more than 10^4 independent realizations. At this value of α , the force due to the gentler and steeper side of the potential is -1.25 and 5, respectively.

The performance of the motor is determined by the transport properties, which include the average particle current $\langle v \rangle$, effective diffusion coefficient D_{eff} and the Peclet number, Pe . They are calculated from numerical simulations via the following equations:

$$\langle v \rangle = \lim_{t \rightarrow \infty} \left\langle \frac{x(t) - x(0)}{t} \right\rangle, \quad D_{eff} = \lim_{t \rightarrow \infty} \frac{MSD}{2t}, \quad Pe = \frac{L \langle v \rangle}{D_{eff}}, \quad (3)$$

where the mean square displacement (MSD) is given by $\langle x^2(t) \rangle - \langle x(t) \rangle^2$. When the drift overcomes diffusion, the transport becomes coherent and the motion becomes regular. This can be identified from the value of the Peclet number (for coherent motion, $Pe > 2$).

RESULTS AND DISCUSSIONS

In Fig. 1(a), we plot the Peclet number as a function of v_0 for different values of D_T in the adiabatic regime ($\tau = 5$). The Peclet number exhibits a monotonic decrease with v_0 and transport is incoherent. A slight bump in Pe is observed in the region where the average current peaks, but it is always less than 2. In the inset of Fig. 1 (a), the average current and effective diffusion coefficient are plotted as functions of v_0 . There is an optimal value of v_0 , whose magnitude coincides with that of the force due to the steeper side of the potential ($v_0 = 5$), at which the average current peaks, while D_{eff} monotonically increases with v_0 . The monotonic rise in D_{eff} shows the particle crossing both sides of the barrier, thus suppressing the average current and the transport coherence.

In Fig. 1 (b), the average current is plotted as a function of D_T for different values of the switching rate τ and v_0 . At low values of τ the particle changes its direction more frequently, and the system is in the non-adiabatic state. The particles do not have enough time to cross the gentle side of the potential, resulting in a smaller current. With increasing τ , the particle has enough time to cross the gentle side of the potential and move in the forward direction, while motion in the reverse direction is suppressed due to the asymmetry of the potential, thus leading to a larger current in the positive direction. We also observe that the current is optimized at finite D_T only at low values of v_0 ($v_0 \leq 1.25$, the magnitude of the force due to the gentler side of the potential), where the amplitude of the fluctuating force is weak or in the non-adiabatic regime ($\tau = 0.1$). At all other values of v_0 and τ , thermal fluctuations do not enhance the particle current. Figure 1(c) shows the variation of D_{eff} as a function of D_T . At low values of v_0 ($v_0 = 1.25$), when less energy is pumped to the system by the fluctuating force, the diffusivity increases rapidly as the thermal energy increases, followed by a gradual increase. At larger values of the fluctuating force, where diffusivity is already high, and at low D_T , D_{eff} changes slowly till large temperatures, when it begins to monotonically increase.

In Fig. 1(d), we plot the Peclet number as a function of D_T with increasing values of v_0 and τ . We observe that in the adiabatic regime, thermal fluctuations increase the coherence only at low values of v_0 . However, Pe is always less than 2, showing that the motion is incoherent. In the non-adiabatic regime ($\tau = 0.1$), marginal transport coherence is achieved ($Pe \approx 2.5$) at low values of D_T but it decreases with increasing magnitude of thermal fluctuations.

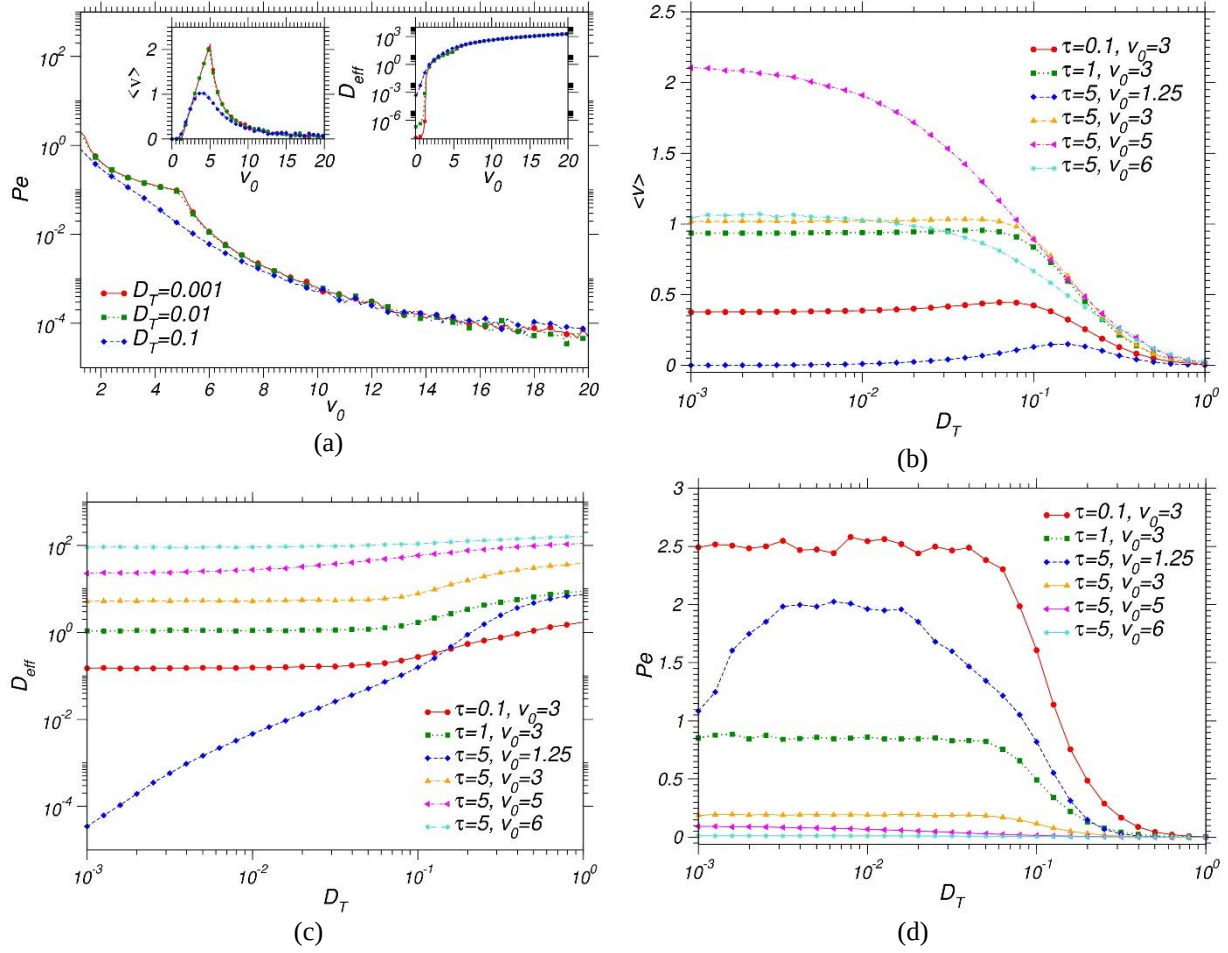


FIGURE 1. (a) Pe versus v_0 at various D_T . Inset of (a) shows $\langle v \rangle$ and D_{eff} as a function of v_0 . Here, $\tau=5$. In (b), (c), and (d), $\langle v \rangle$, D_{eff} , and Pe , respectively, are plotted as functions of D_T for different values of τ and v_0 .

CONCLUSION

In this work, we have explored the transport coherence of Brownian particles in a fluctuating force ratchet. We observed that the particle current can be optimized as a function of the magnitude of the external fluctuating force. Thermal fluctuations increase the current, but only at small magnitudes of v_0 , when the fluctuating force is less than or equal to the force corresponding to the gentler side of the potential. The motor is relatively more coherent in the non-adiabatic regime at low temperatures, but the overall transport coherence is poor.

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Tuning Fluctuation-Induced Casimir Forces in Porous Colloidal Systems Using Embedded Metal Nanoparticles

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Abstract. Casimir force is a direct macroscopic manifestation of quantum field theory and plays an important role in nanoscience and nanotechnology owing to their piconewton strength, short range and tunability with surrounding temperature and shape of the objects involved. This study explores the enhancement of Casimir forces in porous polystyrene microspheres via incorporation of gold nanoparticles (AuNPs). Using the Boundary Element Method we simulated interactions between (i) isolated AuNPs, (ii) porous polystyrene spheres and (iii) hybrid structures with embedded AuNPs. Porous polystyrene spheres increased Casimir forces from sub-piconewton to several piconewtons, and incorporation of AuNPs inside enhanced the interaction range beyond 100 nm. While isolated AuNPs show negligible forces beyond this range, hybrids maintain measurable attraction due to the composite's collective electromagnetic response. The results highlight nanoparticle–polymer hybrids as a tunable platform for controlling fluctuation-induced forces, offering pathways for designing responsive colloidal assemblies and controlling nanoscale interactions in soft matter systems.

INTRODUCTION

Quantum field theory predicts that vacuum is permeated by zero-point electromagnetic fluctuations, giving rise to measurable forces between material boundaries. In 1948, Hendrik Casimir calculated that two parallel metallic plates in vacuum experience an attractive force due to the restriction of electromagnetic mode density between them compared to the surrounding space [1]. Lifshitz subsequently extended this framework to real materials by considering charge fluctuations within the materials themselves, providing a more general theory applicable to dielectric and conducting media [2]. In soft matter and colloidal systems, where typical separations range from nanometers to micrometers, Casimir forces become particularly relevant. These fluctuation-induced interactions can significantly influence colloidal stability, self-assembly processes, and the mechanical properties of nanostructured materials³. The magnitude and range of Casimir forces depend critically on the dielectric properties of the interacting materials and the intervening medium, making them tunable through material selection and structural design.

Porous polystyrene microspheres are widely used in soft matter and materials science due to their controlled porosity, which allows tunable surface area, permeability, and mechanical compliance. These properties enable applications in controlled drug delivery, responsive materials, photonic devices, and tissue engineering scaffolds. Their high surface area supports extensive chemical functionalization, while periodic pore structures can generate photonic effects. Incorporating metallic nanoparticles into such porous matrices yields multifunctional composites with enhanced optical, electronic, and electromagnetic properties [3, 4]. In the present work, we explored the possibility of enhancing the Casimir forces in one such system - porous polystyrene microspheres incorporated with gold nanoparticles.

System Configuration and Force Calculation

Visualizing the zero-point energy cavity modes between the boundaries and simulating the Casimir interactions is discordant and it becomes hard in the case of material media. Simulating the forces using material-fluctuation viewpoint is more advantageous than zero-point energy summation. In this work, to ascribe the forces between the soft matter systems we have used Boundary element method [5] to simulate the system and screen shots of various configurations are shown in figure 1.

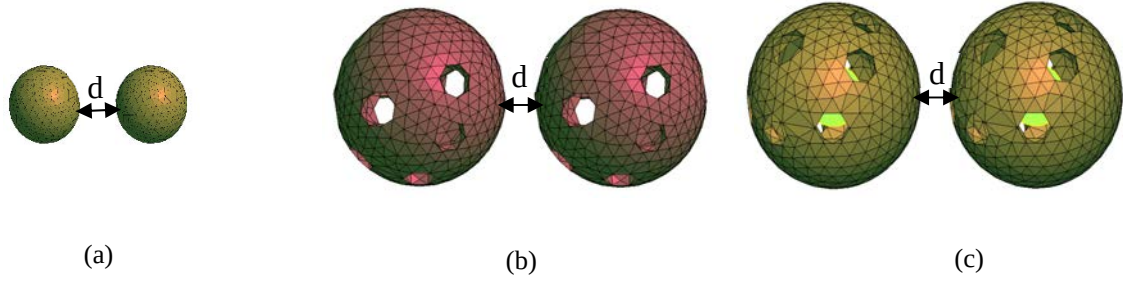


FIGURE 1. (a) Two gold spheres (radius 50 nm). (b) Two porous polystyrene particles (radius 150 nm) with randomly introduced pores. (c) Porous polystyrene particles containing embedded gold spheres (bright green) of radius 50 nm. Casimir interactions are simulated for each configuration at varying separation distances.

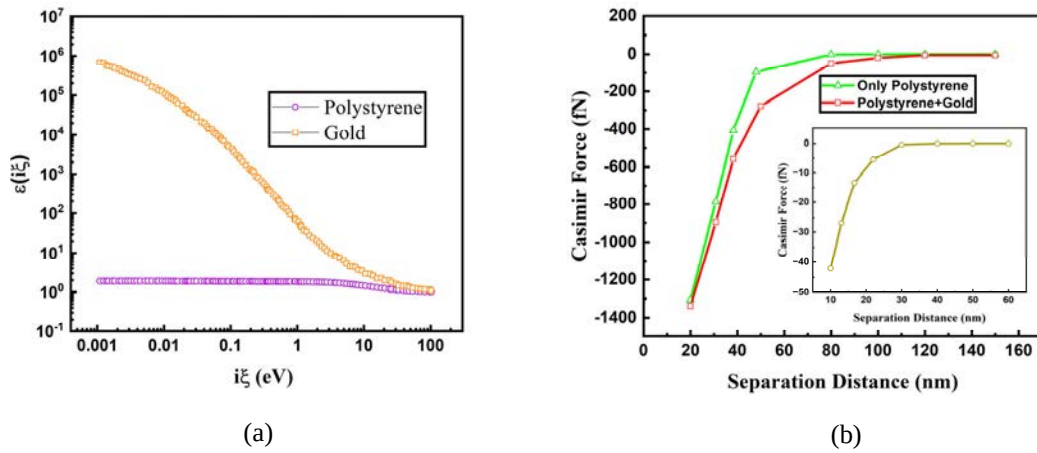


FIGURE 2. (a) Dielectric response of gold and polystyrene spheres versus imaginary frequency, showing gold's much higher permittivity across the spectrum. (b) Casimir interaction between two porous polystyrene particles (green) and polystyrene with embedded gold spheres as a function of separation distance. Inset: interaction between gold spheres alone. Dimensions are as in Fig. 1.

RESULTS AND DISCUSSIONS

To mimic the transient oscillatory behavior of electromagnetic fluctuations travelling with the objects under consideration we calculate the dielectric response as a function of imaginary frequency as shown in fig. 2(a) using Kramer-Kronig relations. Figure 2(a) presents the frequency-dependent dielectric response of both materials evaluated at imaginary frequencies. Gold exhibits a monotonically decreasing dielectric function from approximately 10^6 at low frequencies to near unity at high frequencies, characteristic of metallic response dominated by free electron contributions [6]. In contrast, polystyrene shows a much weaker frequency dependence, with values ranging from 2.5 to 2.0 across the same frequency range [7]. The stark contrast in dielectric responses between gold and polystyrene creates significant electromagnetic field gradients at their interfaces, which is crucial for enhancing Casimir interactions in the hybrid system. The porous structure of polystyrene effectively creates a composite material with an effective dielectric function intermediate between pure polystyrene and the surrounding medium (air). The Casimir force between two 50 nm radius gold spheres shows rapid decay with separation distance (Fig. 2b, inset). Beyond $d = 100$ nm, the force becomes negligible, consistent with the small size spheres. The larger size ($r = 150$ nm) and porous structure of polystyrene spheres result in significantly enhanced Casimir forces to the order of pico-Newtons, compared to isolated gold nanoparticles. The porosity reduces the effective dielectric contrast with the surrounding medium, but the larger interaction area more than compensates for this reduction. Adding gold nanoparticles (AuNPs)

increases the attraction between polystyrene particles even when separated by over 100 nm, whereas forces between gold spheres alone decay rapidly below 100 nm. This indicates that AuNPs modify force magnitude through a collective electromagnetic response, with embedded nanoparticles creating highly polarizable regions that alter the composite's overall electromagnetic behavior.

CONCLUSIONS

This computational study demonstrates that incorporating gold nanoparticles into porous polystyrene microspheres significantly enhances Casimir forces between colloidal particles. The hybrid system shows a 2.5-fold increase in Casimir force magnitude compared to pure porous polystyrene spheres at short separations ($d < 50$ nm). While isolated 50 nm gold nanoparticles show negligible forces beyond 100 nm separation, the hybrid system maintains measurable attractive forces up to 150 nm and beyond. The enhancement arises from the collective electromagnetic response of the composite structure rather than simple addition of individual particle contributions. These results suggest that strategic incorporation of metallic nanoparticles in porous polymer matrices provides a powerful approach for controlling fluctuation-induced forces in soft matter systems. The ability to tune both the magnitude and range of Casimir interactions through material composition and structure opens new possibilities for designing responsive colloidal materials.

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Effect of Macromolecular Crowding on Linear and Ring Polymer

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Abstract: Biopolymers such as DNA, RNA, FtsZ etc, exist in both linear and ring conformations, each exhibiting distinct dynamical and structural behaviours in crowded cellular environments. Using extensive Langevin dynamics simulations, we made a comparative study on the structural and dynamical properties of linear and ring polymer with varying flexibility under different crowding conditions. While the mean time-averaged mean-squared displacement (TAMSD) shows a similar dependence on packing fraction and flexibility for both topologies, the radius of gyration of ring polymers is significantly more sensitive to changes in crowding and flexibility with respect to linear polymers.

INTRODUCTION

The importance of crowding in biology is gaining increasing attention. The cellular interior is highly crowded with macromolecules, which plays a crucial role in various biological processes [1]. Polymer characteristics depend on the different aspects of the crowded medium, for example, packing fraction, ordered, polydispersity etc. In ordered media, compaction of polymer is more and dynamics is slow in long-time [2]. Crowding environment facilitates in the translocation of polymer [3]. The diffusivity of the polymer is regulated due to presence of nanoparticles [4]. Depending on the topology of a polymer, how it responds to an alteration of the crowded medium, is the central theme of this study. However, crowded induced depletion interaction effect the compaction of an isolated ring polymer [5]. Depending on the density of the crowded environment, polymer exhibits distinct behaviors. In our model, we investigated how dynamic crowders effect the migration of the linear and ring polymer differently. We notice there is a considerable difference in conformational properties of linear chain and ring while exploring the complex media.

METHODOLOGY

We mimic the crowded environment by randomly placing static particles inside a 2D square box of size 35σ in both directions. By increasing the number of crowders we can increase the packing fraction of the system. Both linear and ring polymer are modeled as bead-spring polymer where each polymer consists of $N_m = 40$ monomers of size (σ_m) equal to the crowding particle diameter σ_c , i.e. $\sigma_m = \sigma_c = \sigma$. The monomers of each polymer are connected by finitely extensible nonlinear elastic (FENE) bond potential, $U_{FENE}(r) = -(1/2)kr_0^2 \ln[1 - (r/r_0)^2]$, where r is the center-to-center distance between two adjacent monomers. The maximum distance (r_0) between two beads connected via a FENE bond was chosen to be 1.5 with spring constant $k = 30$. The excluded volume interactions between polymer beads and crowders are modeled with the short-ranged and shifted purely repulsive Weeks-Chandler-Anderson (WCA) potential,

$$U_{WCA}(r_{ij}) = \begin{cases} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \epsilon_{ij}, & r_{ij} < 2^{1/6}\sigma_{ij} \\ 0, & r_{ij} \geq 2^{1/6}\sigma_{ij} \end{cases} \quad (1)$$

where r_{ij} is the center-to-center distance between particles i and j and the interaction strength $\epsilon_{ij} = 1$.

The stiffness of the polymers is accounted through the bending potential, $U_{BEND}(\theta_i) = \kappa(1 + \cos \theta_i)$, where κ is the bending modulus and θ_i is the angle between bond vectors i and $i + 1$. We change the flexibility of the polymer

by changing κ values i.e. $\kappa = 0$ means fully flexible and as we increase the κ values the stiffness of the semi-flexible polymer increases.

In our system the total potential energy can be written as, $U(r_i) = U_{FENE} + U_{WCA} + U_{BEND}$. In our simulation, σ , $k_B T$ and $\tau = \sqrt{m\sigma^2/k_B T}$ set the units of length, energy, and time scales, respectively. Where k_B is the Boltzmann constant, T is the temperature and γ is the friction coefficient of the system. Here, we consider a low friction limit i.e. $\gamma = 0.7$. Therefore, the dynamics is practically underdamped. The equation of motion for the system is the underdamped Langevin equation which is defined by

$$m \frac{d^2 r_i}{dt^2} = -\nabla U(r_i) - \gamma \frac{dr_i}{dt} + f_i(t) \quad (2)$$

where m is the mass of each bead or crowders, $\gamma \frac{dr_i}{dt}$ is the viscous drag force. The thermal force $f_i(t)$ is the Gaussian random white noise with zero mean and variance $\langle \hat{f}_i(t') \cdot \hat{f}_j(t'') \rangle = 4\gamma k_B T \delta_{ij} \delta(t' - t'')$ in two dimensions.

The volume occupied by the crowding particles is defined as $V_c = N_c 4\pi\sigma_c^3/3$, where N_c is the number of crowders. The packing fraction, $\phi_c = V_c/V$, where V is the volume of the simulation box. All the simulations are performed at a temperature of $T = 1.0$ using Langevin thermostat, and the velocity-Verlet algorithm is used to integrate the equation of motion. To relax the systems, it is first equilibrated for 10^6 steps at integration timestep of $\Delta t = 10^{-3}$. Then, for data collection of 100 identical systems, each simulation is carried out for 10^7 steps at the same timestep and the coordinates are recorded every 100 steps. Freely available open-source molecular dynamics package Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is used to carry out the simulations.

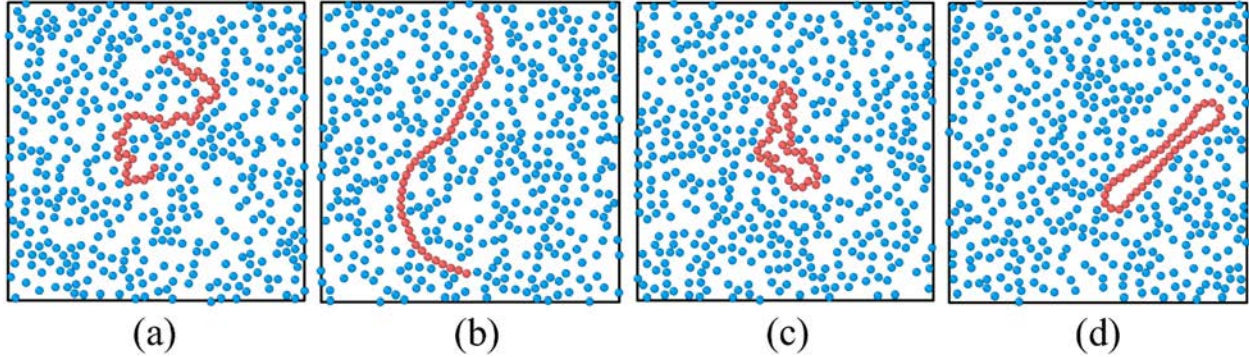


FIGURE 1. Schematic representation of a flexible and a semiflexible polymer in crowded environment with packing fraction ($\phi_c = 0.3$) for linear and ring polymer. Linear polymer: (a) flexible ($\kappa = 0$), (b) semi-flexible ($\kappa = 30$); Ring Polymer: (a) flexible ($\kappa = 0$), (b) semi-flexible ($\kappa = 30$).

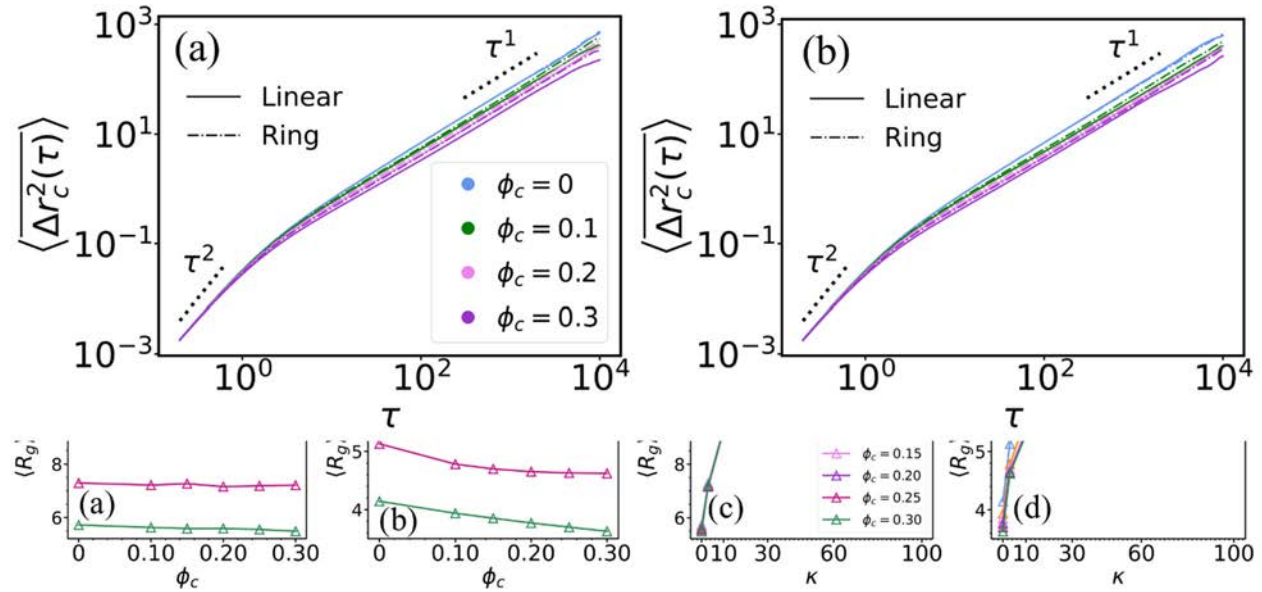
RESULTS

To quantify the dynamical behavior of the linear and ring polymer, first we compute the ensemble-averaged of the individual time-averaged mean squared displacement (TAMSD)[6], $\langle \overline{\Delta r_c^2(\tau)} \rangle$, of the center of mass of both polymers keeping semi-flexibility (κ) fixed, as a function of lag time τ , at different ϕ_c . Both type of polymers show small time super diffusion ($\sim \tau^2$) and longtime normal diffusion ($\sim \tau^1$). Figs. 2(a) and 2(b) show the variation of TAMSD for both flexible ($\kappa = 0$) and semi-flexible ($\kappa = 30$) linear and ring polymer, respectively. As both the crowders and polymers are free to move, crowders cannot impact significant effect on the movement of the polymer. For conformational change of the polymers, we calculated mean Radius of Gyration, $\langle R_g \rangle$. In case of linear polymer, $\langle R_g \rangle$ increases pronouncedly with κ , saturates at higher κ and crowding has no effect on it as shown in Figs. 3(a) and 3(c). For the ring polymer, $\langle R_g \rangle$ varies strongly with κ . Effect of κ is much more prominent for low ϕ_c . In Figs. 3(b) and

3(d), saturation of $\langle R_g \rangle$ is faster for lower ϕ_c . It represents, for intermediate κ values, higher fraction causes a decrease in the average extent of ring polymer.

FIGURE 2. Time-Averaged Mean Squared Displacement (TAMSD) of the centre-of-mass of linear and ring polymer in crowded environments at varying packing fractions (ϕ). (a) flexible ($\kappa=0$) and (b) semiflexible ($\kappa=30$).

FIGURE 3. Mean radius of gyration, $\langle R_g \rangle$ as a function of packing fraction (ϕ_c) at different flexibility (κ) for linear (a) and ring (b) polymers, and as a function of flexibility (κ) at different ϕ_c for linear (c) and ring (d) polymer. In both plots (a) and (b), from



lower to upper, the values of flexibility are $\kappa = 0, 3, 10, 30, 60, 100$ which are represented by different colours.

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Intelligent Multifunctional Hydrogel for Soft Robotic Applications

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Abstract. Intelligent multifunctional hydrogels are compact materials with their unique structural properties and stimulus responsiveness. They have potential applications in domains such as energy harvesting, biomedical fields, soft sensors, micro-biomechanics, and soft robotics for medical care. In this work, we synthesize a polyvinyl alcohol (PVA), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), and graphene oxide (GO)-based multifunctional piezoelectric hydrogel using organic solvents. This study explores the piezoelectricity and piezoresistive property of the hydrogel. The piezoelectric response of the hydrogel was observed under constant force tapping, and piezoresistivity was demonstrated through strain-sensing capability.

INTRODUCTION

Multifunctional hydrogels are soft, intelligent materials composed of hydrophilic polymer networks. The formation of a 3D hydrogel network relies on the physical, chemical, and dual or multiple crosslinking of its constituent polymer molecules. Due to the hydrophilicity of the constituent polymer molecules that comprise the hydrophilic phase, these have a propensity to capture and release water molecules in response to physical stimuli, such as humidity and temperature [1]. As a result, hydrogels have a relatively low elastic modulus [2]. These materials are compact and multifunctional due to their sensitivity to various types of physical or chemical stimulation. Multifunctional hydrogels are composited with various types of nanofillers to develop new functionalities in them or to synergize their existing properties. Recently, Guo *et al.* reported a self-powered, multifunctional, transparent hydrogel-based multimodal IoT system to monitor sunlight and wind speed for plants, paving the way for future smart farming [3]. Lee *et al.* [4] reviewed multifunctional hydrogels for advanced cancer treatment and their potential to integrate multiple types of cancer treatments, thereby synergizing the effectiveness of the treatment.

In this work, we synthesize an intelligent, multifunctional hydrogel composed of polyvinyl alcohol (PVA), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), and graphene oxide (GO) using the freeze-thaw method and study its piezoelectric response and piezoresistivity or strain-sensing property. PVA and PVDF-HFP were chosen for a multicomponent hydrogel matrix, and the GO was taken as a nanofiller material. PVA is a hydrophilic polymer that tends to trap water molecules, and PVDF-HFP is a piezoelectric polymer that introduces the piezoelectric activity and an ionic conductivity due to the presence of amorphous HFP group. Additionally, its optimized fraction in the hydrogel matrix enhances the strength of the hydrogel. GO has a hexagonal honeycomb lattice with various types and an abundant number of functional groups attached across the 2D plane, providing interaction sites for the functional groups of the polymeric units in proximity. GO filler is used to enhance the β -phase fraction, thereby improving the piezo-response of the hydrogel and increasing its potential to generate new functionalities and synergize existing ones.

MATERIALS AND METHODS

Materials and Synthesis of the Hydrogel

1 g of PVA was first dissolved in 10 mL of DMSO, while 1 g of PVDF-HFP was prepared separately in 4 mL of DMF. Each solution was stirred individually for 1 hour, after which they were combined and stirred together for an additional hour. A 0.015 g amount of GO, approximately 0.75% of the total sample, synthesized using Hummer's method [5], is dissolved in 3 mL of DMSO through the ultrasonication process. Subsequently, it is added to the stirred

mixture to obtain the final solution. The final homogeneous solution is freeze-thawed for multiple cycles, followed by a solvent exchange process to obtain the hydrogel.

Piezo-response and Strain-sensing

A device with dimensions $\sim 1.5 \times 1.5 \text{ cm}^2$, having the hydrogel sample sandwiched between the electrodes, is fabricated. This device is connected to the source meter (Keithley, 2611B) to measure the voltage. As the device is tapped with a nearly constant pressure of $\sim 150 \text{ N/m}^2$, this results in voltage peaks. For the demonstration of strain sensing, a hydrogel sample with an initial length (l_0) of 3 cm is prepared and connected to the source meter. The sample is then stretched by 1 cm in each step up to 8 cm and relaxed in the same manner.

CHARACTERIZATION

Fourier transform infrared spectroscopy (FTIR) (Spectrum-400, PerkinElmer) was used to identify and understand the interaction (physical or chemical) between the constituent materials in the hydrogel. An X-ray diffraction (using PAN Analytical EMPYREAN, $\lambda = 1.5409 \text{ \AA}$) test was conducted for confirming the results obtained from the FTIR spectra.

RESULTS AND DISCUSSION

Figure 1 (a) presents the FTIR spectrum of the PVA + PVDF-HFP + GO hydrogel. The peaks highlighted with green asterisks are assigned to the PVDF-HFP phase. In particular, the prominent bands at 839 cm^{-1} , 1234 cm^{-1} , and 1277 cm^{-1} are characteristic of the β -phase, corresponding to the piezoelectric form of PVDF-HFP [6]. Peaks marked with dots (light blue) at 916 , 1143 , and 1325 cm^{-1} correspond to PVA [7] polymer, and those marked with parallelograms (violet) at 1093 , and 1653 cm^{-1} correspond to GO [5] nanofiller.

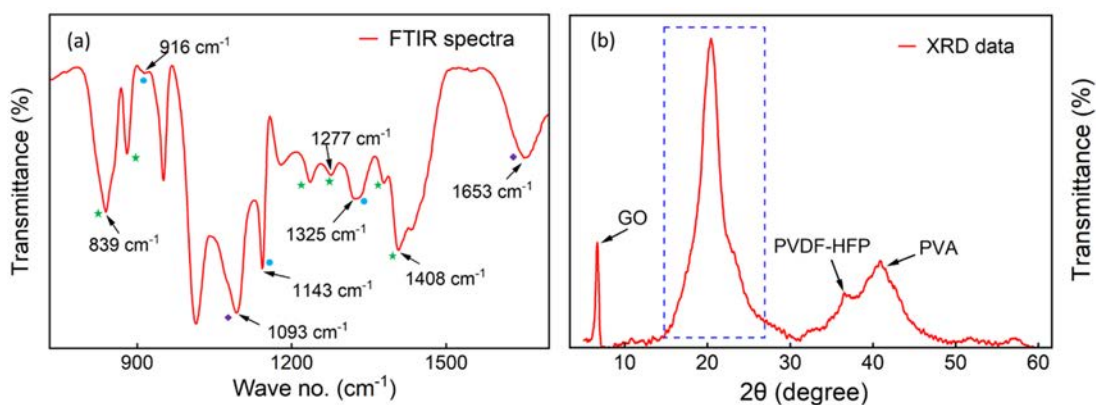


FIGURE 4. (a) and (b) are the FTIR spectra and XRD diffractogram of the PVA + PVDF-HFP + GO hydrogel.

In Fig. 1 (b), the XRD diffractogram of PVA has two peaks corresponding to 101 and $10\bar{1}$ near $2\theta = 20^\circ$ and one peak at 41° [7], PVDF-HFP has multiple peaks at 18.3° , 19.7° , and 21.2° , and one at 37° [6], and a peak at $2\theta = 6.7^\circ$ corresponds to the GO [5]. In the FTIR spectra of the hydrogel in Fig. 1 (a), the overall spectra indicate a physical interaction among the constituent materials. The presence of the individual characteristic peaks of the constituents and a broader peak (enclosed in a dotted box) observed near $2\theta = 20^\circ$ (see Fig. 1 (b)) in the XRD diffractogram, confirms the presence of the constituent materials and physical interactions among them [6]. Figure 2 (a) shows the piezoelectric response of the hydrogel sample when tapped with a constant force with a cycle of 2 seconds. Each tapping event produces a noticeable increase in voltage, which can be attributed to the presence of the β -phase of PVDF-HFP. The fluctuations observed in the signal arise from contact variations at the electrode-hydrogel interface (see Fig. 2 (a)) [6]. Figure 2 (b) illustrates the increase and decrease in resistance during stretching and relaxation of the sample, caused by changes in its dimensions under applied strain, demonstrating its suitability for strain-sensing applications.

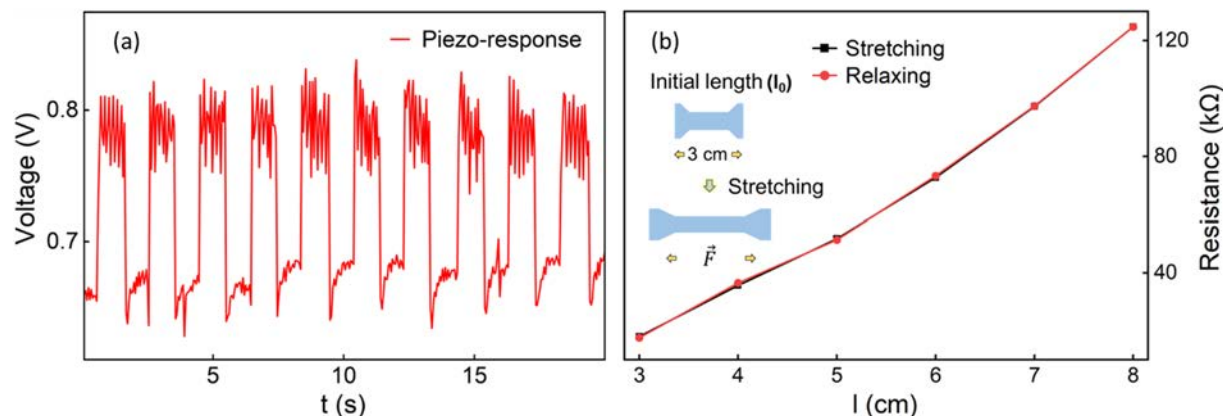


FIG 2.(a) Piezoelectric voltage response of the hydrogel;(b)piezo-resistive property of the hydrogel or strain-sensing.

CONCLUSION

Multifunctional hydrogels are soft materials with numerous applications in various domains. These can be tailored for sought-after properties with suitable nanofillers. Here, we synthesized a multifunctional PVA and PVDF-HFP-based piezo-electric hydrogel incorporated with 2D nanofiller GO. This hydrogel exhibits a piezoelectric response that lasts longer than that of other polymeric materials, and it also possesses strain-sensing capability. In the future, we will investigate various types of nanofillers to synergistically enhance the desired properties of hydrogels, as well as develop hydrogel-based soft metamaterials and explore their applications.

ACKNOWLEDGEMENTS

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Growth and Characterization of $(C_2H_5)_2ZnCl_4$ Hybrid Single Crystals for Nonlinear Optical Applications

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Abstract: The current study aims to explore the organic-inorganic hybrid material diethyl zinc chloride $(C_2H_5)_2ZnCl_4$ single crystal development and nonlinear optical (NLO) characteristics to comprehend its possible uses in photonic and optical devices. A slow-evaporation approach was used to synthesize high-quality single crystals of $(C_2H_5)_2ZnCl_4$ with few defects to initiate the investigation. There is little impurity in the developed crystal, and the crystallites have acceptable quality; thus, we can say that the crystal structure is orthorhombic. Fourier Transform Infrared spectroscopy (FTIR) reveals that the linked chemical has many functional groups. In ultraviolet-visible spectroscopy, the optical band gap is determined. The material exhibits considerable optical switching, frequency conversion, and NLO responses.

1. INTRODUCTION

The combination of organic and inorganic components in hybrid materials has drawn much interest for the fascinating optical properties and their potential applications in areas such as photonic, optoelectronic, and nonlinear optics (NLO). Their single crystals are highly transparent, structurally stable, and have better NLO properties that can be used in the fields of frequency conversion, optical switching, laser technology, etc. Of these materials, Diethyl zinc chloride (DEZC) $(C_2H_5)_2ZnCl_4$ has good optical transparency in the visible and near-infrared (NIR) region. The zinc chloride part is thermo- and chemically stable, and the organic part allows flexibility in crystal engineering. However, investigation of NLO and crystal growth properties of it is still limited [1].

2. EXPERIMENTAL METHODOLOGY

2.1 Materials and Synthesis

Diethyl zinc ($Zn(C_2H_5)_4$): The organozinc compound functions as a highly reactive substance that requires handling under an inert atmosphere due to its pyrophoric properties.

Hydrochloric Acid (HCl): Aqueous solution with high concentration serves to introduce chloride ions.

Formation of $(C_2H_5)_2ZnCl_4$: The combination of diethyl zinc with hydrochloric acid creates diethyl zinc chloride.

Controlled Evaporation: The controlled evaporation process takes place at 25–30°C while maintaining a steady temperature to produce defect-free, large single crystals. The grown crystal of $(C_2H_5)_2ZnCl_4$ is shown in Figure 1.

2.2 Solubility Test: For the solubility test took a small amount of diethyl zinc chloride in its solid form. In the present investigation, different solvents such as Distilled water, Ether, and Ethanol [2] were used. The solubility graph is shown in Figure 2.

3. CHARACTERIZATION METHODS

X-Ray Diffraction (XRD) Analysis

The X-ray diffraction (XRD) was to be done on a powder sample of diethylzinc chloride $(C_2H_5)_2ZnCl_4$. The XRD of $(C_2H_5)_2ZnCl_4$ is shown in Figure 3. The Miller indices (hkl) values were calculated by using Bragg's equation $n\lambda = 2d\sin(\theta)$. The crystallite size, which was calculated using Scherer and $[\delta = 15^\circ \beta \cos(\theta) / 4aD]$, the formula. The lattice parameter of $(C_2H_5)_2ZnCl_4$ calculated from XRD is in close correlation with the reported value in literature [3]. XRD analysis provides accurate lattice measurements, supporting optimized optical device development.

TABLE 1. XRD data of $(C_2H_5)_2ZnCl_4$ single crystals

Parameters	(C ₂ H ₅) ₂ ZnCl ₄ single crystal
Crystal Structure	Orthorhombic
Crystallography angle (Degree)	$\alpha = \beta = \gamma = 90^\circ$
Highly intense peak at 2θ (degree)	20.10°
Miller Indices (hkl) value at the prominent peak	(102)
Lattice Constants (Å)	a = 8.123 Å, b = 10.456 Å, c = 12.789 Å.
Unit cell volume (Å) ³	1086.222
Mean Crystallite size (nm)	40.14

Fourier Transform Infrared (FTIR) Spectrum

The analysis of functional groups in a molecule is shown by the Fourier Transform Infrared (FTIR) spectrum, which displays important absorption bands. The FTIR spectra were acquired using a spectrometer between 4000-400 cm⁻¹. Figuring out the FTIR spectrum (4). The spectra reveal vibrations at 2935 cm⁻¹ caused by the ethyl groups. This could happen because of the ethyl groups' symmetric and asymmetric C-H bond stretching [4]. At 532 cm⁻¹, the stretching of the Zn-Cl bond is seen in the lower frequency range.

Ultraviolet–Visible (UV–Vis) Spectrum

The UV-Vis spectrum data bring out information about the absorption spectrum, optical energy band gap, which depends on the electronic transition between the molecules of the compound. UV-Vis spectrum is taken in the range of wavelength 200-1000 nm. UV-Vis absorption spectrum of (C₂H₅)₂ZnCl₄ Single Crystal shown in Figure 5. The figure (6) shows the optical energy band gap. The measurement of absorbance was used to compute the absorption coefficient (α), and the photon energy value ($h\nu$) was derived by dividing 1240 by λ (eV). The material's huge optical band gap, along with its remarkable chemical and thermal stability, makes it an ideal candidate for high-power laser applications [5].

Nonlinear Optical (NLO) Property

Kurtz and Perry powder technique was used to test the SHG efficiency of the produced crystals. The Nd: YAG laser's output ($\lambda = 1064$ nm) was utilized as the source. A capillary tube with a diameter of 0.154 mm was filled with powdered samples, and this LASER was utilized to light them. Table 2 shows the conversion efficiency of the (C₂H₅)₂ZnCl₄ crystal.

TABLE 2. SHG efficiency data of (C₂H₅)₂ZnCl₄ crystal

NLO Sample	Input (mJ/pulse)	SHG output Signal in (mV)	SHG efficiency
KDP (reference material)	2.9	55	1
(C ₂ H ₅) ₂ ZnCl ₄ crystal (w.r.t KDP)	2.9	70	1.27

The enhancement of the second-order nonlinear response in (C₂H₅)₂ZnCl₄, compared to KDP, indicates its potential for NLO applications. Its phase-matching capabilities and strong SHG effect make it suitable for optical modulation, optical switching, and optical limiting devices.

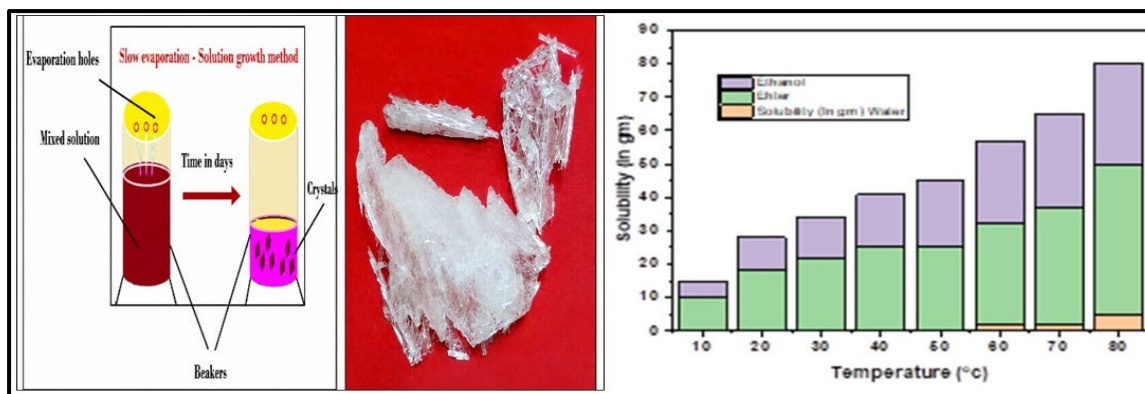


FIG 1. Solution Growth Setup, $(C_2H_5)_2ZnCl_4$ grown single crystal

FIG 2. Solubility test graph of $(C_2H_5)_2ZnCl_4$

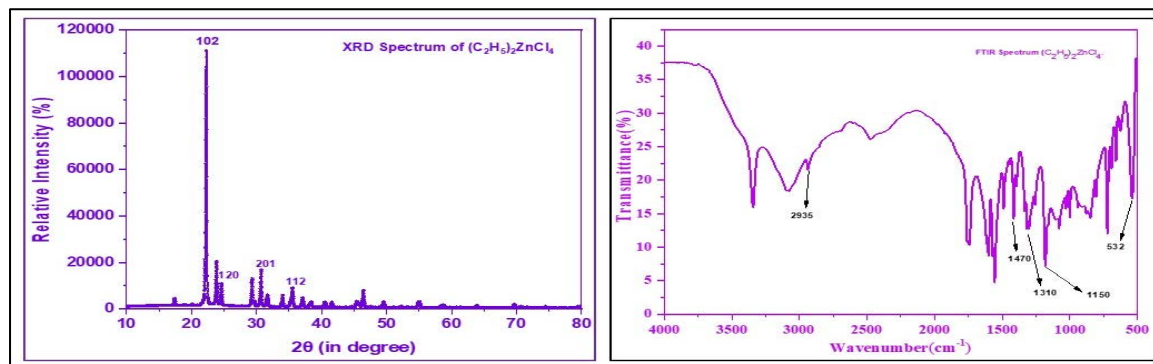
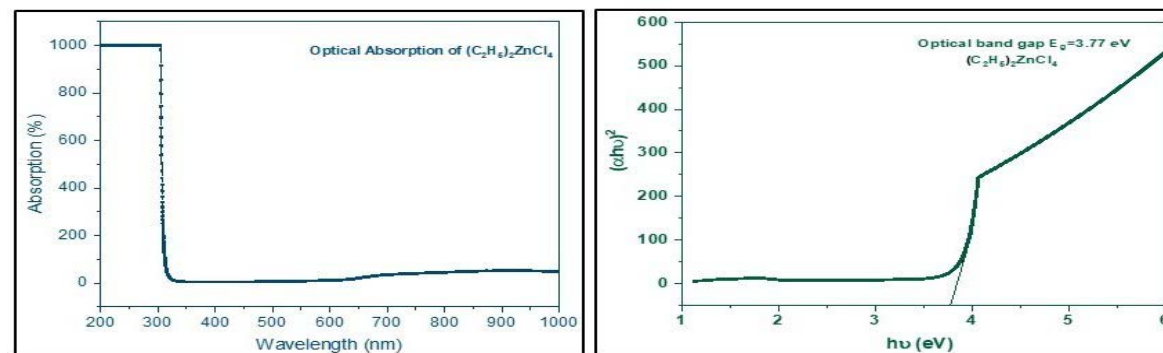


FIG 3. XRD Peak Positions of $(C_2H_5)_2ZnCl_4$ Single Crystal

FIG 4. FTIR spectrum of $(C_2H_5)_2ZnCl_4$ Single Crystal



Figure(5): UV-Vis Absorption graph of $(C_2H_5)_2ZnCl_4$ Single Crystal

Figure(6): Optical Energy band gap of $(C_2H_5)_2ZnCl_4$ Single Crystal

4. CONCLUSION

The study focuses on the preparation and study of nonlinear optical (NLO) properties of the single crystal of the hybrid compound $(C_2H_5)_2ZnCl_4$. Its crystal structure is confirmed by XRD and its functional groups & stability are confirmed by FTIR. The outcomes show that the materials have good NLO characteristics for photonic, laser and optical applications.

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Highly Responsive NiO/MCM-48 Humidity Sensor For Sleep Hypopnea- Apnea Detection

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Abstract. To identify Sleep Hypopnea-Apnea Syndrome (SHAS), a common sleep disorder characterized by breathing disruptions, a novel humidity sensor utilizing a NiO/MCM-48 nanocomposite has been developed. Scanning electron microscopy (SEM) verified that the hydrothermal synthesis of the NiO/MCM-48 composite produced distinct spherical nanostructures. The sensor utilizes the semiconducting qualities of NiO and the porous structure of MCM-48, both of which are critical for humidity detection. The sensor exhibits quick response and recovery times of 10.8 s and 9 s, respectively. In order to detect apnea episodes, it was also used in a real-time monitoring system to track changes in humidity associated with human breath.

INTRODUCTION

Sleep Hypopnea-Apnea Syndrome (SHAS) is a common but mostly underdiagnosed respiratory disorder marked by recurrent episodes of partial or complete upper airway blockage during the sleep, that causes reduced or halted airflow [1]. Early and accurate detection of SHAS is, therefore, crucial for timely detection and cure, which can improve patient's quality of sleep and life as well. Traditional diagnostic methods such as polysomnography, although highly accurate, are expensive, time-consuming, and often require overnight hospital stays [2]. In recent years, non-invasive, and real-time sensing techniques have been emerged as promising alternatives. Semiconducting metal oxides have been highly explored for humidity sensing applications due to their high sensitivity, easy fabrication, and stable electrical properties. The ideal material for humidity sensors is nickel oxide (NiO), a p-type semiconductor known for its excellent chemical stability, environmental compatibility, and hydrophilic nature with water molecules [3]. However, its sensing abilities can be enhanced by combining it with mesoporous materials. MCM-48 is notable among different mesoporous silica structures because of its large pore volume, extensive surface area, and three-dimensional cubic pore network. These features enhance water molecule adsorption, diffusion, and overall response performance [4]. In this work, a NiO/MCM-48 nanocomposite was synthesized via a hydrothermal method, resulting in well-dispersed spherical nanostructures. In order to detect Sleep Hypopnea-Apnea Syndrome (SHAS), a novel humidity sensor based on a NiO/MCM-48 nanocomposite has been created. In order to detect apnea episodes, the sensor was incorporated into a real-time monitoring system that observed humidity changes associated with human breathing.

SYNTHESIS AND CHARACTERIZATION

To synthesize NiO/MCM-48, 2.6 g of CTAB was mixed in 120 g of distilled water and stirred vigorously till a homogeneous solution was prepared. To this, 12 mL of aqueous ammonia was added. 0.096 g nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ was dissolved in deionized water. Subsequently, 3.5 g TEOS under continuous stirring was added, and the stirring continues for 5 hours. The resulting suspension was then subjected to hydrothermal treatment at an elevated temperature. After cooling, the solid product was filtered, washed and dried at 100°C. The final NiO/MCM-48 powder was calcined at 650°C for 7 hours in air. Further, the structural characteristics of the prepared samples were studied using X-ray diffraction (XRD) on a Rigaku Ultima IV (RU IV) diffractometer

furnished with a Cu K α X-Ray radiation source ($\lambda = 1.54 \text{ \AA}$), operating in the 2θ range suitable for identifying crystalline phases. The morphology and surface morphology of the NiO/MCM-48 nanocomposite was examined using a ZEISS Scanning Electron Microscope (SEM), providing detailed insights of the shape, size, and dispersion of the nanoparticles within the mesoporous silica matrix. The NiO/MCM-48 nanocomposite was dispersed in ethanol (0.3 g in 2 mL) and finely ground into a uniform slurry using a mortar and pestle. This paste was drop-casted onto a pre-cleaned Ag–Pd interdigitated electrode using a $10 \mu\text{L}$ micropipette. The coated sensor was then subjected 70°C of temperature for 2 hours to remove ethanol.

STRUCTURAL ANALYSIS (XRD & SEM)

XRD pattern confirmed the successful integration of NiO into the MCM-48 silica framework, illustrating characteristic amorphous hump at 22° corresponding to MCM-48 along with distinct peaks of crystalline NiO at 37.31° , 43.35° , 62.9° , demonstrating the coexistence of both phases as shown in Fig. 1(a) [5]. SEM analysis shows that the nanocomposite have a uniform spherical morphology with well-dispersed NiO nanoparticles across the silica matrix as illustrated in Fig. 1(b) [6].

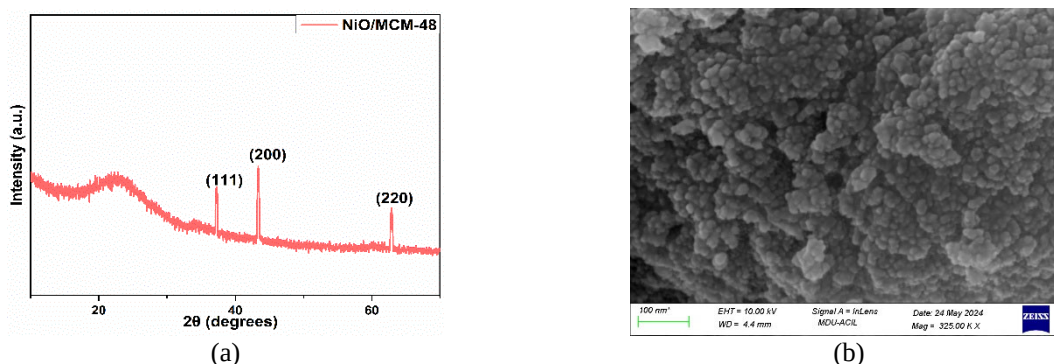


FIGURE 1. (a) XRD plot, (b) FESEM image of as synthesized NiO/MCM-48

HUMIDITY SENSING PROPERTIES

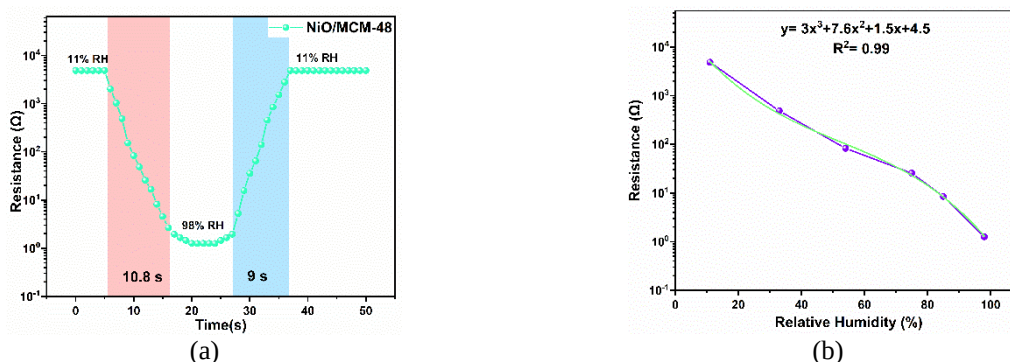


FIGURE 2. (a) Response and Recovery time of NiO/MCM-48, and (b) Cubic Polynomial fitting of resistance with %RH

The sensor depicts a rapid response time of 10.8 s and a recovery time of 9 s, showing efficient adsorption and desorption of water molecules as shown in Fig. 2(a). Sensitivity was quantitatively evaluated by calculating the change in resistance per unit change in RH (%), with an average sensitivity of $55.74 \Omega/\text{RH}\%$ as illustrated in Fig. 2(b).

BREATH MONITORING

Sleep Hypopnea-Apnea Syndrome (SHAS) is a respiratory disorder described by recurring episodes of reduced or completely blocked airflow during sleep, mainly due to the partial or complete failure of the pharyngeal airway [7]. To simulate the respiratory irregularities associated with SHAS, mimicking conditions of temporary cessation and holding breath for 10 seconds was done as illustrated in Fig. 3(a,b). The resulting respiratory signal, captured during this controlled simulation, reveals distinct electrical patterns corresponding to both abnormal breathing phases.

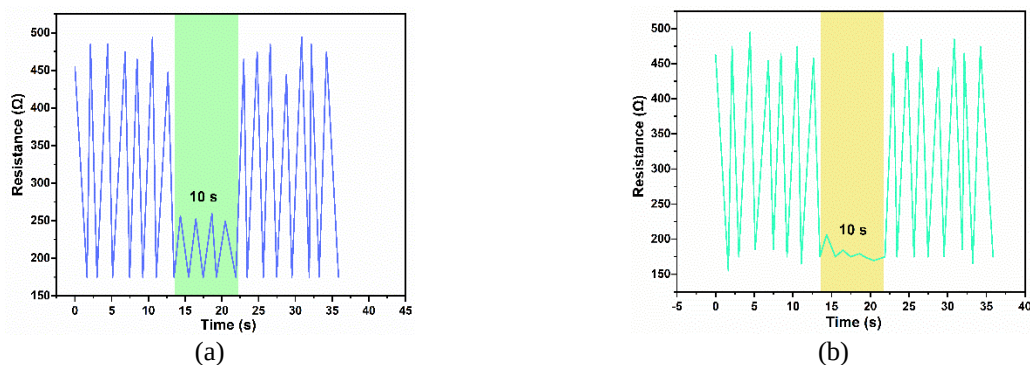


FIGURE 3. Real time resistance variation for simulated (a) sleep hypopnea, (b) sleep apnea breathing patterns

CONCLUSION

The NiO/MCM-48 nanocomposite was successfully synthesized via a hydrothermal method and employed as a high-performance humidity sensor for detecting Sleep Hypopnea- Apnea Syndrome (SHAS). The sensor demonstrated a quick response & recovery time of 10.8 s & 9 s, respectively, along with high sensitivity within a linear RH range. Real-time breath monitoring experiments, including simulated apnea and hypopnea episodes, validated the sensor's capability to detect abnormal respiratory patterns.

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Assembling of Atomic Gold Clusters to Photodetector Devices

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Abstract. Gold nanoclusters captivate researchers with their finely tunable electronic and optical properties, shaped by atomic-scale structures. This study demonstrates the ligand-driven assembly of eight-atom gold clusters (Au_8) into a locally periodic nanostructured framework, highlighting their potential for advanced optical applications. A distinct absorption peak at 371 nm in the optical absorbance spectrum corresponds to an excitonic transition between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Analysis of two oppositely signed excitonic features in the circular dichroism spectra confirms the coupling of excitons with distinct chiral characteristics. Magnetic behavior analysis reveals superparamagnetic ordering driven by spin-orbit interaction. Furthermore, the discretization of electronic states and spin-orbit coupling produces a favorable HOMO-LUMO gap, indicative of semiconductor behavior. The Schottky junction-based device exhibits promising photoresponse in the ultraviolet region, representing a significant advancement toward next-generation UV-active photodetectors.

INTRODUCTION

Atomic gold (Au) nanocluster (NC) assemblies have emerged as a promising nanomaterial for quantum communication, sensing technologies, and high-speed photodetector applications [1–3]. In contrast to conventional gold nanoparticles (Au NPs), Au NCs possess well-defined core–shell architectures, typically composed of a metallic Au (0) core surrounded by an Au(I)–thiolate (S) shell. Au NCs, with sizes ranging between 1–3 nm, lie in an intermediate regime between individual atoms and nanoparticles. Within this size range, pronounced quantum confinement effects arise, resulting in discrete electronic energy levels similar to those observed in single atoms [4]. This leads to unique optical features, such as well-defined UV–Vis absorption peaks associated with HOMO–LUMO transitions and distinct photoluminescent behavior [5]. Moreover, Au NCs (Au_n , with $n < 20$) exhibit deviations from the diamagnetism observed in bulk gold due to quantum confinement effects and surface atom stirred spin polarization. These effects primarily arise from relativistic splitting of the 5d and 6s bands, resulting in unpaired electrons, as well as finite-size-induced band merging in ligand-protected clusters, yielding semiconducting behavior [6]. Again, ultraviolet (UV) radiation offers both benefits and hazards to human health, making UV sensors essential for monitoring exposure safely and using UV effectively. Although wide bandgap semiconductor-based UV detectors are used for UV sensing applications, the high photoresponse and low power consumption are major concerns. This work highlights the (i) growth of assembled gold clusters with UV active electronic states, (ii) fabrication of Schottky junction-based photodetector, and (iii) evaluation of UV responsivity suitable for practical applications.

EXPERIMENTAL METHODS

The Au NCs (atomicity ~ 8) were prepared by a chemical route using a surfactant, L-Cysteine methyl ester (LCME), a gold chloride solution as the precursor, and sodium borohydride as the reducing agent. The detailed methodology is described elsewhere [7]. The final solution was centrifuged and washed with anhydrous ethanol to yield the powder sample. Further, the powder samples were dispersed in distilled water for various spectroscopic characterization. A gold cluster-based photodetector was fabricated using spin coating technique in a Schottky-junction configuration, followed by device characterization.

RESULTS AND DISCUSSION

The optical absorption properties of the Au₈ NCs were investigated using a SHIMADZU UV–Vis spectrophotometer at room temperature. Figure 1(a) displays a sharp optical absorption peak at 371 nm corresponding to an electronic transition between the discrete HOMO and LUMO energy levels emanated from the confinement effect of *sp*-conduction band and its occupied *d*-band. Figure 1(b) presents the circular dichroic (CD) spectra of the sample, revealing their inherent chirality. The strong CD signal at 374.3 nm and a weaker band at 346.9 nm, with opposite intensities, confirm the negative chiral nature of the nanoclusters. The magnetic properties of the samples were characterized using a Quantum Design Dynacool vibrating sample magnetometer (PPMS, Quantum Design) set up. Figure 1(c) shows the M–H curve of Au₈ NCs at 300 K, displaying a reversible S-shaped magnetization response without hysteresis loops (zero coercivity and remanence), followed by saturation of magnetization (*M*_s) at 6.04×10^{-5} emu/g. This behavior indicates the superparamagnetic (SPM) nature of the Au₈ NCs. The origin of SPM properties may be due to the collective superatomic spins in rigid structures that resist distortion, enabling high moments that are reversible by thermal fluctuations [8].

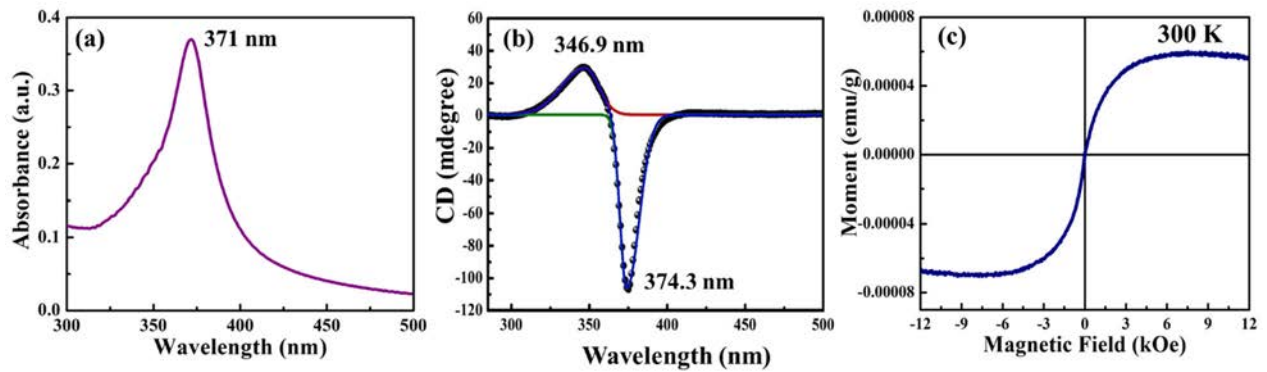


FIGURE 1. (a) Optical absorption spectrum and (b) Circular dichroic spectra of Au₈ NCs. (c) M–H loop of the sample measured at temperatures of 300 K.

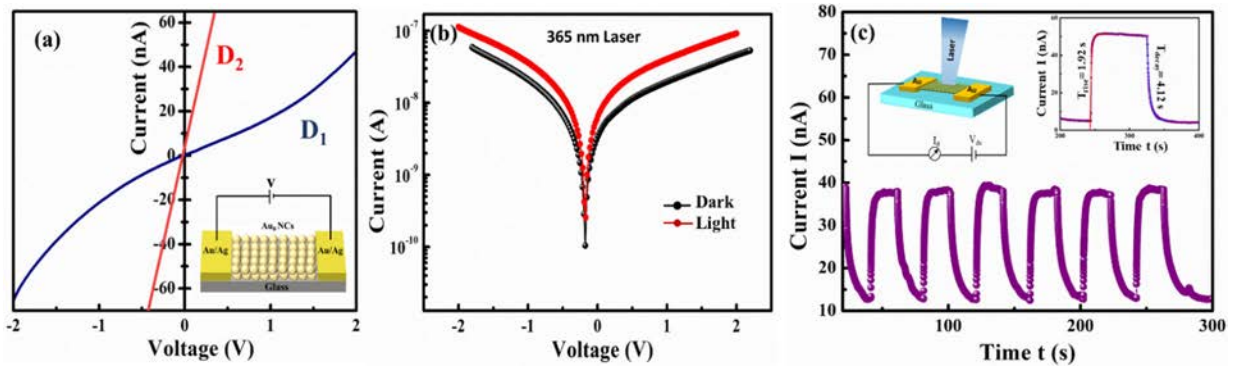


FIGURE 2. (a) The I–V characteristics of the devices D₁ and D₂, and the inset of (a) shows the schematic diagram of the devices. (b) I–V characteristics of the photodetectors under dark (black) and 365 nm UV illumination (red). (c) Temporal photoresponse of device D₁ operated at a bias of 2 V and 365 nm light irradiation.

The electrical properties of the fabricated devices were investigated by constructing two types of metal–semiconductor junctions: Au–NCs–Au (D₁) and Ag–NCs–Ag (D₂). Current–voltage (I–V) measurements of both devices (D₁ and D₂) were carried out at room temperature using a Keithley 2450 source meter, as shown in Figure 2 (a). As observed from Figure 2(a), the Au₈ NCs exhibit Schottky behavior for Au–NCs–Au while Ohmic behavior for Ag–NCs–Ag. This may be due to the metal work function-dependent band alignments. Further, the photodetector performance of our device was evaluated. Figure 2(b) illustrates the I–V behavior of the device, D₁, both in the dark and under illumination with a 365 nm UV light operated at a bias of 2 V. Figure 2(c) demonstrates the stability and repeatability of the photodiode's response for a period of 300 seconds. The device exhibited excellent reproducibility

with a consistent and stable photocurrent output. A sharp exponential increase in current was observed upon UV photoexcitation, followed by a steady saturation phase. The photodiode displayed a rise time of 1.92 seconds and a decay time of 4.12 seconds. These relatively short lifetimes may be attributed to the charge separation dynamics and modified carrier mobility.

CONCLUSIONS

In conclusion, fabrication of an assembled gold cluster-based photodetector has been established with promising photoresponse properties in the ultraviolet regime. A clear absorption peak at 371 nm in the optical spectrum indicates a HOMO–LUMO excitonic transition, with oppositely signed features in the circular dichroism spectra, confirming chiral exciton coupling. Magnetic analysis suggests superparamagnetic ordering influenced by spin–orbit interaction, while discrete electronic states and spin–orbit coupling yield a suitable HOMO–LUMO gap characteristic of semiconducting behavior. As observed from the I–V characteristics, the Au–Au₈ NC–Au based junction exhibits Schottky characteristics where the majority carriers are contributing to the transport properties as fast carriers. The I–V behavior under dark and UV light excitation reveals the generation of distinguishable photocarriers contributing to the photocurrents. The temporal photoresponse exhibits a rise and decay time of 1.92 s and 4.12 s, respectively. This response is comparable to an expensive wide-band gap photodetector. The present study provides new opportunities for designing gold NCs-based wide-bandgap semiconductor homojunction architectures toward the development of high-performance, environmentally friendly UV photodetectors for advanced detection and sensing applications.

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Tailoring COK-19 Mesoporous Silica for Enhanced Cefepime Encapsulation and Sustained Release

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Abstract. Mesoporous silica materials are leading the way in drug delivery systems based on nanotechnology. Mesoporous silica COK-19 has homogeneous pore size distribution, high surface area and good biocompatibility, which enabling the encapsulation and controlled release of drug molecules. This study looks into the development of a controlled drug delivery system by assimilating cefepime inside COK-19. Cefepime loaded COK-19 formulations were analyzed with UV-Vis spectroscopy, FTIR and BET. The release profile exhibits the sustained release of cefepime over a period of 72 hours. This scrutiny represents that COK-19 can be used as a vehicle for sustained and controlled drug delivery.

INTRODUCTION

Cefepime is a fourth-generation β -lactum antibacterial agent having the ability to hinder the growth of Gram-positive and Gram-negative bacteria [1,2]. Efficiency of this drug is very low because of less solubility, non- sustained release and poor bioavailability, all of these require repeated administration. In order to get overcome these constraints, nanostructured drug delivery systems are employed to enable sustained and targeted delivery. Mesoporous silica nanomaterials (MSNs) have gained lots of attention due to their properties such as biocompatibility, high surface area, tunable pore size, etc., which make them suitable carriers for both hydrophilic and hydrophobic drugs [3]. A newly manufactured MSN COK-19, which was prepared using Pluronic F-127 as surfactant, has large surface area, biocompatible and well-arranged pore structure [4]. Its larger pore size assists high drug encapsulation and good release profile. This scrutiny aims to enhance the drug entrapment, explain structural features and analyse in vitro release physiologically.

EXPERIMENTAL

Synthesis of COK-19

COK-19 was produced using the propounded hydrothermal method in the literature [5]. Firstly, 2.58 g of Pluronic F-127 was dissolved in 107.5 g of deionized water with continuous stirring. Trisodium citrate dihydrate (2.55 g) and citric acid monohydrate (3.7 g) were added to produce a buffered solution. A milky suspension was formed as soon as 10.4 g of a pre-diluted sodium silicate solution (in 30 g of deionized water) was quickly added. This mixture was filtered, cleaned and dried at 80°C after being statically aged for 24 hours at 70°C. Ultimately, pure white COK-19 was produced by calcining at 350°C for 24 hours at a rate of 0.5°C per minute, which eliminated the surfactant.

Calibration Curve of Cefepime, Drug Loading and Releasing

A stock solution was serially diluted to concentrations varying from 0.5 to 7 $\mu\text{g/mL}$ in order to create a calibration curve for cefepime. Using a UV-Vis spectrophotometer, measurements were made for absorbance at 515 nm, using distilled water as the blank. To quantify cefepime in unknown samples, the linear regression equation $A = mC + b$ was created.

Using a post-impregnation technique, cefepime was loaded into COK-19 by combining an aqueous COK-19 dispersion dropwise with a cefepime solution while stirring continuously for 24 hours. The resulting composite was then gathered and vacuum-dried after the mixture was centrifuged for an hour at 5000 rpm. To determine drug entrapment efficiency (DEE), the following formula was used:

$$DEE = (C_i - C_f) * 100 / C_i$$

Where, C_i is initial concentration of drug (mg/ml) and C_f is final concentration of drug in the supernatant (mg/ml).

For in vitro release, about 50 mg of drug-loaded COK-19 was put in a dialysis bag and incubated for 72 hours in 150 mL of PBS (pH 6.8) at 37°C. Occasionally, 2 mL samples were taken out, swapped out for new PBS, and examined at 515 nm. Triplicate trials served as the basis for release profiles.

RESULTS AND DISCUSSION

BET Interpretation and Fourier Transform Infrared Spectra

According to the IUPAC classification, mesoporous materials are characterized by type IV nitrogen adsorption-desorption isotherms and are displayed in Fig. 1(a). BET analysis demonstrated a reduction in pore size, volume, and surface area after drug loading, as indicated in Table 1, suggesting that cefepime was well integrated into the COK-19 mesoporous channels. This decrease confirms successful drug trapping and points to partial or total pore filling [6].

Sample	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (nm)
COK-19	815.78	0.3092	4.4007
Cefepime-COK-19	357.89	0.1972	3.6543

TABLE 1. BET analysis of COK-19 and cefepime loaded COK-19

Cefepime's efficient loading into the COK-19 was confirmed by FTIR spectra. Figure 1(b)(iii) shows COK-19 has distinctive peaks at 1610 cm⁻¹ (H-O-H bending), 3634 cm⁻¹ (O-H stretching), and significant Si-O-Si vibrations at 1088 and 804 cm⁻¹, which suggested a silica framework that was well-ordered. Following drug loading, new bands that matched the functional groups of cefepime at 3457, 2344, 1437, and 793 cm⁻¹ emerged, indicating its incorporation as seen in Fig. 1(b)(ii). In the loaded sample, a small shift and expansion of the O-H stretching band indicates physical adsorption or hydrogen bonding between the surface silanol groups and cefepime [7]. FTIR research confirms efficient drug loading via physical encapsulation and hydrogen bonding.

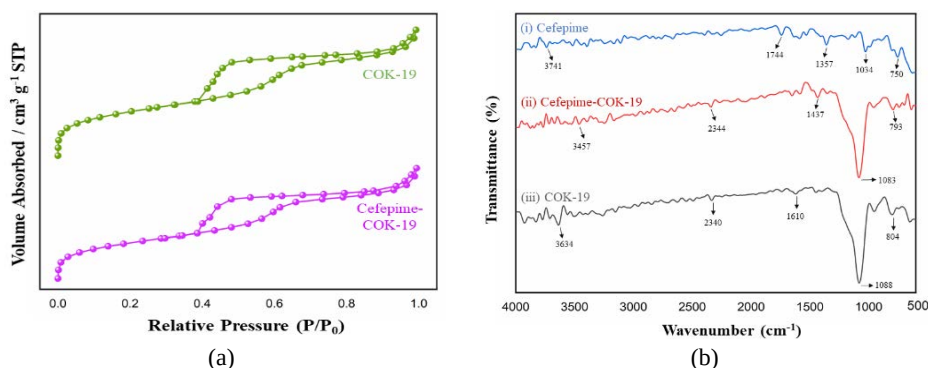


FIGURE 1. (a) Isotherms showing nitrogen adsorption-desorption of COK-19 and Cefepime-COK-19 and (b) FTIR Spectra of (i) Cefepime, (ii) Cefepime-COK-19 and (iii) COK-19.

Drug Entrapment Efficiency and pH Responsive Drug Release

Drug entrapment efficiency of cefepime in COK-19 was calculated using equation from calibration curve as shown in Fig. 2(a) and high entrapment efficiency of 75.87% was acquired. Figure 2(b) instances the cefepime from COK-19 exhibits a biphasic release pattern, with a quick release phase at the beginning and sustained release at the end of the 72-hour cumulative drug release study. Much of the medication is released in the first 24 hours and the release rate progressively drops after 24 hours, suggesting diffusion-controlled release from inside the mesoporous channels.

Strong interactions between the drug and the silica matrix are suggested by the release of 34% of the drug by the end of the study. The potential of COK-19 as a long-term, regulated drug delivery vehicle is demonstrated by this profile.

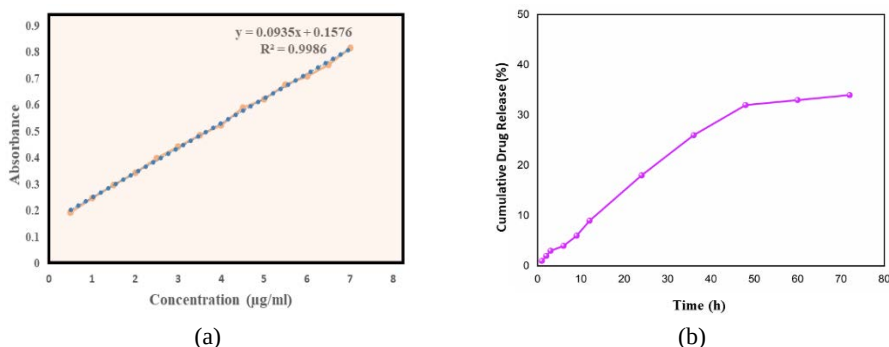


FIGURE 2. (a) Calibration curve of cefepime drug and (b) In vitro drug release profile of cefepime loaded COK-19 composite.

CONCLUSIONS

Using COK-19 mesoporous silica, a targetable drug-loaded composite was successfully created with high loading efficiency of 75.87%. Effective drug encapsulation and stable retention were made possible by COK-19's special physicochemical characteristics, which included a large pore size, high surface area and an organized mesostructure. This system promotes the controlled, sustained, and site-specific release of hydrophobic drugs, thereby greatly increasing their bioavailability. Its potential as a secure and expandable platform for cutting-edge drug delivery is further supported by COK-19's biocompatibility and structural integrity. It is a safe and effective nanovehicle that has great promise for the commercial and medicinal use of hydrophobic medications.

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Alteration Of Structural and Magnetic Properties Of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ Nanomaterials Synthesized By Citrate Autocombustion Method

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Abstract. Synthesis of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.1$ and 0.3) nanomaterials were carried out using citrate autocombustion method. XRD analysis confirms the formation of pure cubic phase of the products annealed at 650°C . The average crystallite sizes (D) were 40 nm , 36 nm and 40 nm for $x = 0.0, 0.1$ and 0.3 in $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$, respectively. The lattice parameters show an overall decrease from $8.3551\text{ \AA}$ to $8.3360\text{ \AA}$ for $x = 0.0$ to 0.3 , respectively. FTIR studies confirm the characteristic M–O bonding frequencies observed in range of $616 - 630\text{ cm}^{-1}$ for T_d site occupancy whereas $414 - 416\text{ cm}^{-1}$ and $451 - 455\text{ cm}^{-1}$ showing the O_h site occupancy in all $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ materials. The magnetic parameters were obtained using vibrating sample magnetometer (300 K). The significant linear decrease in the saturation magnetization (M_s) was from 74.3 emu/g to 60.7 emu/g for ' x ' varying from 0.0 to 0.3 in $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$, respectively. The observed coercivity (H_c) values was 780 Oe to 453 Oe for $x = 0.0$ to 0.3 , respectively. All the magnetic parameters studied in this work for $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ nanomaterials could be correlated to the insertion of Cr^{3+} ions in CoFe_2O_4 , cation redistribution and size and surface effects.

INTRODUCTION

Cobalt ferrite (CoFe_2O_4) is one of the most studied nano-sized spinel ferrites due to its significant magnetic properties such as moderate M_s , high values of H_c and magnetocrystalline anisotropy constant (K_1), making it a suitable candidate for various technological applications [1-3]. Various factors that affect these magnetic parameters are particle size, cation distribution, choice of substituent metal ion, composition of materials, substitution of metal cation at Co or Fe site, synthesis routes adopted etc. [2]. Several refractory transition metal elements such as Cr, V and Nb, have been chosen for potential substituents in CoFe_2O_4 in order to alter the structural and magnetic properties [4-6]. Chromium is a valuable substituent in CoFe_2O_4 as it can couple with the existing magnetic order of existing ions, reduce nanoparticle size and alter cation redistribution. Therefore, we have focused on $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.1$ and 0.3) nanomaterials, in order to understand the alteration in the structural properties, spectroscopic characteristics and magnetic properties of CoFe_2O_4 , in detail.

EXPERIMENTAL METHODS

Synthesis of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ nanomaterials was carried out by using citrate autocombustion method [4]. Various metal salts used were $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Here, citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (CA) was used as chelating agent and fuel. First, calculated amounts of the metal salts were weighed and dissolved in minimum quantity of double distilled water, separately. These clear metal salt solution mixtures were then mixed together quantitatively. Then, 10 g of CA was added and dissolved completely followed by addition of 1 M HNO_3 to obtain clear solution without any precipitation. This final solution was refluxed at 80°C for 3 h . Then, gel formation started with loss of excess solvent at 95°C to obtain a sticky gel. The complete dried gel product was obtained at 95°C which was crushed into coarse powder and heated in an alumina crucible at 450°C for 4 h in a muffle furnace. This $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ product was ground into fine powder, confirmed for phase purity and further annealed at 650°C for 4 h . The annealed materials were then analyzed using XRD (Bruker, D8 Advance), FTIR spectroscopy (Shimadzu, IRAffinity-1S) and VSM measurements carried out by using the instrument– make: Quantum Design, model: PPMS Evercool II with VSM.

RESULTS AND DISCUSSION

XRD studies

XRD patterns of the annealed $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.1$ and 0.3) nanomaterials are represented in figure 1. The cubic spinel phase of the materials was confirmed by comparing the XRD patterns with the ICDD card no. 00-022-1086. The XRD lines were indexed with (220), (311), (222), (400), (422) (511), (440) and (531) planes. The Scherrer formula was used to estimate D wherein marginal variation was observed i.e. 40 nm, 36 nm and 40 nm for $x = 0.0, 0.1$ and 0.3 , respectively. From the WH plots, the intercepts obtained from the linear fit of the linear plots of $\beta\cos(\theta)$ vs. $4\sin(\theta)$, were used to estimate particle size, $D' = 239$ nm, 128 nm and 226 nm for $x = 0.0, 0.1$ and 0.3 , respectively. Lattice parameters (a) decreases from $8.3552 \text{ \AA}$ to $8.3360 \text{ \AA}$ for $x = 0.0$ to 0.3 in $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$, respectively. However, there is a slight increase in ' a ' for $x = 0.1$, calculated as $8.3614 \text{ \AA}$. This can be due to the smaller crystallite size with larger surface fractions causing lattice expansion and ascertained by occurrence of canted spin structures at the surfaces [7].

FTIR spectroscopic analysis

FTIR spectra of the annealed $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.1$ and 0.3) nanomaterials are represented in Fig. 2. The variation in frequencies for characteristic M–O bonding in spinel ferrites i.e. ν_1 (615 to 630 cm^{-1} for T_d site occupancy) and ν_2 (451 to 455 cm^{-1} O_h site occupancy) has been represented in table 1 for all $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ compositions. As the aq. citrate method was used for synthesis of materials, few medium to low intensity IR bands were observed as follows: 1338 – 1393 cm^{-1} assigned to (NO_3^-) ions whereas bands at $\sim 1513 \text{ cm}^{-1}$, $\sim 1546 \text{ cm}^{-1}$ and $\sim 1639 \text{ cm}^{-1}$ can be assigned to (M–COO–Organic linkages) [4]. Also, medium intensity bands at 2349 cm^{-1} can be attributed to adsorbed $\text{CO}_2(\text{g})$ and broad bands with very low intensity was observed at $\sim 3446 \text{ cm}^{-1}$ can be assigned to OH stretching of adsorbed water molecule ($\text{H}_2\text{O}(\text{l})$) [6].

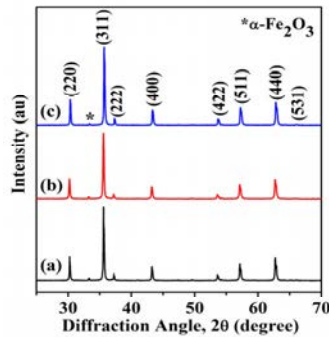


FIGURE 1. XRD patterns of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ nanomaterials; (a) $x = 0.0$, (b) $x = 0.1$ and (c) $x = 0.3$

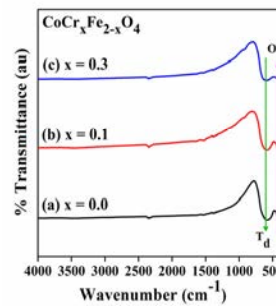


FIGURE 2. FTIR spectra of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ nanomaterials; (a) $x = 0.0$, (b) $x = 0.1$ and (c) $x = 0.3$

Magnetic properties

Figure 3 depicts the M vs. H curves for the $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ nanomaterials annealed at 650°C . The values of intercept estimated from the linear fitting of the plot M vs. $(1/H^2)$ equals values to saturation magnetization. The reduction in the values of M_s followed linear trend, i.e. from 74.3 emu/g to 60.7 emu/g , for $x = 0.0$ to $x = 0.3$, respectively. However, alteration in H_c values was highly significant varying from 780 Oe ($x = 0.0$) to 453 Oe ($x = 0.3$). The remanent magnetization (M_r) values were obtained from the MH curves changes from 28.7 emu/g to 17.7 emu/g (Table 1). The (M_r/M_s) ratios were noted as 0.3863 , 0.3513 and 0.2916 for $x = 0.0, 0.1$ and 0.3 respectively. The magnetocrystalline anisotropy constant (K_1) was calculated using following expressions [6]:

$$M_s \times \sqrt{\frac{(105 \times b)}{8}} \quad \text{----- (1)}$$

The values of ' b ' and M_s were obtained from the plot of M vs. $(1/H^2)$ which can be attributed to the equation given below:

$$M = M_s \left(1 - \frac{b}{H^2}\right) \quad \text{----- (2)}$$

Therefore, for $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ materials in this work, K_1 values vary as $2.0563 \times 10^4 \text{ J/m}^3$ ($x = 0.0$) to $1.5023 \times 10^4 \text{ J/m}^3$ ($x = 0.3$) (see table 1). All these alterations in the magnetic parameters can be correlated to the effective incorporation of Cr in the lattice structure, cation redistribution and nano-size and surface effects [6, 7].

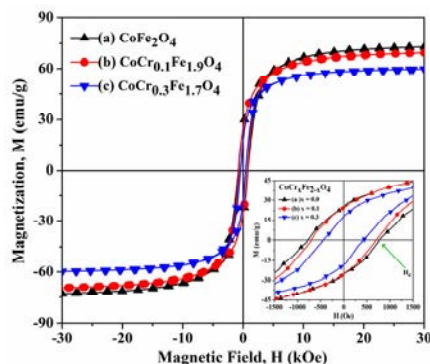


FIGURE 3. MH curves measured at 300 K of $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ nanomaterials; (a) $x = 0.0$, (b) $x = 0.1$ and (c) $x = 0.3$ (Inset shows zoom-in plots for depicting H_c)

TABLE 1. Details of estimated structural parameters from XRD analysis, FTIR studies and Magnetic parameters for all the $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ compositions

Cr content, (x)	D (Scherrer formula), (nm)	D' (WH plot), ($\times 10$ nm)	Lattice strain, ϵ , ($\times 10^{-3}$)	Lattice constant, a, (Å)	FTIR frequencies (cm^{-1})		Magnetic Parameters			
					v1 (T_d site)	v2 (O_h site)	M_s (emu/g)	H_c (Oe)	M_r (emu/g)	K_1 ($\times 10^4$) (J/m^3)
$x = 0.0$	40	23.9	2.15	8.3552	615	455	74.3	780	28.7	2.0563
$x = 0.1$	36	12.8	1.96	8.3614	617	453	70.6	712	24.8	1.9132
$x = 0.3$	40	22.6	2.13	8.3360	630	451	60.7	453	17.7	1.5023

CONCLUSION

We have successfully synthesized pure phase $\text{CoCr}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0, 0.1$ and 0.3) nanomaterials by using modified citrate autocombustion method. Various structural properties were studied using XRD and FTIR technique. Magnetic properties were studied using VSM measurements at 300 K. XRD analyses prove the pure cubic spinel phase of products. The considerable alteration in v1 frequency (T_d site) with increase in Cr content signifies cation redistribution. The considerable decrease in the values of M_s and H_c proves the impact of incorporation of Cr, cation redistribution along with the nano-size and surface effects.

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A Highly Selective Gas Sensor Based on WO₃/MCM-48 Nanocomposite

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Abstract. Gas sensing materials with high sensitivity and rapid response are essential for monitoring toxic gases in environmental and industrial applications. In this study, tungsten oxide-incorporated MCM-48 nanocomposite was successfully synthesized via an in-situ hydrothermal technique. Subsequently, a highly selective Carbon Monoxide (CO) based sensor was fabricated using the drop-casting approach. The structural characteristics of the synthesized material were analyzed using Wide-Angle X-ray Diffraction (WAXRD) within the 20°-80° 2θ range and Fourier Transform Infrared (FTIR) spectroscopy spanning 500-4000 cm⁻¹, confirming the formation of the intended nanocomposite. The fabricated sensor reveals a rapid response time of 21.3 seconds and a recovery time of 19.5 seconds at ambient temperature.

INTRODUCTION

In this neotechnic world, the extensive use of pesticides, insecticides, and fossil fuels has significantly increased environmental pollution, releasing harmful gases such as NO_x, NH₃, CO, and H₂S, which adversely affect all forms of life. Carbon monoxide (CO) is found to be a colorless, odorless, and tasteless gas. It basically originates from the emissions of chemical industries, vehicle exhausts, and its excess release causes a serious risk to the natural environment. According to the World Health Organization, exposure to an atmosphere containing 26 ppm of CO for one hour may result in adverse health effects [1, 2]. Tungsten Oxide (WO₃) is one of the most widely used metal-oxide based chemiresistive sensor due to its tunable sensing properties toward different analytes by modulating its concentration and being a n-type semiconductor, it is sensitive towards various gasses for different host materials [3]. In this context, mesoporous materials especially those like MCM-48 have garnered significant research interest due to their high surface area, distinctive 3D pore architecture, and well-ordered cubic symmetry, all of which are advantageous for gas sensing applications [4]. Addressing the existing research gap, we have synthesized a WO₃ loaded MCM-48 nanocomposite and evaluated its performance for carbon monoxide sensing application.

SYNTHESIS ROUTE

Tungsten Oxide was incorporated into MCM-48 matrix through in-situ method. Initially, 0.8g of Na₂WO₄·2H₂O (Sodium Tungstate dihydrate) and 4.8g CTAB were mixed in a solution of 100mL of distilled water, 100mL of ethanol, and 24mL of NH₃ solution on a magnetic stirrer at about 400 rpm for about 2 hours at room temperature. Further, 6.8g of TEOS (Tetraethyl orthosilicate) was added dropwise into this solution and stirred for about 5 hours on magnetic stirrer at 300 rpm. The obtained white solution was poured into a teflon beaker and sealed in a stainless-steel autoclave, which was further processed for hydrothermal treatment at 100°C for 24 hours. Finally, solid white colored product was retrieved termed as WMCM after the centrifugation and washing until the pH becomes 7.0 and this obtained powder was dried and calcined at 75°C and 350°C for 6 hours respectively.

CARBON MONOXIDE SENSOR FABRICATION

A Carbon Monoxide based sensor was fabricated using the drop-casting technique. To begin, a slurry was prepared by thoroughly mixing the synthesized WO_3 -based MCM-48 nanocomposite with ethanol, following manual grinding using a mortar and pestle. The resulting mixture was subjected to ultrasonication to ensure homogeneity and then dried in an oven at 60°C for 3 hours. Subsequently, a portion of the prepared paste was deposited onto a silver-palladium electrode with dimensions of $6.7\text{ mm} \times 3.1\text{ mm} \times 0.6\text{ mm}$. The thickness of the deposited sensing layer was measured to be approximately $300\text{ }\mu\text{m}$. Finally, the fabricated sensor was further dried at 70°C for 2 hours to ensure proper adhesion and stabilization of the sensing film.

STRUCTURAL ANALYSIS (XRD & FTIR)

Figure 1 depicts the structural features of as synthesized WMCM nanocomposite. The Wide-Angle X-ray Diffraction (WAXRD) pattern, as shown in Fig. 1(a), reveals a broad hump centered around 23.16° , which can be attributed to the uniform distribution of WO_3 within the MCM-48 matrix [5]. The corresponding FTIR spectrum, illustrated in Fig. 1(b), which exhibits the structural incorporation of tungsten species. As observed absorption bands include the O–H bending vibration at 1634 cm^{-1} , the W–O bending mode at 584 cm^{-1} , and the W–O–W stretching vibration at 803 cm^{-1} [6]. This spectrum confirms the successful integration of tungsten oxide into the mesoporous framework.

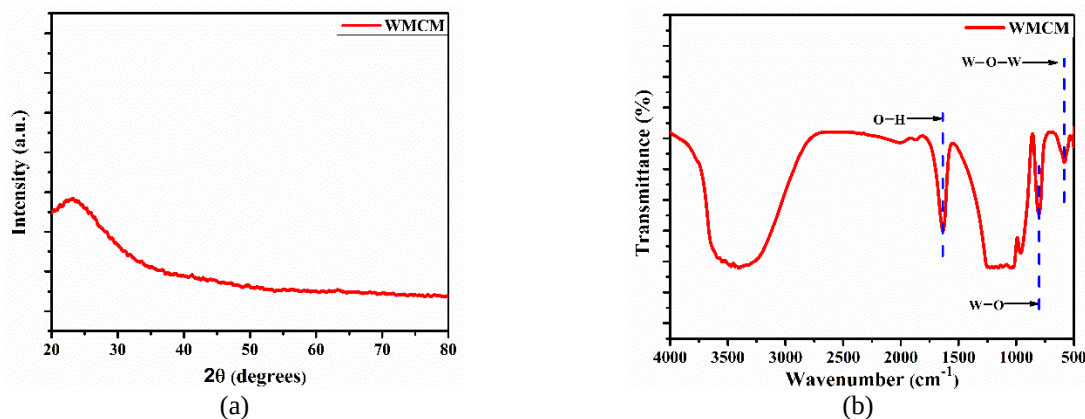


FIGURE 1. (a) WAXRD plot of WMCM, (b) FTIR spectra of WMCM

GAS SENSING ANALYSIS

There are three main parameters which plays important role for analyzing the gas sensing performance of a sensor i.e., Gas Sensing response, Response time, and Recovery time. The gas sensing response can be calculated by using equation (1)

$$R (\%) = \frac{R_g}{R_a} \times 100 \quad (1)$$

In this context, $R (\%)$ represents the gas sensing response, where R_g and R_a denote the sensor resistance in the presence of gas and in ambient air, respectively [7]. Now, based on the experimental observations as shown in Fig.2, the gas sensing response of fabricated sensor for various gases at room temperature was 71.33% for CO, 22.87% for NH_3 , 14.0% for Ethanol, 17.51% for Formaldehyde and 11.16% for Liquefied Petroleum Gas (LPG) as illustrated in Fig.2(a). Further, the response and recovery times were determined for CO and found to be 21.3 seconds and 19.5 seconds, respectively as shown in Fig.2(b). Now, based on these results it can be concluded that the fabricated sensor is suitable and promising candidate for CO detection due to the significant availability of adsorbed O^- ions on the surface of the material, facilitating the effective interaction and adsorption of CO molecules.

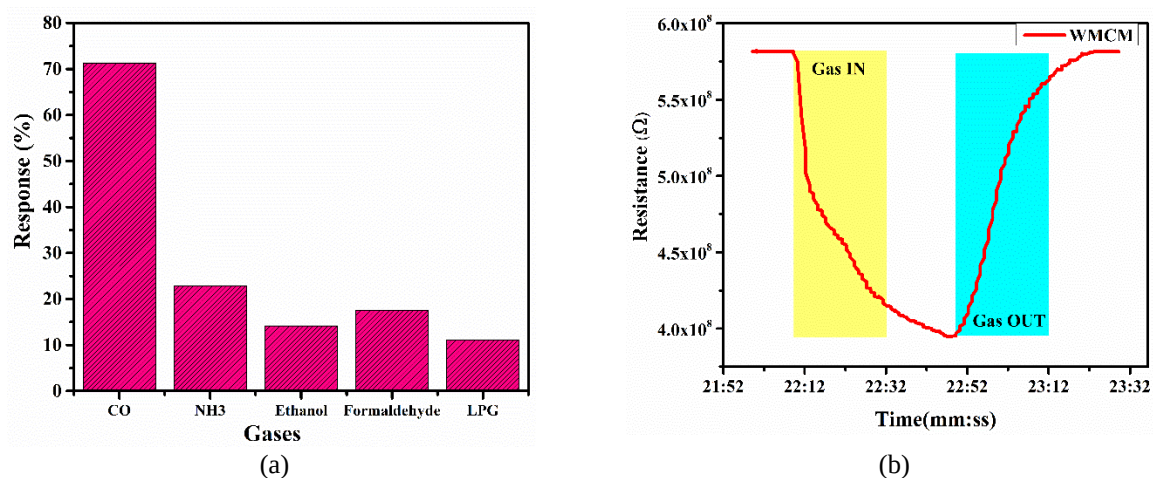


FIGURE 2. (a) Sensing response of WMCM nanocomposite for different gases. (b) Gas Sensing Response of WMCM nanocomposite for CO.

CONCLUSION

The successfully synthesized WO₃-loaded MCM-48 nanocomposite demonstrated excellent structural integrity and gas sensing performance. The fabricated sensor was highly selective towards CO and exhibited a high response of 71.33% with rapid response and recovery times of 21.3 and 19.5 seconds, respectively, highlighting its potential for efficient room-temperature carbon monoxide detection.

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Facile Synthesis of Microspherical CuBi_2O_4 a Promising Electrode for Next-Generation Supercapacitors

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Abstract. In this study, Copper bismuth oxide (CuBi_2O_4) was synthesized via a facile co-precipitation method and investigated as a potential electrode material for supercapacitor application. XRD analysis confirmed the formation of CuBi_2O_4 in a pure phase, with no detection of extra peaks. The morphology of the prepared material exhibits a microsphere-like morphology offering a high surface area favorable for electrochemical properties. In contrast, electrochemical properties were studied in 6 M KOH, exhibiting specific capacitance of 614.33 F/g and 572.82 F/g at 10 mV/s and 1 A/g, respectively, making it promising electrode material for supercapacitors.

INTRODUCTION

Supercapacitors are gaining lots of interest owing to their excellent power density, fast charge/discharge behavior, and extended cycle life. These properties make them suitable candidates for next-generation energy storage [1]. The choice of electrode material plays a crucial role in determining their overall performance [2]. Transition metal oxides, particularly CuBi_2O_4 are a beneficial electrode material for supercapacitors because the presence of copper and bismuth introduces multiple redox-active sites which enhances the charge storage capabilities, along with low toxicity which helps develop the eco-friendly supercapacitor [3]. In this work, CuBi_2O_4 was studied as a supercapacitor electrode material which remains unexplored in the field of energy storage. Here, CuBi_2O_4 is synthesized through co-precipitation method, forming microspheres with a high surface area to facilitate efficient ion transport. Additionally, electrochemical testing in 6 M KOH confirms CuBi_2O_4 is a promising electrode material for advanced supercapacitors.

PREPARATION OF CuBi_2O_4 NANOPARTICLES

CuBi_2O_4 nanoparticles were prepared via a co-precipitation technique. Initially, 0.002 mol copper nitrate trihydrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$] and 0.004 mol bismuth nitrate pentahydrate [$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$] were dispersed in 10 mL deionized water in presence of 2 mL of nitric acid (HNO_3) under constant stirring to prepare a homogeneous solution (solution 1). Another solution 2 is prepared by adding 1 M sodium hydroxide (NaOH) to 70 mL of deionized water. Subsequently, solution 2 was gradually introduced into solution 1 in a dropwise manner while maintaining constant stirring for 11 h. During this process, brown precipitates were obtained and collected by the filtration process. Afterward, resulting precipitate was washed with ethanol as well as deionized water, then dried at 70 °C in a vacuum oven to obtain CuBi_2O_4 nanoparticles.

RESULT AND DISCUSSION

X-ray diffraction (XRD) study

FIGURE 1. illustrates the XRD pattern of CuBi_2O_4 sample prepared by co-precipitation method matched with the JCPDS card No. 42-0334 [2]. It is observed that diffraction peaks of CuBi_2O_4 at $2\theta = 20.9^\circ, 28^\circ, 29.6^\circ, 30.76^\circ, 33.33^\circ, 34.2^\circ, 37.3^\circ, 45.3^\circ, 53.4^\circ, 55.8^\circ, 60.8^\circ, 64^\circ, 66.2^\circ$, and 68° are in good agreement with reference pattern, indicating the phase purity of CuBi_2O_4 . There is no additional peak associated with secondary phase. The broadening of peaks suggests the improved crystallinity of CuBi_2O_4 (see FIGURE 1). Average crystallite size of CuBi_2O_4 nanoparticles is 14 nm which was calculated by using Scherrer equation [1].

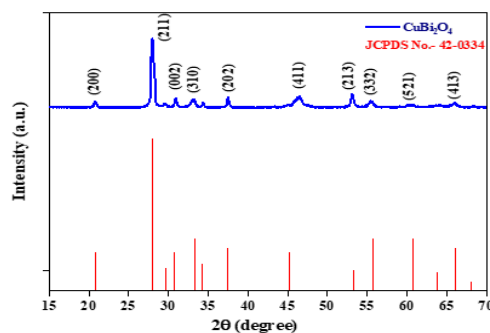


FIGURE 1. XRD patterns of CuBi₂O₄ nanoparticle.

Surface analysis

Surface morphology of the synthesized CuBi₂O₄ nanoparticles was studied using FESEM. FIGURE 2(a) shows FESEM image of CuBi₂O₄ at magnification X10,000 and reveals microsphere-like morphology. This structure provides a large surface area and porous pathways, which are beneficial for electrolyte ion diffusion and increase the electrochemical properties. FIGURE 2 (b) displays the EDS spectrum confirming the presence of Cu, Bi and O elements without any extra peaks indicating the purity of CuBi₂O₄. Furthermore, elemental mapping has also been done which demonstrates a uniform distribution of Cu, Bi, and O throughout micro-spherical morphology as shown in FIGURE 2 (c-e). Surface analysis reveals that CuBi₂O₄ exhibits excellent phase purity and a porous micro-spherical structure, which enhances ion transport and improves electrochemical performance.

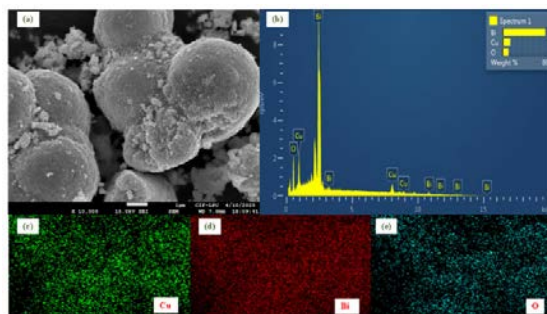


FIGURE 2. (a) FESEM image of CuBi₂O₄ at X10,000. (b) Energy dispersive X-ray spectroscopy (EDS) of CuBi₂O₄. (c-e) Elemental mapping images of Cu, Bi and O respectively.

Electrochemical properties

FIGURE 3 (a) illustrates cyclic voltammetry (CV) profiles of CuBi₂O₄ nanoparticles recorded across a range of scan rates ranging from 10-80 mV/s within potential window of 0 to 0.6 V in 6M KOH aqueous electrolyte. Specific capacitance of the prepared electrode was calculated by [4]:

$$C_s = \frac{A}{ms\Delta V} \quad (1)$$

where, C_s is the specific capacitance, A is area under the curve, m represents active mass, scan rate is denoted by s , Δt discharging time as well as V is the potential window. The specific capacitance value of CuBi₂O₄ is 614.33, 552.86, 513.17, 451.42, 438.61, 411.44, 386.29, 364.45 F/g at 10, 20, 30, 40, 50, 60, 70 and 80 mV/s scan rate, respectively. It is noted that with the increment in scanning rates the capacitance value decreases because at higher scan rates, ions do not have enough time to interact with electrode-electrolyte interface. FIGURE 3 (b) presents the galvanostatic charge-discharge (GCD) profiles of CuBi₂O₄ measured at varying current densities with 0 to 0.46 potential range. The capacitance value of CuBi₂O₄ was determined by using equation [5]:

$$Cs = \frac{I \Delta t}{m \Delta v} \quad (2)$$

The specific capacitance of CuBi_2O_4 is 572.88, 521.73, 476.08, 426.08, 391.30 F/g at 1, 2, 3, 4 and 5 A/g, respectively. From electrochemical analysis, it is revealed that the CuBi_2O_4 electrode demonstrates remarkably specific capacitance retention even at high current densities, highlighting its potential as a promising material for advanced supercapacitor applications.

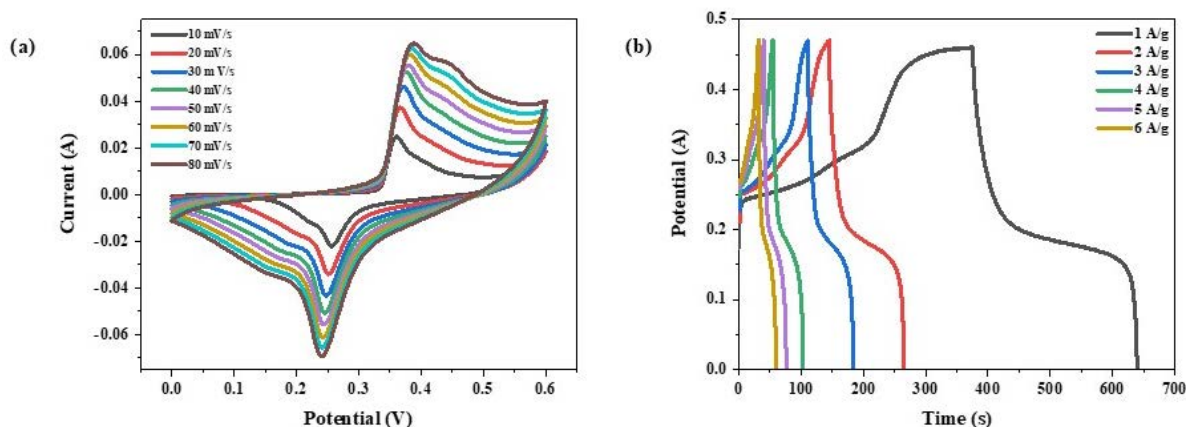


FIGURE 3. a) Cyclic voltammetry (CV) profiles of CuBi_2O_4 recorded at various scan rates. (b) Galvanostatic charge–discharge (GCD) curves of CuBi_2O_4 measured under different current densities.

CONCLUSION

A microsphere-like CuBi_2O_4 electrode was successfully prepared via co-precipitation method. From XRD analysis and surface analysis, it is confirmed that CuBi_2O_4 is in pure phase with effective surface morphology for electrochemical properties. Electrochemical evaluation in 6 M KOH further demonstrated its potential as a promising electrode material for supercapacitors.

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Investigating the Role of Enhanced Surface Area of Dry Electrodes on the ECG Signal Quality

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Abstract. Accurate and noise-free Electrocardiogram (ECG) monitoring is essential for clinical diagnosis and in wearable ECG devices. There are several factors that affect the ECG signal quality, with skin-electrode interface impedance being a key parameter. This study investigates the effect of enhanced electrode surface area on the skin-electrode impedance and ECG signal quality. A comparison between silver thin-film electrodes and nanostructured silver nanorod-based electrodes was performed, which were fabricated by the glancing angle deposition technique (GLAD). Human trials were conducted using both electrode types. Results show that electrodes with a larger effective surface area exhibit significantly lower skin-electrode impedance compared to the flat thin-film electrodes. ECG signal quality assessed using signal-to-noise ratio was higher for silver nanorod electrodes (12 dB) than the silver thin film electrodes (8.8 dB). These findings highlight the role of surface engineering to improve the performance of dry electrodes, providing better quality ECG signals and offering valuable insights for the development of high-fidelity wearable biosensors.

INTRODUCTION

Cardiovascular diseases (CVDs) are a major global health concern affecting millions of people [1]. Diagnosis of CVDs is performed in both clinical settings and with wearable devices. High-quality ECG signals are essential, as accurate diagnosis and analysis depend heavily on signal integrity, whether performed by physicians or by machine learning algorithms in wearable devices. ECG signals are recorded through electrodes, which serve as transducers that convert biological signals from the human body into electrical signals [2]. The quality of the acquired ECG signals largely depends on the electrode's characteristics. Commonly used hospital-grade electrodes include metal and Ag/AgCl wet electrodes. However, metal electrodes lack flexibility, while wet electrodes suffer from gel dehydration during prolonged use, resulting in signal degradation and potential skin irritation. Hence, gel-free dry electrodes, including textile and polymer types, are currently being investigated for clinical applications [3,4]. Key factors which influence ECG signal quality are electrical conductivity, skin-electrode impedance (SEI), skin conformance which reduces noise due to electrode movements and physiological factors such as sweat. Increasing the electrode's effective contact area with the skin reduces the interface impedance, as it increases the capacitance, and impedance is inversely proportional to capacitance. To achieve this, some of the methods adopted are varying electrode size or modifying surface morphology to enhance effective contact area [5,6]. In this study, two types of electrodes were fabricated, one with a silver nanorods (AgNRs) surface and the other with a silver thin film (AgTF) surface, to investigate the effect of surface morphology on ECG signal quality. The comparison highlights that increased effective contact area significantly reduces SEI and enhances ECG signal quality, as evidenced by an improved signal-to-noise ratio (SNR).

EXPERIMENT

For the fabrication of both the electrodes, 2g of silver was used for deposition by thermal evaporation on silicon (Si) substrate. To fabricate AgTF, the substrate holder was positioned perpendicular to the incoming vapor flux, resulting in a uniform silver film with a thickness of approximately 2 μm , illustrated in Fig.1(a). For the AgNRs formation, the substrate holder was tilted to an angle of 85° relative to the vapor flux, employing the Glancing Angle Deposition (GLAD) technique to promote the formation of vertically aligned nanorod structures, illustrated in Fig.1(b). AgNRs were formed on Si substrate with lengths and diameters of approximately 1 μm and 150 nm, respectively. A vacuum of 10^{-6} mbar was maintained during deposition using a rotary and a turbomolecular pump. Both the AgTF and AgNRs structures were transferred from Si substrate to polydimethylsiloxane (PDMS) to be used as ECG electrodes resulting in Ag thin film on PDMS and AgNRs embedded on PDMS electrodes. The fabrication

steps to make ECG electrodes using these deposited structures were followed as mentioned in the work of Yogita et al. [7].

RESULTS AND DISCUSSION

Field emission scanning electron microscopy (FESEM) confirms the formation of thin film (Fig.1(c)) and nanorods of Ag (Fig.1(d)). Atomic force microscopy (AFM) reveals a smooth AgTF (Fig.1(e)) and uniform columnar structures of AgNRs (Fig.1(f)) obtained from deposition using GLAD on Si wafer.

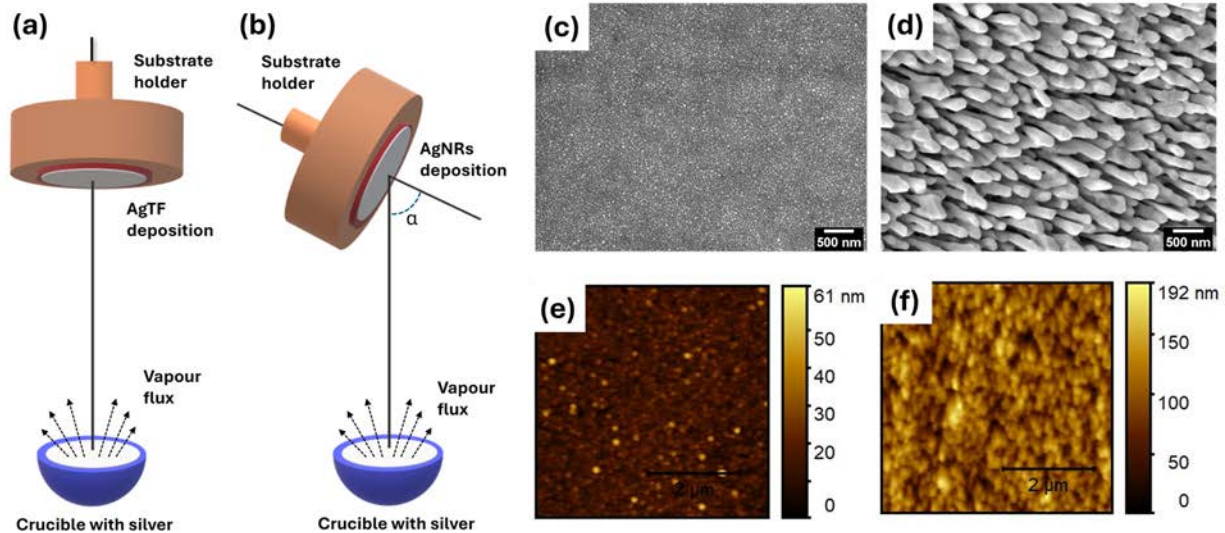


FIGURE 1. Formation via thermal deposition of (a) AgTF (b) AgNRs by GLAD. FESEM image of (c) AgTF (d) AgNRs. AFM image of (e) AgTF (f) AgNRs on Si substrate.

IMPEDANCE AND ECG SIGNAL ANALYSIS

The fabricated electrodes were placed on the forearm at an interelectrode distance of 3 cm. Impedance measurements were conducted using a Keysight E4980 LCR meter over a frequency range of 40 Hz to 1000 Hz, applying a sinusoidal voltage of 10 mV. SEI can vary from person to person, hence all measurements were conducted on same participant on a single day for comparison. The impedance vs frequency characteristics of AgNRs, AgTF and Ag/AgCl electrodes are shown in Fig.2(a). For all three electrodes, impedance decreases with an increase in frequency. AgNRs electrodes exhibited the lowest impedance value across the frequency range, followed by AgTF and Ag/AgCl electrodes. This reduction can be attributed to the enhanced surface area due to the presence of AgNRs on the electrode surface, despite both AgNRs and AgTF electrodes having high conductivity due to silver layer on top of the electrode. As capacitance is proportional to surface area and impedance is inversely proportional to capacitance, the increased effective contact surface area resulted in lower impedance. ECG signals were recorded from a human participant using AgNRs and AgTF electrodes with informed consent from the participant. Electrode placement on the participant for ECG acquisition is shown in Fig.2(b). Figure 2(c-d) display the raw ECG waveforms, including P wave, QRS complex and T wave, recorded using AgNRs and AgTF electrodes. ECG signals were recorded using a standard clinical ECG machine, Philips TC10. To quantitatively evaluate the ECG signal quality acquired using both the electrodes, SNR was computed. SNR is defined as ratio of power of signal to the power of noise. The AgNRs electrode gave an SNR of 12 ± 0.4 dB, while the AgTF electrodes exhibited an SNR of 8.8 ± 1.6 dB., which is graphically represented in Fig.2(e). This shows the effect of enhanced effective contact area of the electrode which reduces the SEI, enabling better acquisition of ECG signals by minimizing the impact of noise.

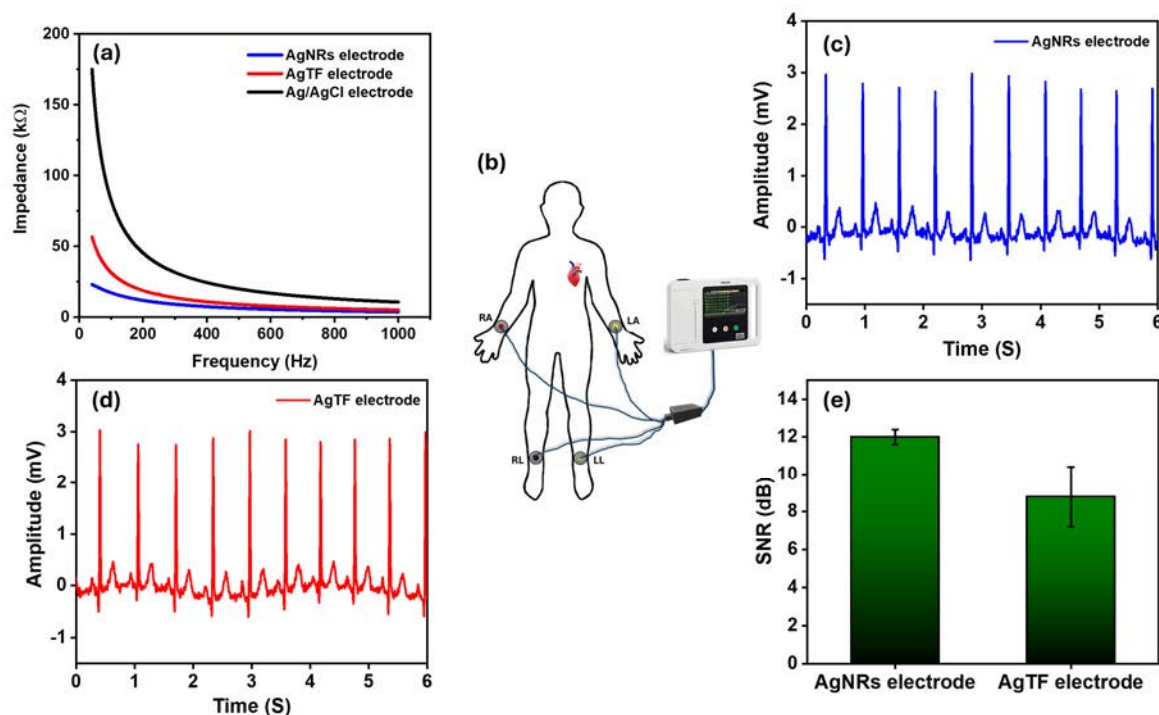


FIGURE 2. (a) Impedance vs frequency plot for AgNRs, AgTF and Ag/AgCl electrode (b) Illustration of electrode placement of human subject. ECG signals of (c) AgNRs (d) AgTF electrodes (e) SNR comparison of AgNRs and AgTF electrode

CONCLUSION

In summary, two types of electrodes with differing effective surface area were fabricated, one with a flat thin film and the other with a nanorod-shaped surface morphology. The impact of enhanced surface area for skin electrode impedance was evaluated using impedance frequency plots, showing significantly lower impedance for the AgNRs electrode. ECG signal quality was compared in terms of SNR, with AgNRs electrode showing superior performance. These results demonstrate the importance of surface engineering for improving the ECG signal quality in healthcare.

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Structural, Optical, Morphological, Photo-catalytic and Antioxidant activities Of Green Synthesized Ag doped ZnO Nanoparticles by Using Orange Peel

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Abstract. This paper explores the green synthesis of Ag-doped ZnO nanoparticles using orange peel extract as a natural stabilizing and reducing agent. Morphological and structural characterization confirmed hexagonal wurtzite structure and uniform Ag distribution. The optical band gap decreased from 3.40 to 2.99 eV with Ag doping. Photocatalytic performance reached 90.99% dye degradation, and antioxidant activity also improved significantly. These findings highlight the enhanced multifunctional properties of Ag-doped ZnO NPs for environmental and biomedical use.

INTRODUCTION

The rapid industrial expansion, especially in textile and dyeing sectors, has significantly increased the discharge of synthetic dyes into water bodies, leading to serious environmental and ecological concerns. These dyes, due to their complex and stable structures, resist degradation and pose toxicity risks [1]. Traditional water treatment methods often fail to remove such persistent pollutants completely. Advanced Oxidation Processes (AOPs), especially those involving metal oxide nanoparticles, have gained attention for their ability to produce Reactive Oxygen Species (ROS) capable to degrade down complex dye molecules. Among these, ZnO nanoparticles stand out due to their favorable properties—non-toxicity, cost-effectiveness, and high photocatalytic activity. Doping ZnO with metals like silver (Ag) further enhances its efficiency by improving light absorption, reducing electron-hole recombination, and promoting surface reactions. Silver-doped ZnO nanoparticles have demonstrated superior photocatalytic performance in degrading various dyes under UV and solar light, with multiple studies confirming enhanced degradation at optimal doping levels. Ag doping also improves antimicrobial properties, broadening its scope for environmental and biomedical use. In this work, Ag-doped ZnO nanoparticles were prepared using a co-precipitation method, with orange peel extract as a green capping agent. The resulting nanoparticles were characterized using EDS, SEM, XRD, FTIR, and UV-visible spectroscopy [2,3]. Their photocatalytic performance was assessed by monitoring the degradation of methylene blue (MB) under visible light. Results indicated that Ag incorporation significantly enhanced photocatalytic efficiency. Thus, Ag-doped ZnO nanoparticles emerge as promising candidates for wastewater treatment, offering a sustainable solution for water purification and environmental protection.

METHOD AND CHARACTERIZATION

In this work, Ag-doped ZnO nanoparticles were synthesized via a green co-precipitation approach using orange peel extract as a natural reducing agent. The nanoparticles were characterized using UV-Vis, FTIR, XRD, SEM, and EDS techniques to analyze their structural, optical, and morphological properties. Photocatalytic efficiency was evaluated through methylene blue dye degradation under visible light, showing enhanced performance with Ag doping. Antioxidant activity was assessed using the DPPH radical scavenging assay, demonstrating improved free radical inhibition. These findings highlight the potential of Ag-ZnO NPs for environmental and biomedical applications.

RESULT AND DISCUSSION

Fig 1 shows the XRD spectra of pure and Ag-doped ZnO nanoparticles, confirming the hexagonal wurtzite structure (JCPDS 36-1451) and FCC structure of Ag (JCPDS 04-0783). Bragg peaks match ZnO's lattice planes, while additional Ag peaks confirm successful doping. As Ag content increases, distinct metallic Ag peaks emerge, and crystallite size decreases due to strain and boundary effects. Rietveld refinement and Scherrer's method reveal consistent crystallite sizes (28.2–38.5 nm) and lattice parameters aligning with ZnO's structure (Table 1). Ag likely segregates at grain boundaries rather than substituting Zn²⁺ within the ZnO lattice [3].

Fig 2 shows a UV absorption edge between 300–420 nm for ZnO and Ag-doped ZnO nanoparticles. Tauc plot analysis reveals a decrease in band gap from 3.40 eV (ZnO) to 2.98 eV (5% Ag-ZnO) (Table 1) due to Ag-induced acceptor levels. This band gap tunability enhances their potential for optoelectronic applications [4].

FTIR spectroscopy (Fig 3) of Ag-doped ZnO nanoparticles reveals distinct peaks confirming various functional groups and bonding characteristics. Peaks between 600–900 cm^{-1} correspond to Zn–O stretching vibrations, indicating successful ZnO formation. Absorption bands at 1643 cm^{-1} and 1394 cm^{-1} are attributed to hydroxyl groups, suggesting surface hydroxylation. These groups enhance the nanoparticles' reactivity and photocatalytic efficiency by facilitating charge transfer. Additional peaks indicate possible moisture-related bands due to environmental exposure. Such impurities can be minimized through proper calcination or heat treatment [5].

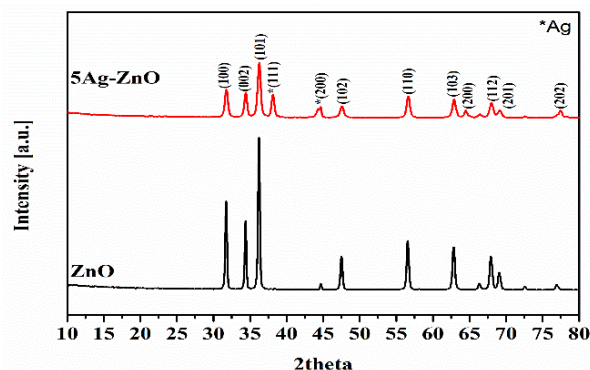


Fig 1: XRD data for ZnO & 5Ag- ZnO NPs.

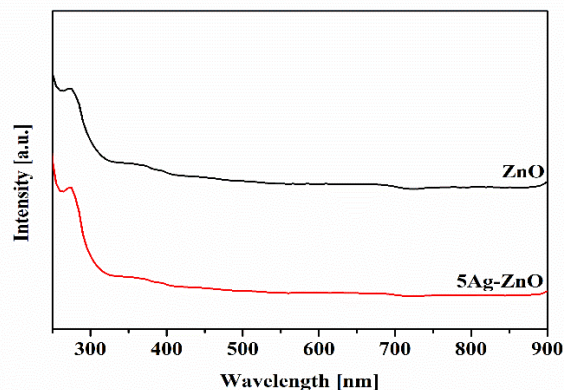


Fig 2: UV spectra for ZnO & 5Ag- ZnO NPs.

The photocatalytic activity of ZnO and Ag-doped ZnO nanoparticles was evaluated using methylene blue (MB) dye degradation under visible light. Ag doping enhanced degradation efficiency, reaching up to 90.99% after 60 minutes, compared to 84.21% for pure ZnO (Fig 4). Improved activity is attributed to reduced crystallite size, increased surface area, and active sites. Ag acts as an electron sink, forming a Schottky barrier that facilitates charge separation and suppresses $e^- - h^+$ recombination. Reactive radicals generated during this process aid in effective MB degradation[1,6-7].

Table 1: Lattice parameters and Crystalline size calculated from Scherrer's Method, Rietveld Refinement and Energy Band Gap of the prepared nanoparticles.

Samples	Lattice parameters (Å)					Crystalline size, D (nm)			Energy Band Gap (eV)
	Scherrer's Method		Rietveld Refinement			Scherrer's Method	Rietveld Refinement		
	a=b	c	a=b	c	Ag		ZnO	Ag	
					$a = b = c$				
ZnO	3.142	5.236	3.254	5.223	-	38.5	44.2	-	3.40
5Ag-ZnO	3.121	5.022	3.242	5.214	4.086	28.2	34.3	29.1	2.99

Fig 5 (a–d) shows SEM images of pure and Ag-doped ZnO nanoparticles, revealing spherical, uniformly distributed nanocrystallites with slight agglomeration. The morphology remains consistent across doping levels, confirming isotropic growth and uniform dispersion of Ag. SEM observations align with XRD results, indicating structural stability. EDS analysis (Figure 8) confirms the presence of Zn, O, and Ag, validating successful Ag incorporation. Elemental composition varies with doping, showing increased Ag content from 3.18% to 9.76%. EDS mapping demonstrates homogeneous distribution of elements across all samples [8-9].

The antioxidant activity of Ag-doped ZnO nanoparticles was evaluated using the DPPH radical scavenging assay, showing a clear color change from violet to yellow, indicating free radical reduction. Antioxidant activity increased with higher Ag doping, reaching 42.25% for 5Ag-ZnO at 100 $\mu\text{g/ml}$. This enhancement is attributed to the synergistic effect of Ag and ZnO in scavenging free radicals. The ROS-generating capability of ZnO and electron transfer interactions contribute to this effect. Functional groups from plant extract synthesis may also enhance activity. These results align with previous antioxidant studies on doped ZnO systems [9-10].

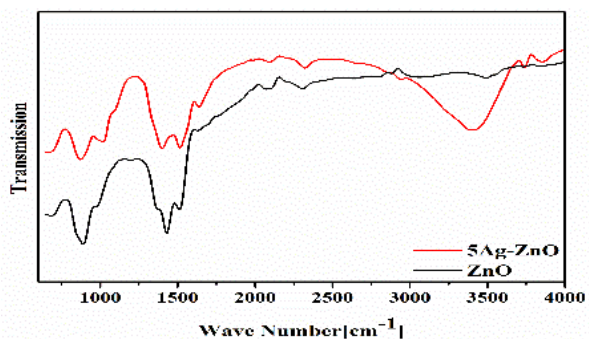


Fig 3: FTIR spectra for ZnO & 5Ag- ZnO NPs

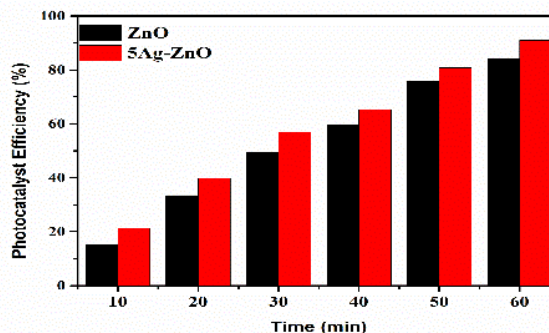


Fig 4: Photocatalytic degradation for ZnO & 5Ag- ZnO NPs

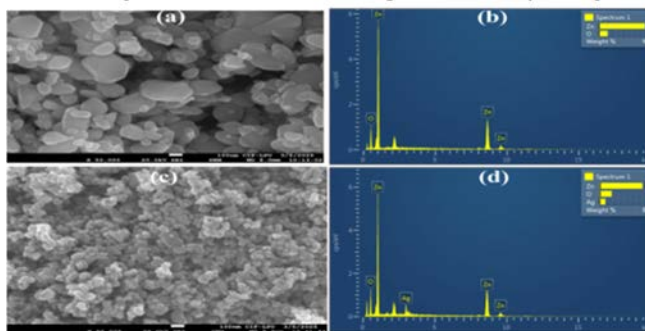


Fig 5: (a & c) SEM, (b & d) for ZnO & 5Ag- ZnO NPs

CONCLUSION

Ag-doped ZnO nanoparticles were synthesized using orange peel extract, offering a green and cost-effective approach. Structural and optical analyses confirmed Ag incorporation, leading to reduced band gap and enhanced light absorption. The nanoparticles showed strong antioxidant activity (~52%) and improved photocatalytic efficiency, achieving 97.7% MB dye degradation with 5% Ag-ZnO. These enhancements result from better charge separation and narrowed band gap. The study highlights their potential for environmental applications like wastewater treatment. Future research will focus on their anticancer and antibacterial potential in biomedical field.

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Sol-gel Synthesis and Crystallographic Study of ZnO/f-MWCNTs Nanocomposites

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Abstract. Zinc oxide nanoparticles (ZnO NPs) and functionalized multi-walled carbon nanotubes (ZnO/f-MWCNTs) nanocomposites were successfully synthesized using the Sol-gel method. The incorporation of ZnO onto the surface of f-MWCNTs led to a composite material that may exhibit significantly enhanced electrical, optical, catalytic, and sensing properties as compared to bare ZnO nanoparticles and MWCNTs. The crystallographic properties of ZnO nanoparticles, f-MWCNTs and ZnO/f-MWCNTs nanocomposites were investigated using X-ray diffraction (XRD) techniques. The XRD patterns confirmed the presence of a hexagonal wurtzite crystal structure. ZnO/f-MWCNTs. This study has potential future applications in the fields of science & technology and industry.

INTRODUCTION

The combination of the remarkable properties of both carbon nanotubes (CNTs) and semiconductor nanostructures is leading to the development of an advanced class of nanocomposite materials, opening up a vast range of applications across various scientific fields [1,2]. Among the numerous nanomaterials, ZnO nanoparticles have attracted significant attention in materials science, chemistry, physics, and industry [3]. Zinc oxide is considered one of the most valuable and versatile n-type semiconductor materials, possessing a direct band gap of 3.3 eV at room temperature and an exciton binding energy of 60 meV [4]. ZnO primarily exists in three crystal structures: wurtzite, rock salt, and zinc blende, with the thermodynamically most stable phase being wurtzite under ambient conditions. The morphology of ZnO nanoparticles depends significantly on the synthesis method employed. They can appear as nanotubes, nanorods, nanobelts, nanosheets, or nanowires. The physical and chemical properties of ZnO are heavily influenced by its structure, grain size, and the synthesis technique used.

The present work focuses on the synthesis and characterization of nanocomposites, particularly ZnO/multi-walled carbon nanotube (MWCNT) composites, which have garnered considerable interest due to the high porosity, hollow structure, and large specific surface area of MWCNTs [5]. These nanotubes possess unique physical properties and excellent electrical conductivity, making them highly effective in enhancing adsorption and facilitating charge transfer between semiconducting materials—thus improving overall conductivity [6]. We have synthesized ZnO nanoparticles using the sol-gel method, and subsequently functionalized MWCNTs (f-MWCNTs) to fabricate the nanocomposite. The sol-gel approach enables the formation of materials with complex molecular architectures in a gel-like state. The synthesized materials have been characterized using X-ray diffraction (XRD), to gain critical information on the crystal structure and phase composition of the samples.

EXPERIMENTAL DETAILS

For this study, pristine multi-walled carbon nanotubes (MWCNTs) with an outer diameter of 10–20 nm and a length of 10–30 μm , having a purity greater than 95% and less than 3% impurities, were used. Other chemicals employed included high-purity zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$, nitric acid (HNO_3 , 67%), sulfuric acid (H_2SO_4 , 95%), sodium hydroxide (NaOH), ethanol, and deionized (DI) water. All reagents were used as received, without further purification. Zinc oxide nanoparticles were synthesized via the sol-gel method, a bottom-up approach illustrated in Fig.1. Initially, 2 g of zinc acetate dihydrate was dissolved in 15 mL of DI water and stirred for 20 minutes. In a separate container, 8 g of sodium

hydroxide was dissolved in 10 mL of DI water and similarly stirred for 20 minutes. The two solutions were then combined under constant stirring for 5 minutes. Subsequently, 100 mL of ethanol was titrated dropwise into the mixed solution using a burette, resulting in the formation of a milky white precipitate, indicative of ZnO precursor formation. The suspension was left undisturbed for 5 hours to allow gel formation. The resulting gel was washed 3–4 times with deionized water, dried in an oven at 80 °C overnight, and finally calcined at 250 °C to obtain ZnO nanoparticles [8].

To functionalize the MWCNTs, 600 mg of raw MWCNTs was dispersed in 100 mL of a mixed acid solution containing nitric acid (15.8 M) and sulfuric acid (18.4 M) in a 1:3 volume ratio. The mixture was sonicated at 40 °C for 2.5 hours to ensure homogeneous dispersion and the introduction of functional groups on the nanotube surfaces. After cooling to room temperature, the suspension was filtered using Whatman filter paper, and the resulting black solid was washed repeatedly with deionized water until a neutral pH was achieved. The product was then dried at 60 °C for 5 hours to yield functionalized MWCNTs (f-MWCNTs). For preparing ZnO–MWCNT nanocomposites, 100 mg of ZnO nanoparticles was dispersed in DI water and sonicated for 1 hour at room temperature. A separate dispersion of 100 mg of f-MWCNTs in DI water was also sonicated under identical conditions. The two suspensions were then combined and stirred for 3 hours at a constant speed. The resulting suspension was centrifuged multiple times with deionized water to remove unbound particles, and the final product was filtered and dried in an oven at 60 °C for 24 hours to eliminate residual moisture and ensure material stability for further characterization [9].

The synthesis process involves a series of chemical reactions. The overall chemical reaction for ZnO nanoparticles formation is when sodium hydroxide was used as solvent as in Eq. (1)

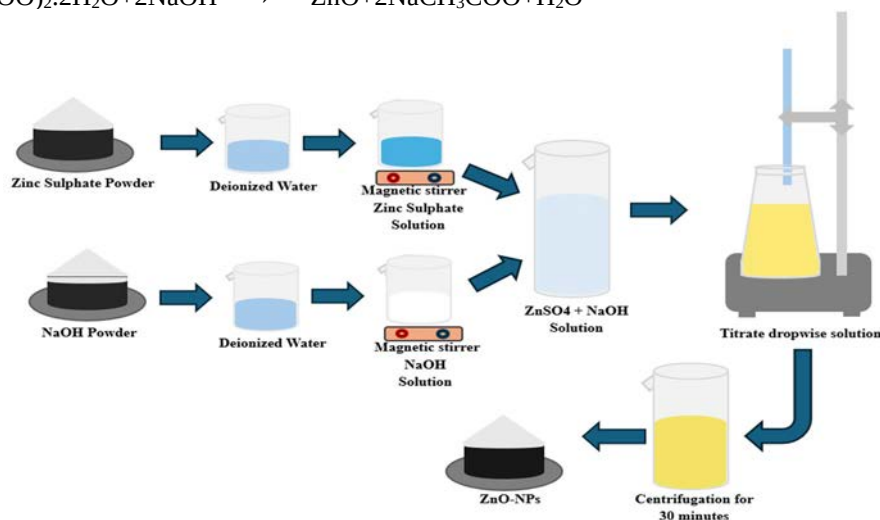
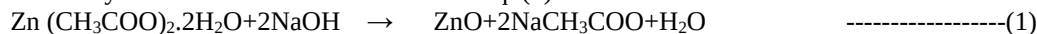


FIGURE 1. Synthesis of ZnO Nanoparticles using Sol Sol-Gel Method

RESULTS AND DISCUSSION

The crystallinity and structure of pure ZnO, functionalized MWCNTs (f-MWCNTs), and ZnO/f-MWCNT nanocomposites were analyzed using a PANalytical X'Pert Pro diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), over a 2θ range of 10° – 70° at a scan rate of $3^\circ/\text{min}$. As shown in Fig. 2, the ZnO/f-MWCNT nanocomposite exhibited prominent diffraction peaks at $2\theta = 25.925^\circ, 31.775^\circ, 34.475^\circ, 36.275^\circ, 47.525^\circ, 56.625^\circ, 62.875^\circ, 68.030^\circ, \text{ and } 69.233^\circ$, corresponding to the (002), (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) characteristic planes of ZnO, confirming its wurtzite hexagonal structure (JCPDS 36-1451). The absence of additional peaks or anomalies indicates that the synthesized ZnO/f-MWCNT nanocomposite is free from detectable impurities or defects, signifying its high phase purity—an essential factor for effective performance in advanced applications. A distinct peak at $2\theta = 25.925^\circ$, also observed in f-MWCNTs, corresponds to the (002) plane of graphitic carbon, verifying the presence and structural integrity of MWCNTs. This peak is commonly associated with sp^2 -hybridized carbon in graphite-like structures. Additional f-MWCNT peaks appeared at 44.1° and 53.72° , indexed to the (100) and (004) planes. All detected peaks align well with standard ZnO diffraction data (JCPDS Card No. 36-1451), confirming the wurtzite hexagonal crystal structure of the ZnO nanoparticles. The crystallite size of ZnO was estimated using the Debye–Scherrer equation

$$D = K\lambda / \beta \cos\theta \quad \text{-----(2)}$$

where:

- D is the average crystallite size,
- K is the Scherrer constant (0.9),
- λ is the X-ray wavelength ($1.54 \text{ \AA}$),
- β is the full width at half maximum (FWHM) of the diffraction peak (in radians), and
- θ is the Bragg angle.

Using this equation, the average crystallite size of the synthesized ZnO nanoparticles was calculated to be in the range **34–36 nm**, confirming their nanoscale dimensions.

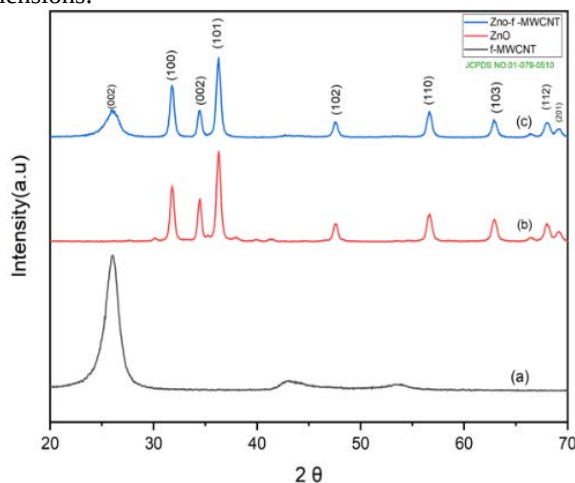


FIGURE 2. The XRD patterns of ZnO, f-MWCNT & ZnO-MWCNTs nanocomposites

CONCLUSION

In summary, ZnO/MWCNT nanocomposites were successfully synthesized using the sol-gel method. X-ray diffraction (XRD) analysis confirmed that the composite exhibits a hexagonal wurtzite crystal structure, with a strong preferred orientation along the (101) plane. A prominent diffraction peak at $2\theta = 36.75^\circ$ indicates a highly crystalline nature of the material. The average crystallite size of pure ZnO nanoparticles was found to be approximately 36 nm, confirming their nanoscale dimensions. The results suggest that the incorporation of MWCNTs does not disrupt the crystalline structure of ZnO but may contribute to an increase in crystallite size and improved structural integrity of the composite.

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Stability Evaluation of Nanostructured AAO-Au Substrate for SERS Applications

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Abstract. For precise and accurate sensing applications, substrates must maintain stability over time and across different conditions. This makes the stability of Surface-Enhanced Raman Scattering (SERS) substrates especially important, as it directly affects their performance and durability in real-world environments. This study evaluated the Raman signals of gold nanoparticles (AuNPs) coated on porous anodic aluminum oxide (PAAO) thin films with three different pore lengths on day 1 and day 30 to assess their stability. Formation and uniformity of the AAO thin films were confirmed by scanning electron microscopy (SEM). The sample S1, which has a shorter pore length than samples S2 and S3, demonstrated exceptional signal stability with a slight increase (~6.3%) in SERS intensity after 30 days. This suggests potential self-enhancement effects, which may be attributed to a gradual increase in analyte attachment, better exposure of plasmonic hot spots, or slight surface changes that make the substrate more favorable for molecular interaction.

INTRODUCTION

The stability of SERS (Surface-enhanced Raman spectroscopy) substrates is an important area of research because they are inherently related to the performance and reliability of SERS applications. In recent years, researchers have focused on improving the stability, reproducibility, and sensitivity of SERS substrates to avoid their known limitations [1]. Developing a unexpensive technique to produce SERS substrates with excellent stability and reproducibility over large areas is necessary. The self-assembling method has been proven to be favorable and effective in fabricating regular nanostructures on an AAO substrate. The nanoporous structure of AAO provides a large surface area that can be improved through specific fabrication conditions (Applied voltage, Anodization time, Temperature) [2]. The stability of SERS signals is improved by using highly ordered arrays of SERS substrates, which is achievable through AAO template-assisted methods. The stability of specific metal-based SERS substrates, such as Ag/Au nanostructures, has been noted. P. Gu et.al [3] reported that strong SERS peaks were observed after 3 months of storing substrates in air. This study focuses on testing the stability of AAO-Au nanostructure SERS substrates over a period of thirty days on different samples with different pore lengths.

EXPERIMENTAL

To synthesize self-ordered nanoporous anodic aluminum oxide (AAO), aluminum foils (1.2 cm × 4 cm, 1 mm thickness, purity 99.999%) were the anode, and a platinum sheet was the cathode, both parallel and 2 cm apart. The aluminum foil and platinum sheet were degreased in an ultrasonic ethanol bath for 30 minutes. The aluminum foil was electropolished in perchloric acid and ethanol (1:4) for 60 seconds at 20 volts to remove surface irregularities. Samples were washed and dried. A two-step potentiostatic anodization was used. The first step used 0.3M oxalic acid for 360 minutes at 10°C, with 40 volts. The first anodization layer was removed by immersing samples in 1.8 wt/g chromic acid and 6 mL phosphoric acid for 1 hour at 65°C. The second anodization used the same conditions, with durations of 1 minute for sample S1, 5 minutes for S2, and 10 minutes for S3. Both specimens were coated with 40 nm diameter gold nanoparticles using spin coating. An analyte, R6G, at 10⁻⁴ concentration, was drop-cast on each specimen, and Raman spectroscopy was performed on the first and thirtieth days to investigate the SERS behavior.

RESULTS AND DISCUSSIONS

The morphology of porous substrates is crucial for enhancing SERS because porous structures provide a high density of hot spots where the local electromagnetic field is significantly intensified. Figure 1 (a), (b), and (c) present

the SEM image of sample S1, which was anodized for one minute in the second step of anodization, sample S2, and sample S3, which were anodized for 10 minutes and 15 minutes in the second step, respectively. The average pore diameters of all samples are the same at approximately 44 nm. The variation in the anodization time during the second step for each sample resulted in differing pore lengths among the samples [4]. The tunability of the pores is noticeable at S1 and S3. Figure 1 (d), (e), and (f) present the SERS spectra of R6G molecules adsorbed on the Au-AAO thin film at a wavelength of 532 nm, with a power setting of 1 mW for samples S1, S2, and S3 on the first and thirty days, respectively. The spectra reveal several characteristic Raman peaks of R6G at 613, 773, 1363, 1510, and 1652 cm^{-1} on both day 1 and day 30. Notably, the most intense and well-resolved peak is observed at 613 cm^{-1} , which is attributed to the C–C–C in-plane ring bending mode of R6G [5]. The intensity variation of the Raman signals for all samples was calculated. For sample S1, the intensity increased by 6.3%, whereas it decreased by 49.7% for sample S2 and 34% for sample S3. The substantial decrease in intensity for S2 compared to S3 is likely due to S3 possessing tunable and uniform pores in contrast to S2. The stability of sample S1 maybe a result of a consistent enhancement of local electric fields at the surface, thereby enhancing Raman signals [6]. Additionally, changes in the chemical environment [7] and alterations in the dielectric environment over time due to solvent evaporation or moisture changes can affect plasmon resonance conditions, leading to enhanced Raman scattering [8].

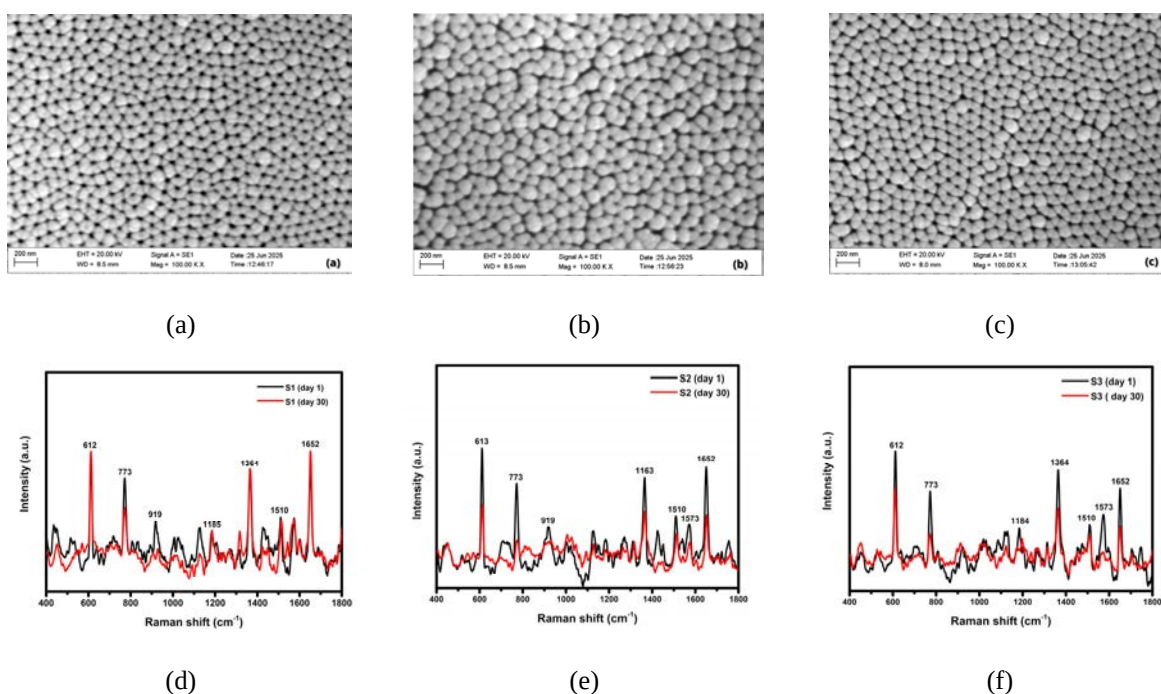


FIGURE 1. Presents, (a) SEM image of sample S1, (b) SEM image of sample S2, and (c) SEM image of sample S3. (d) Raman spectra of R6G adsorbed on S1, (e) Raman spectra of R6G adsorbed on S2, and (f) Raman spectra of R6G adsorbed on S3.

CONCLUSION

The Stability of SERS-based sensing platforms. Our findings demonstrate that although all three samples—S1, S2, and S3—exhibited similar pore diameters (~ 44 nm), the variation in anodization time led to significant differences in pore length and ordering, which directly impacted SERS performance and stability over time. Sample S1, with the shortest pore length, notably showed exceptional signal stability, even exhibiting a slight increase ($\sim 6.3\%$) in Raman intensity after 30 days. This unexpected enhancement suggests potential long-term self-optimization of analyte–substrate interactions, possibly driven by improved hotspot exposure, surface reorganization, or environmental changes affecting the plasmonic response. These results highlight the importance of controlled pore engineering in achieving durable and high-performing SERS substrates for real-world sensing applications.

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Characterization And Biocompatibility Assessment of Collagen-Hydroxyapatite Scaffolds For Tissue Engineering Applications

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Abstract. Collagen-hydroxyapatite (HA) composite scaffolds were fabricated using the freeze-drying method for potential application in bone tissue regeneration. Structural and morphological characterization was carried out using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and field emission scanning electron microscopy (FESEM) techniques. XRD analysis confirmed the formation of hydroxyapatite with well-defined peaks and FTIR spectra showed characteristic functional groups of both collagen and HA, indicating successful composite formation. FESEM images revealed a highly porous and interconnected structure, which is beneficial for cell infiltration and nutrient diffusion. The biocompatibility of the scaffolds was evaluated through an *in vitro* MTT assay using mesenchymal stem cells (MSCs), which showed good cell viability and proliferation over a 7-day culture period. These results suggest that the freeze-dried collagen-HA scaffold is a promising candidate for bone tissue engineering applications.

Keywords: Freeze-drying, Collagen-hydroxyapatite scaffold, Bone tissue engineering, Biocompatibility, MTT Assay.

INTRODUCTION

Over the past few decades, tissue engineering has gained recognition as a promising multidisciplinary strategy for repairing and regenerating damaged bone tissue. This approach involves the integration of osteogenic cells and osteo-inductive signalling molecules with a suitable scaffold [1]. These scaffolds must be biocompatible and offer a temporary and spatially organized 3D framework to guide tissue formation. Additionally, they serve as an artificial extracellular matrix, supporting cell attachment, growth, and proliferation, while also providing structural support for the developing tissue [2]. Natural bone tissue is composed of an organic matrix, primarily collagen, and an inorganic crystalline phase like hydroxyapatite. The organic component contributes to flexibility and on the other hand, the inorganic phase provides mechanical strength and durability [3]. Collagen-based scaffolds are commonly used due to collagen's inherent bioactivity, which supports favourable biological responses. These scaffolds typically exhibit high porosity and good permeability; however, they suffer from weak mechanical strength [4]. Therefore, owing to its excellent biological characteristics, collagen can be combined with other materials like HA to enhance its mechanical strength. HA is known for its biocompatibility and osteoconductive properties [5]. Collagen-HA scaffolds are commonly synthesized using the freeze-drying method, which allows for the creation of highly porous structures with interconnected pores. This technique not only preserves the bioactivity of the components but also supports cell infiltration, nutrient diffusion, and tissue ingrowth—making the scaffolds suitable for bone tissue engineering applications [6].

Owing to these advantages of collagen–HA scaffolds, the authors fabricated the composite scaffolds using the freeze-drying method. Subsequently, the scaffolds were characterized using X-ray diffraction, Fourier-transform infrared spectroscopy, and scanning electron microscopy. In addition, their biocompatibility was evaluated through MTT assay using mesenchymal stem cells.

MATERIALS AND METHOD

HA nanoparticles were synthesized using the co-precipitation method reported in our previous study [7], which ensures controlled crystallite size and phase purity suitable for scaffold fabrication. The synthesized HA powder was then utilized to fabricate bio-ceramic porous scaffolds using the freeze-drying technique. Briefly, collagen type I was

suspended in 0.1 M acetic acid to form a homogeneous collagen slurry, which was then subjected to lyophilization. The slurry was first degassed and placed in the freeze-dryer chamber at room temperature. Both the chamber and shelf were cooled at a controlled rate to a final temperature of -40°C , resulting in uniformly porous scaffolds. For scaffold functionalization, HA nanoparticles were incorporated into the collagen slurry before freeze drying [8,9].

RESULTS AND DISCUSSION

The XRD pattern of the collagen-HA scaffold is shown in Figure 1(a). Characteristic diffraction peaks were observed at $2\theta = 25.8^{\circ}$ and 31.7° , corresponding to the (002) and (211) crystallographic planes of HA (JCPDS card no.072-1243) which confirms the formation of HA phase. The presence of sharp and well-defined peaks indicates a crystalline nature of the HA nanoparticles incorporated within the collagen matrix. In contrast, the XRD pattern of pure collagen exhibited a broad hump around 20° , indicating its amorphous nature. The successful incorporation of crystalline HA into the collagen scaffold is further supported by the absence of any secondary phase peaks. The FTIR spectrum of the collagen-HA scaffold (Figure 1b) confirmed the presence of characteristic functional groups corresponding to both collagen and HA. The spectra displayed characteristic peaks around $\sim 634\text{ cm}^{-1}$ and $\sim 1025\text{ cm}^{-1}$, corresponding to the vibrational modes of hydroxyl (OH^+) and phosphate (PO_4^{3-}) groups in HA. Additionally, absorption bands related to collagen were observed, including amide I ($\sim 1640\text{ cm}^{-1}$), amide II ($1500\text{--}1590\text{ cm}^{-1}$), and bands near $\sim 1446\text{ cm}^{-1}$ and $\sim 1330\text{ cm}^{-1}$ attributed to pyrrolidine ring vibrations and carboxyl groups [10].

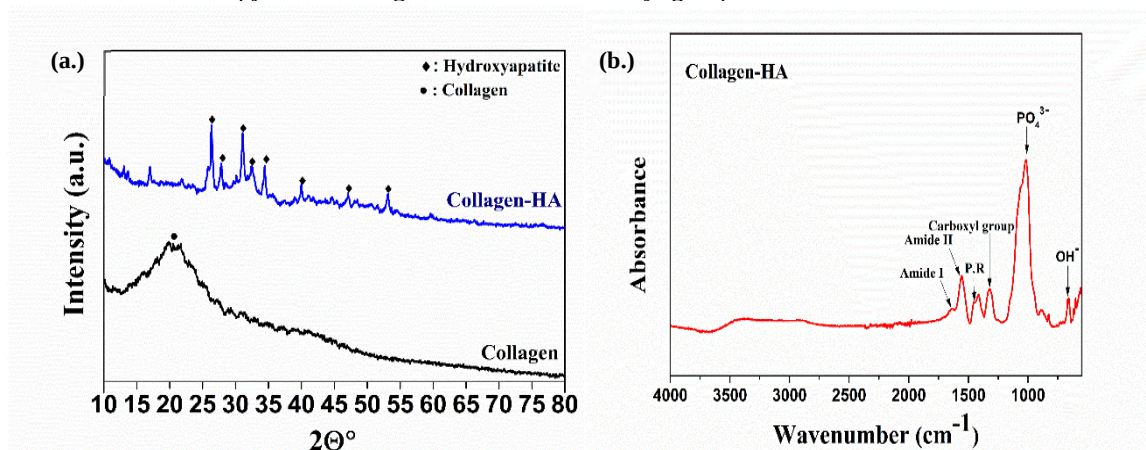


FIGURE 1. (a) XRD patterns of collagen and collagen-HA scaffolds, (b) FTIR spectrum of the collagen-HA scaffold.

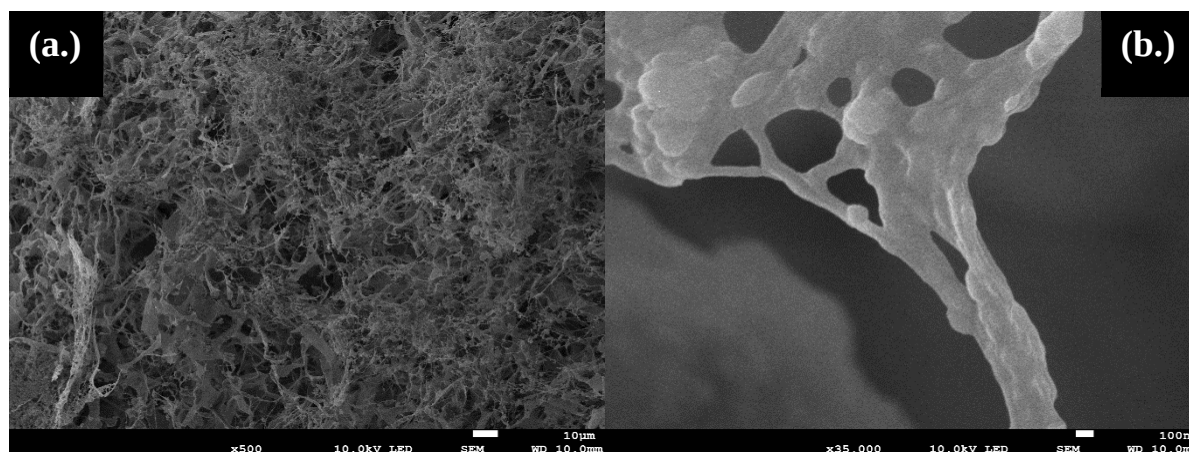


FIGURE 2. FESEM images of collagen-HA scaffold at (a) $\times 500$ and (b) $\times 35,000$ magnifications.

FESEM micrographs of the collagen-HA scaffold at different magnifications are shown in Figure 2. The low magnification image reveals a highly porous and interconnected network, which is essential for facilitating nutrient

transport, cell infiltration and vascularization in tissue engineering applications. The interconnected pores indicate the effectiveness of the freeze-drying method in preserving the scaffold's microstructure. At higher magnification, the surface morphology shows uniformly distributed HA nanoparticles embedded within collagen matrix. The scaffold structure mimics the extracellular matrix, suggesting its suitability for bone tissue regeneration.

The biocompatibility was evaluated using the MTT assay and the results are presented in Figure 3. Cell viability was assessed after 3, 5 and 7 days of incubation, and the optical density (O.D.) was measured at 570 nm. A consistent increase in cell viability over time was observed for both the control and scaffold treated groups, indicating cell proliferation. Notably, the Collagen-HA scaffold showed significantly higher cell viability compared to the control at all time points. After 3 days, the O.D. for the Collagen-HA group was approximately double that of the control, demonstrating excellent initial cytocompatibility. By day 7, the viability in the scaffold group reached an O.D. value of ~1.2, indicating enhanced cellular attachment and proliferation. These findings suggest that the Collagen-HA scaffold supports the proliferation of MSCs and holds strong potential for use in bone tissue regeneration applications.

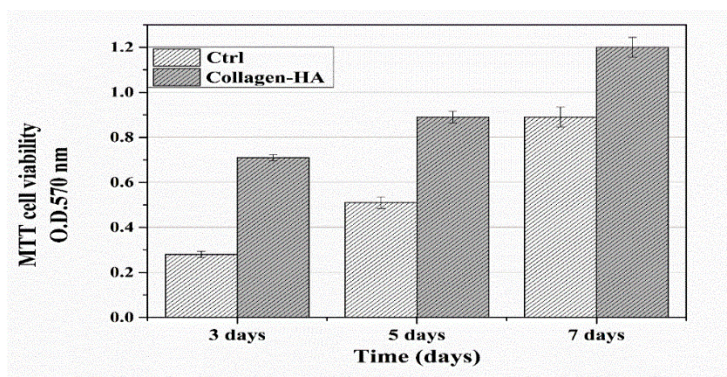


FIGURE 3. MTT assay results showing cell viability of mesenchymal stem cells cultured with collagen-HA scaffold and control over 3, 5 and 7 days.

CONCLUSION

In this study, collagen-hydroxyapatite scaffolds were successfully developed using the freeze-drying method. Structural analysis confirmed the presence of characteristic hydroxyapatite and collagen phases through XRD and FTIR techniques. FESEM analysis revealed a porous, interconnected morphology. The MTT assay demonstrated excellent biocompatibility of the scaffolds over 7 days. These results suggest that the fabricated scaffold possesses the necessary physicochemical and biological characteristics to serve as a promising candidate for bone tissue engineering applications.

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Influence of Low-Concentration Thallium Doping on the Structural, Optical, and Transport Properties of Bi₂Se₃ Nanoparticles

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Abstract. Bi_{1.98}Tl_{0.02}Se₃ nanoparticles were synthesized using the hydrothermal method to investigate the effects of low-level thallium doping on Bi₂Se₃. XRD analysis confirmed a hexagonal crystal structure, FTIR spectra indicated Bi(Tl)-Se vibrational modes, and the optical band gap was determined to be 1.187 eV from the DRS analysis. Electrical transport property measurement were conducted within the range of room temperature to 430 K, which shows the negative seebeck coefficient with increasing magnitude from -60 μVK^{-1} at room temperature to -78 μVK^{-1} at 430 K. The power factor of the material after doping also improved with the temperature, reaching $0.39 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ at 430 K. These result demonstrate that even low-concentration thallium doping can effectively optimize the thermoelectric properties of the Bi₂Se₃ for energy conversion application.

INTRODUCTION

Bismuth selenide (Bi₂Se₃) is a chalcogenide compound from the V-VI group and it has gained attention due to its promising thermoelectric properties and topological insulating behavior. It has layered crystal structure and narrow band gap which make it suitable for various electronic and energy related applications [1]. However, its thermoelectric application is limited by high intrinsic carrier concentration and low seebeck coefficient [2]. Controlled elemental doping has been widely investigated to enhance thermoelectric performance of Bi₂Se₃. Thallium (Tl) doping at the bismuth site can effectively modulate its electronic structure, lattice dynamics, and charge carrier transport properties. In the present study, hydrothermal method was used to synthesize Bi_{1.98}Tl_{0.02}Se₃ nanoparticles. The structural, optical, and transport properties were investigated using XRD, FTIR, UV-Vis DRS, and Hall effect measurements, along with temperature-dependent electrical conductivity and Seebeck coefficient analysis to evaluate the thermoelectric potential of the material.

EXPERIMENTAL DETAILS

In this experimental procedure [3], 15 mmol of NaOH was dissolved in 40 mL deionized water, followed by the addition of 9.2 mmol selenium powder and 1 mL hydrazine hydrate. The mixture was stirred for 1 hour. Separately, 6.0 mmol Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) and 0.03 mmol thallium(I) sulfate (Tl₂SO₄) were dissolved in triethanolamine and added to the selenium solution, followed by 30 minutes of stirring. The prepared mixture was transferred to a hydrothermal autoclave and heated in a muffle furnace for 24 hours at 160 °C. After that solution was allowed to cool naturally, and the obtained sample was washed multiple times with ethanol and deionized water, after that placed into muffle furnace for drying process for at 80 °C for 4 hours.

RESULTS AND DISCUSSION

The structural phase analysis of Bi_{1.98}Tl_{0.02}Se₃ nanoparticles was carried out using a Rigaku SmartLab SE X-ray diffractometer. XRD pattern of Bi_{1.98}Tl_{0.02}Se₃ confirming a hexagonal phase with R-3m space group consistent with

JCPDS card no. 00-033-0214, as shown in Figure 1. The Rietveld refinement (Using Fullprof Suite Software) provided refined lattice parameters $a = 4.1395 \text{ \AA}$, $c = 28.6243 \text{ \AA}$. The Williamson-Hall plot (Fig. 2) was used to calculate average crystallite size and micro strain, which were found to be 17.48 nm and 2.54×10^{-3} , respectively.

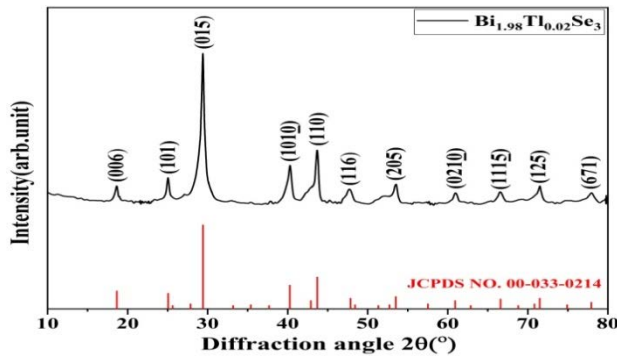


FIGURE 1. XRD pattern of $\text{Bi}_{1.98}\text{Tl}_{0.02}\text{Se}_3$ nanoparticles

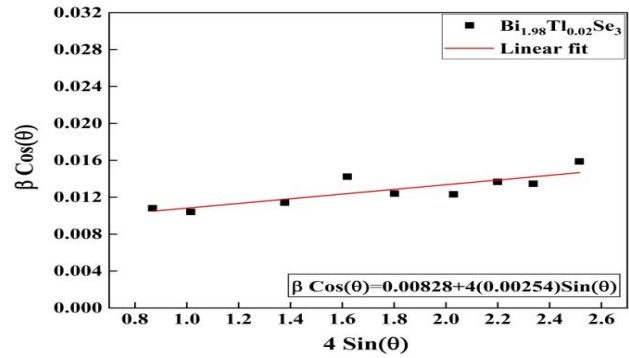


FIGURE 2. W-H plot of $\text{Bi}_{1.98}\text{Tl}_{0.02}\text{Se}_3$ nanoparticles

The FTIR spectrum of $\text{Bi}_{1.98}\text{Tl}_{0.02}\text{Se}_3$ nanoparticles was recorded using a JASCO FTIR-4100 spectrometer within the range of $400\text{--}4000 \text{ cm}^{-1}$, as shown in Fig. 3. Characteristic bands were observed, with key peaks around 438 cm^{-1} and 522 cm^{-1} corresponding to Bi(Tl)-Se stretching vibrations [4, 5]. Additional peaks and their respective vibrational assignments are listed in table 1. Diffuse reflectance measurements were conducted using an Evolution 260 Bio UV-Vis spectrometer. The diffuse reflectance spectrum (inset of Fig. 4) and the corresponding Tauc plot (Fig. 4) were used to determine optical band gap using the Kubelka-Munk method. The estimated direct band gap was approximately 1.187 eV .

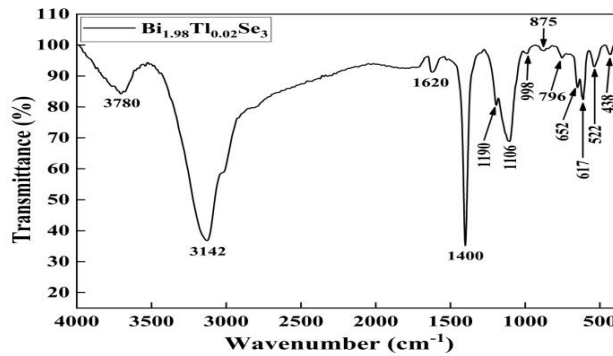


FIGURE 3. FTIR spectra of $\text{Bi}_{1.98}\text{Tl}_{0.02}\text{Se}_3$ nanoparticles

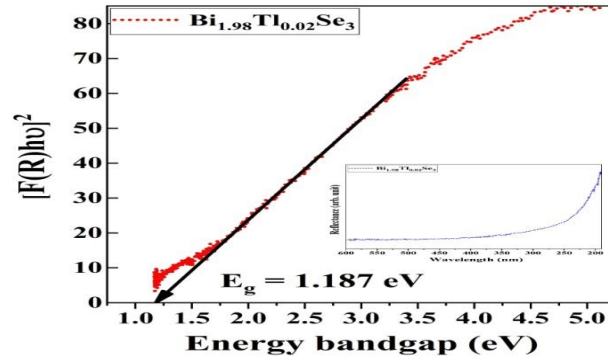


FIGURE 4. Tauc plot of $\text{Bi}_{1.98}\text{Tl}_{0.02}\text{Se}_3$ nanoparticles

TABLE 1. FTIR wave numbers and corresponding vibrational assignments.

Wave number (cm^{-1})	Assignments	Wave number (cm^{-1})	Assignments
617	Bi-O-Bi	1106, 1190	C-O bending
652	NO_2 wagging	1400	C-N bending
796	Se-O stretching	1620	C=O bending
875	C-H aromatics	3142	O-H stretching
998	CH_2 bending	3780	C=C-H bond

Hall effect measurements at room temperature confirmed n-type conductivity in $\text{Bi}_{1.98}\text{Tl}_{0.02}\text{Se}_3$, with electrons as the dominant charge carriers. The calculated mobility was $190 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$, and the charge carrier concentration was estimated to be $2.57 \times 10^{19} \text{ cm}^{-3}$ after the thallium doping, indicating moderately conductive behavior influenced by doping.

Electrical transport measurements were conducted using the standard four-probe method to investigate the temperature-dependent electrical conductivity. Electrical conductivity (σ) shows the decreasing trend with increasing temperature, declining from $0.798 \times 10^5 \Omega^{-1}\text{m}^{-1}$ at room temperature to $0.631 \times 10^5 \Omega^{-1}\text{m}^{-1}$ at 430 K, as shown in Fig. 5. This phenomenon may be attributed to reduced free carrier concentration due to substitution of Bi^{3+} with the aliovalent

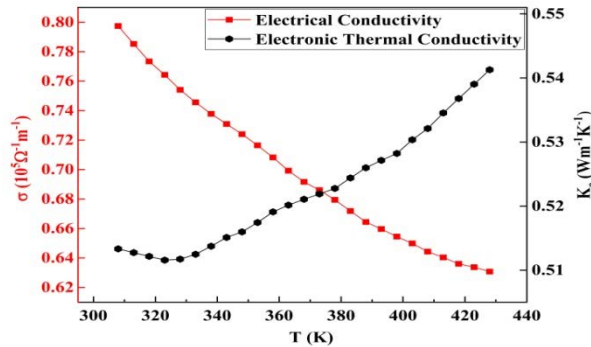


FIGURE 5. Electrical conductivity and Electronic thermal conductivity of $\text{Bi}_{1.98}\text{Tl}_{0.02}\text{Se}_3$ sample.

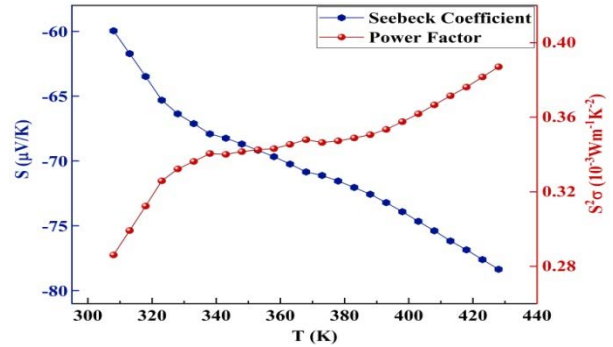


FIGURE 6. Seebeck coefficient and power factor of $\text{Bi}_{1.98}\text{Tl}_{0.02}\text{Se}_3$ sample.

dopant Tl^+ , as well as to enhanced scattering mechanisms at increasing temperature. Electronic thermal conductivity can be calculated from electrical conductivity using the Wiedemann-Franz relation: $\kappa_e = L_0 \sigma T$, where L_0 is the Lorenz number [6]. The observed decrease in electrical conductivity with increasing temperature leads to corresponding reduction in electronic thermal conductivity, which contributes the overall thermoelectric performance of material.

The differential method was used for thermoelectric power measurements by creating a controlled temperature gradient across the sample, and the resulting voltage difference between the hot end and cold end was recorded [5]. The seebeck coefficient (S) increases from $-60 \mu\text{VK}^{-1}$ at room temperature to $-78 \mu\text{VK}^{-1}$ at 430 K, as shown in Fig. 6. This results shows improved thermoelectric voltage generation at higher temperature, which may be due to the reduction in charge carrier concentration and possible energy-dependent scattering. The Power factor ($S^2\sigma$) increased with temperature, from $0.28 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ at room temperature to $0.39 \times 10^{-3} \text{ Wm}^{-1}\text{K}^{-2}$ at 430 K. This improvement in power factor is due to the enhancement in seebeck coefficient caused by the thallium doping in Bi_2Se_3 , which shows the potential application of material in the thermoelectric devices.

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Green Route To Blue Emission: Rare Earth Doped Amorphous Silica From Agriculture Waste

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Abstract. Solid-state reaction method was used to prepare the Tb³⁺ doped amorphous silica (SiO₂: x Tb³⁺) samples with various concentrations, x = 0, 1, 2, 3, 4, 5 mol %. The method of extraction of SiO₂ from groundnut shells (GS) is easy, involving only two steps, and eco-friendly. To confirm the amorphous phase of prepared SiO₂, the X-ray diffraction (XRD) analysis was used. The FTIR study was carried out for the analysis of chemical bonds present in the prepared samples. The optical properties were investigated with photoluminescence studies. The maximum PL intensity on excitation of 243 nm was observed for SiO₂: 2 mol% Tb³⁺ with chromaticity coordinates (0.2159, 0.1780) and color purity (CP) 56.2% giving blue light emission. The blue light emitting phosphor materials have uses in lighting and photonics devices.

INTRODUCTION

The potential applications of rare-earth doped silica phosphor materials in photonics devices have gained the interest of researchers for their remarkable mechanical strength and stability[1]. The high production of agriculture waste, its disposal in an inadequate way, and cost-effective alteration into valuable products are some factors that need to be dealt with from an economic parameters[2]. The common silica precursors used are less economical, and thus GS ash, rice straw ash, and other residual materials having SiO₂ can be used as a substitute[3]. In this work, the acetic acid was selected for acid wash of the groundnut shells. Followed by solid-state mixing of rare-earth ions (Tb³⁺) into the obtained silica powder from GS ash, samples with various concentration of Tb³⁺ were prepared[4]. The synthesized phosphor material further analyzed by X-ray diffraction (XRD) study, FT-IR spectroscopy, and Photoluminescence (PL) spectroscopy confirm the phase purity, functional groups and optical properties of the synthesized phosphor material.

MATERIALS AND METHODS

Materials Used and Preparation Method

The materials used were groundnut shells, acetic acid (99.8%, Thermo Fisher Scientific), Deionized (DI) water, and Terbium (III) acetate hydrate (99.9%, Sigma Aldrich).

The groundnut shells (GS) thoroughly washed with DI water dried at room temperature for 1 day followed by 0.1 M acetic acid wash and again dried in microprocessor oven at 70 °C for 10 hours. After complete combustion in a muffle furnace at 550 °C for 120 minutes to produce GS ash, the Tb³⁺ ions into the SiO₂ ash was doped via solid-state reaction approach. Stoichiometric amount of Terbium (III) acetate hydrate was added to the SiO₂ and ground for 30 minutes and calcined at 600 °C for 4 hours to obtained phosphor material.

MATERIAL CHARACTERIZATIONS

The X-ray diffraction (XRD) studies were obtained using a high-resolution Bruker D8 Discover X-ray diffractometer. The Fourier transform Infra-red (FT-IR) spectroscopy analysis was conducted using Perkin-Elmer spectrometer (spectrum 65). Photoluminescence (PL) studies were obtained with an excitation source of 150 W Xenon lamp of Shimadzu Spectro-fluorophotometer (RF-6000).

RESULTS AND DISCUSSION

The XRD plots for SiO_2 : x mol% Tb^{3+} are shown in Fig. 1(a) confirming the presence of an amorphous phase of SiO_2 characterized by broad hump located at $2\theta \approx 15$ to 25° with Si (111) peak at 29.6° , quartz (SiO_2) peak at 39.9° , carbon peak at 26.2° , quartz (SiO_2) at 28.61° , Si (220) peak at 47.90° , and Si (311) peak at 57.2° confirming the silica rich nature of material prepared[5], [6].

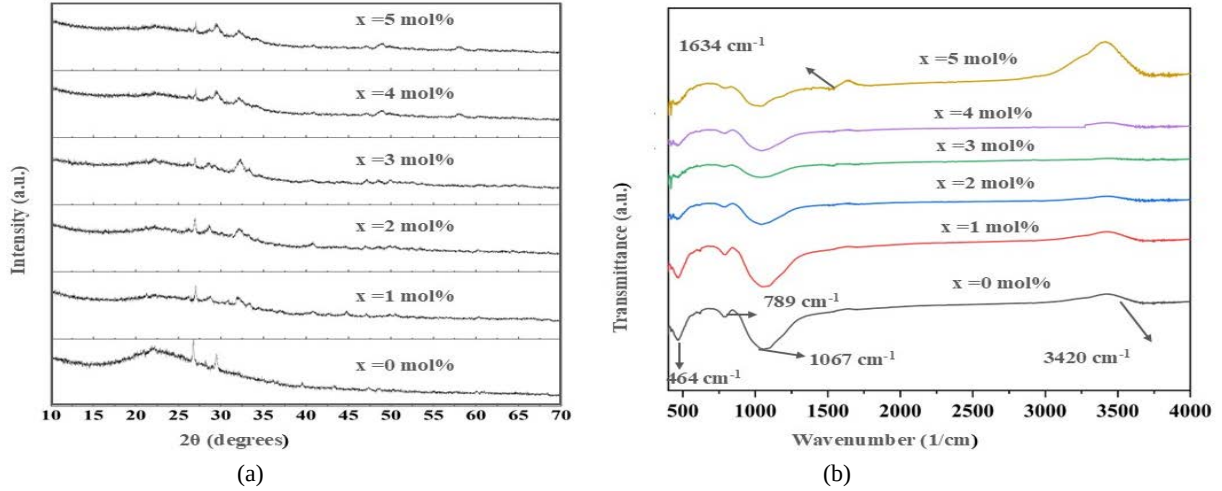


FIGURE 1. (a) XRD patterns for SiO_2 : x mol% Tb^{3+} ($x = 0, 1, 2, 3, 4, 5$), and (b) FT-IR spectrum for SiO_2 : x mol% Tb^{3+} ($x = 0, 1, 2, 3, 4, 5$)

The FT-IR plots of prepared phosphor material closely matched with the commercial silica gel giving bands at 464 cm^{-1} and 789 cm^{-1} correlate to the Si-O-Si bending modes and stretching modes respectively as shown in Fig. 1(b). The dominant band at 1069 cm^{-1} shows the presence of SiO_2 as primary component. The bands at 1634 cm^{-1} and 3420 cm^{-1} indicates bending and stretching vibrations of water molecules [5].

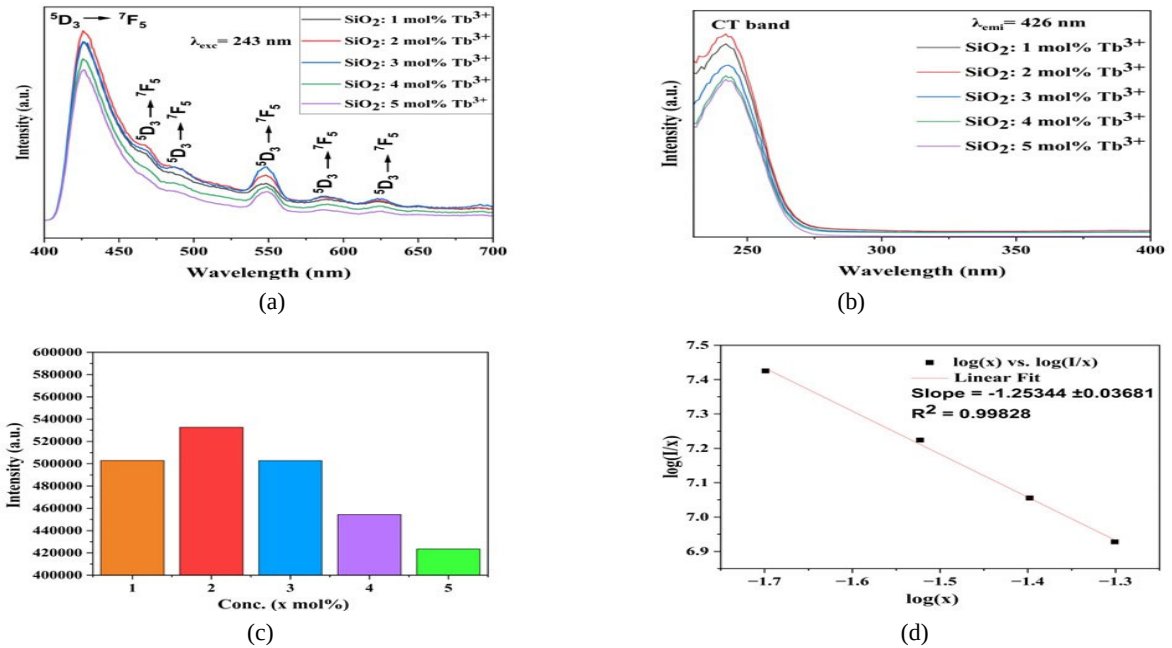


FIGURE 2. (a) PL, (b) PLE spectra, (c) concentration-dependent PL emission spectra, and (d) linear plot for $\log(I/x)$ vs. $\log(x)$ for SiO_2 : x mol% Tb^{3+} ($x = 1, 2, 3, 4, 5$)

Photoluminescence emission (PL) spectra of SiO_2 : x mol% Tb^{3+} was observed upon $\lambda_{\text{exc}} = 243 \text{ nm}$ as shown in Fig. 2(a)[7]. The photoluminescence (PLE) excitation spectrum consisting of charge transfer (CT) band around 243 nm is shown in Fig. 2(b). The concentration-dependent PL spectra is depicted in Fig. 2(c). The nature of interaction between ions causing concentration quenching can be concluded from the slope (Q/3) of plot between $\log(x)$ vs. $\log(I/x)$, which is given in Fig. 2(d) using Dexter's energy transfer theory equation, which comes out to be 3.7 confirming nearest neighbour ion interactions. The 1931 CIE chromaticity diagram for the samples is given in Fig. 3(a), and (b) showing blue light emission[7]. The color purity was calculated for SiO_2 : x mol% Tb^{3+} , where $x = 1, 2, 3, 4, 5$ and it came out to be 56.9%, 56.2%, 53.4%, 60.6%, and 67.3% with color coordinates (0.2166, 0.1729), (0.2159, 0.1780), (0.2208, 0.1879), (0.2103, 0.1604), (0.1982, 0.1387) respectively.

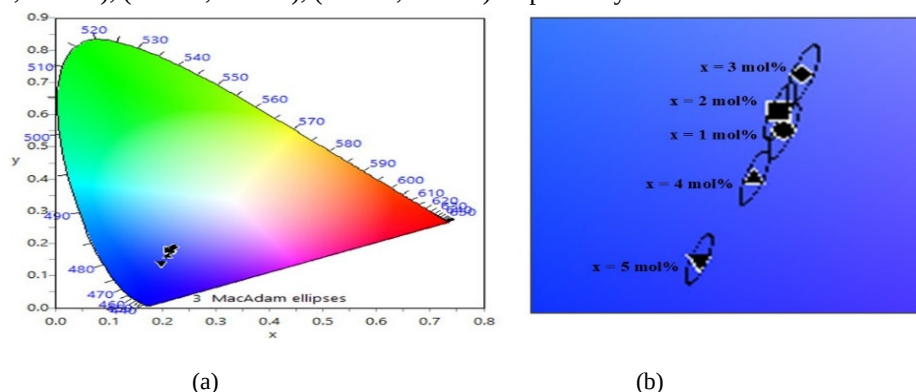


FIGURE 3. (a) CIE diagram under 243 nm excitation, and (b) enlarged view of color coordinates in CIE chromaticity diagram for SiO_2 : x mol% Tb^{3+} ($x = 1, 2, 3, 4, 5$)

CONCLUSIONS

The GS ash waste has been used to synthesize the SiO_2 : x mol% Tb^{3+} ($x = 0, 1, 2, 3, 4, 5$) phosphor material via solid-state reaction method as phosphor material. XRD and FT-IR studies validated the structural and functional groups characteristics. The CIE chromaticity coordinates diagram for prepared phosphor material revealed blue light emission under 243 nm excitation. The blue light emitting phosphor material has wide applications in decorative lighting and various optical devices.

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Synthesis of Binder-Free Ni_3S_2 for Supercapacitor Applications

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Abstract: In this study, one-pot hydrothermally synthesized nanostructured granular-like Ni_3S_2 was used as electrode material for advanced supercapacitors. Structural and morphological characterization of Ni_3S_2 electrode was determined using X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM). Surface morphology shows granular nanostructure on the surface of Ni substrate. XRD analysis confirms the formation of a high-purity phase and crystallinity of Ni_3S_2 . The electrochemical behavior of synthesized Ni_3S_2 electrode was analysed by cyclic voltammetry (CV), and galvanostatic charge-discharge (GCD). Analysis showed at 1 Ag^{-1} current density 6 M KOH exhibits enhanced capacitance of 1542.5 Fg^{-1} . The Ni_3S_2 nanostructured electrode exhibits excellent electrochemical properties due to its sufficient electroactive sites for redox action and a promising electrode material for supercapacitor applications.

INTRODUCTION

High-performance material development of energy storage devices has gained attention recently on a global scale. Numerous studies on various electrode materials have been reported and are continuing. Globalization and the growing need for smart, flexible gadgets have led to a lot of research into supercapacitors owing to their maximum energy density, eco-friendliness and long-term stability [1]. Among various electrode materials, metal sulfides have emerged as a promising electrode due to their excellent electrochemical behavior [2]. Ni_3S_2 has gained interest due to its superior theoretical capacitance, high redox reaction, unique Ni-Ni metallic bonds, and good electrical conductivity [3]. In this work, Ni_3S_2 nanostructure was prepared as binder-free electrode by hydrothermal route. The outstanding performance of synthesized Ni_3S_2 serves as a strong electrode for next-generation supercapacitor applications.

EXPERIMENTAL SECTION

The steps involved in synthesizing nanostructured Ni_3S_2 grown on Ni foam via hydrothermal route. Initially, nickel foam was washed by ultrasonication with 2 M HCl solution for 30 minutes. Separately, 50 ml of ethylene glycol and 0.009 M were ultrasonicated to obtain transparent solution. In presence of Ni, the solution was poured into a 100 ml autoclave and heated for 4 hours at 150°C . After that, electrode was dried at 70°C in oven to achieve binder-free Ni_3S_2 electrode. 3. Result and discussion

Morphology study

FIGURE 1(a) displays FESEM images of Ni_3S_2 electrode. The FESEM revealed the formation of a granular-like nanostructure of Ni_3S_2 . The EDS analysis is performed to investigate the elements of Ni_3S_2 electrode. The presence of Ni, O, S and C as shown in FIGURE 1(b) confirms their uniform distributions which enhance the surface area, ion transport and electrochemical performance of Ni_3S_2 electrode.

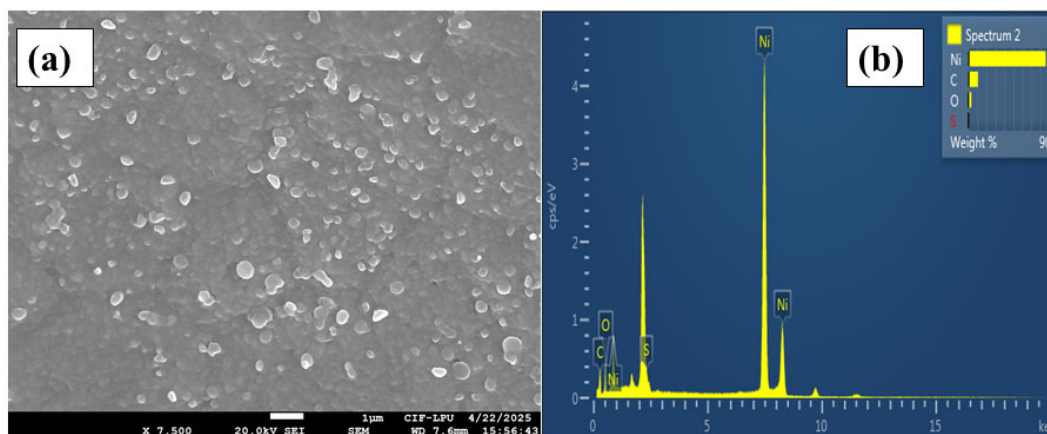


FIGURE 1. (a) FESEM image of Ni₃S₂ shows granular morphology at X 7,500. (b) Shows the Energy dispersive X-ray spectroscopy.

XRD Analysis

FIGURE 2(a) shows the X-ray diffraction pattern of Ni₃S₂. At 2θ values 21.8°, 31.1°, 37.7°, 49.7°, and 55.2° different diffraction peaks were detected corresponding to the (101), (110), (003), (113), and (122) planes of hexagonal Ni₃S₂ respectively [4]. In FIGURE 2(a) the intensity of Ni foam is high due to which Ni₃S₂ peaks are not clearly visible however, the W-rocking curve as shown in FIGURE 2(b) clearly reveals sharp and narrow diffraction peaks confirming high crystallinity of electrode. No additional peaks or impurities that would have indicated any other phases of nickel sulfide were detected. Therefore, XRD analysis indicates high purity phase and crystallinity of Ni₃S₂ electrode.

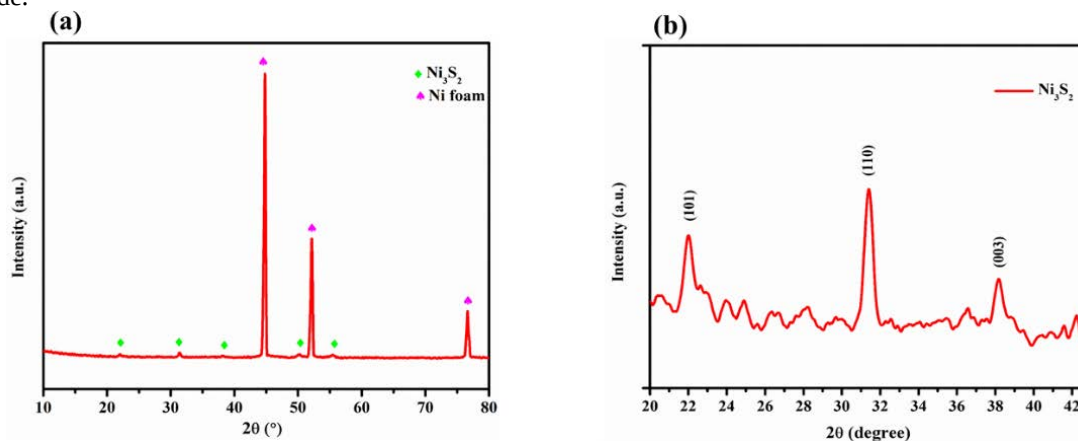


FIGURE 2. (a) XRD pattern of Ni₃S₂ electrode. (b) W- Rocking curve of Ni₃S₂ electrode.

Electrochemical Analysis

FIGURE 3(a) reports that CV peaks in 6 M KOH electrolyte for Ni₃S₂ electrode were recorded at distinct scan rates (10 to 40 mV/s) within voltage window 0-0.6 V. The CV curves with distinct redox peaks demonstrate that Ni₃S₂ electrode shows pseudocapacitive behaviour. The fabricated electrode specific capacitance was calculated by [5]:

$$Cs = \frac{A}{m s V} \quad (1)$$

where, Cs is the specific capacitance, A is the area under the curve, m is the mass loading of the active material, s is the scan rate and V is the potential window. The specific capacitance value of Ni₃S₂ electrode is 1412.72, 1287.35,

1152.93, 1037.79, 929.56, 829.33, and 744.55 Fg^{-1} at 10, 15, 20, 25, 30, 35, and 40 mV/s scan rate, respectively. Moreover, the specific capacitance increases as the redox peak increases with an increment of scan rates which shows excellent electrochemical reversibility and high charge transfer efficiency.

FIGURE 3(b) at a range of current densities from 1 to 5 Ag^{-1} , GCD measurements of electrode performed within potential range 0–0.4 V in 6M KOH electrolyte. Due to faradic redox reaction, GCD curves under different current densities exhibit a non-linear shape indicating good electrochemical reversibility and pseudocapacitive behaviour. By using the following equation, the capacitance is determined by [6]:

$$C_{\text{sp}} = \frac{I \times \Delta t}{m \times \Delta V} \quad (2)$$

Where, current density is represented by I , discharge time is denoted by Δt , and potential window is denoted by ΔV used in GCD curve. The Ni_3S_2 electrode exhibited specific capacitance values of 1542.5, 1280, 1095, 1010, and 750 Fg^{-1} at 1 to 5 Ag^{-1} current density, respectively.

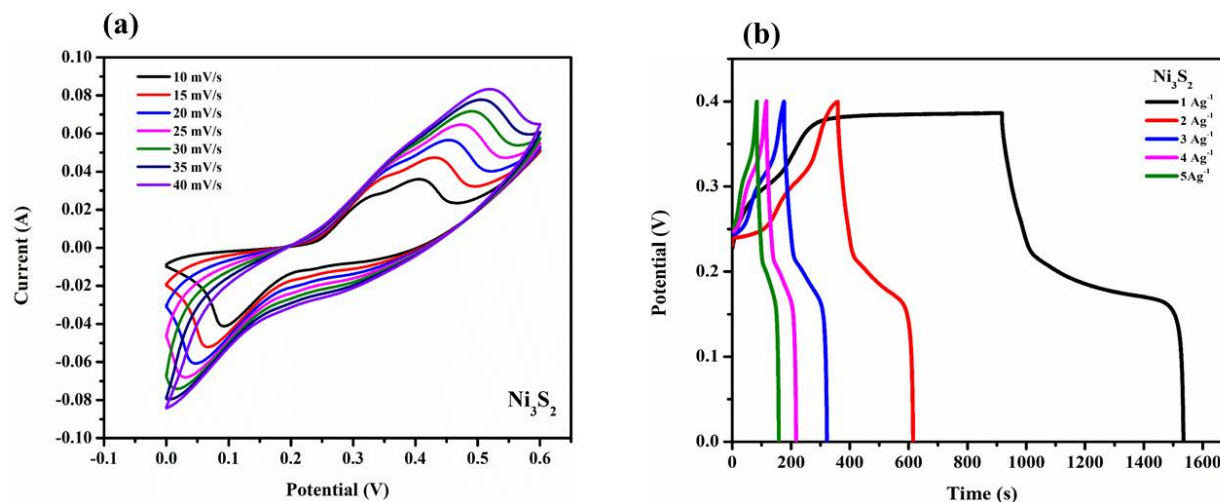


FIGURE 3. (a) CV (b) GCD of Ni_3S_2 electrode.

CONCLUSION

In conclusion, granular-like Ni_3S_2 nanostructures have been successfully synthesized by one-pot hydrothermal method useful as a binder-free electrode. XRD analysis confirmed the high phase purity and crystallinity of material. At 1 Ag^{-1} current density enhanced capacitance of 1542.5 Fg^{-1} was recorded for Ni_3S_2 . These experimental results highlight Ni_3S_2 as a great potential electrode material for advanced supercapacitor applications.

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Visible-Blind UV-C Photodetection Using NiO-ZnO Nanorods on a Flexible Substrate

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Abstract- A flexible, visible-blind ultraviolet (UV) photodetector was fabricated using NiO–ZnO (NZ) nanocomposites, consisting of one-dimensional ZnO nanorods with a hexagonal wurtzite structure decorated with cubic NiO quantum dots (QDs). The device shows a significant photocurrent response under UV-C illumination, even at low light intensity, while remaining insensitive to visible light.

INTRODUCTION

UV photodetectors play a crucial role in diverse applications, including environmental monitoring, flame sensing, optical communication and biomedical diagnostics [1,2]. ZnO and NiO are wide band gap semiconductors, with ZnO exhibiting n-type conductivity and NiO showing p-type behavior [3, 4]. ZnO, with its strong UV absorption and an exciton binding energy of ~60 meV, is particularly attractive for such applications, although its photoresponse is often limited by surface oxygen adsorption and desorption processes. NiO, possessing a higher exciton binding energy (~110 meV) and good lattice compatibility with ZnO, serves as an effective p-type counterpart. The formation of a p–n heterojunction between NiO and ZnO introduces a built-in electric field that facilitates efficient charge separation, enhancing the sensitivity and response speed of the photodetector, are frequently employed for UV detection [2,5]. In this study, we fabricated a flexible NZ nanocomposite-based UV-C photodetector and systematically investigated its structural, morphological, and optoelectronic properties for efficient deep-UV sensing applications.

MATERIALS AND METHODS

NZ nanocomposites were synthesized by incorporating pre-formed NiO quantum dots (QDs) [4] into an aqueous 0.4 M zinc acetate (99.5%) solution. The suspension was stirred thoroughly to ensure uniform dispersion of the NiO QDs. Subsequently, aqueous ammonia (extra pure, 30%) was added dropwise under continuous stirring until the pH of the mixture reached ~10. The resulting solution was further stirred and maintained at 70°C in a hot water bath for 4 hours. A pale white precipitate formed during the process was collected by filtration, rinsed several times with deionized water, and dried in a hot air oven at 60°C for 12 hours. The obtained powder was then heated on a hot plate at 100°C for 1 hour to obtain the final NZ nanocomposite. For sensor fabrication, indium tin oxide (ITO)-coated polyethylene terephthalate (PET) substrates were used. An etched region was introduced in the ITO layer to isolate the electrodes and define the active sensing region. A suspension of the synthesized nanocomposite in isopropanol was prepared and drop-cast onto the patterned ITO surface. The films were left to dry naturally under ambient conditions to complete the fabrication process. X-ray diffraction (XRD) analysis was performed using a Rigaku MiniFlex II powder diffractometer equipped with a Cu K α radiation source. The surface morphology and elemental composition of the sample were investigated using field emission scanning electron microscopy (FESEM) and energy-dispersive X-ray spectroscopy (EDS) (Quanta FEI-450 FEG). Optical absorption spectra were recorded using a UV–vis spectrophotometer. Photoconductive measurements were conducted using a Source Measure Unit (Keithley SMU-2450), with a halogen lamp (400–800 nm) serving as the visible light source and a xenon lamp used for ultraviolet (UV) illumination.

RESULTS AND DISCUSSION

Structure and morphology

The XRD pattern (Figure 1a) confirms the presence of both ZnO and NiO phases in the nanocomposite. All major diffraction peaks correspond to the hexagonal wurtzite structure of ZnO (JCPDS No. 36-1451). An additional peak observed around 43.2° is indexed to the (200) plane of cubic NiO (JCPDS No. 47-1049), indicating the successful incorporation of NiO. The overlapping of ZnO (101) and NiO (111) reflections results in an enhanced intensity at that region. No impurity phases are detected, confirming the phase purity of the composite. Figure 1b displays the absorption spectrum, indicating a band edge ~ 380 nm. Figure 1c shows the FESEM image of the synthesized material. The morphology reveals the 1-D nanorods and appear decorated with nanoparticles. Figure 1d depicts the EDS spectrum. Quantitative analysis indicates atomic concentrations of approximately 45% Zn, 5% Ni, and $\sim 50\%$ oxygen, confirming the presence of Zn, Ni, and O in the sample and verifying the compositional purity of the synthesized nanocomposite.

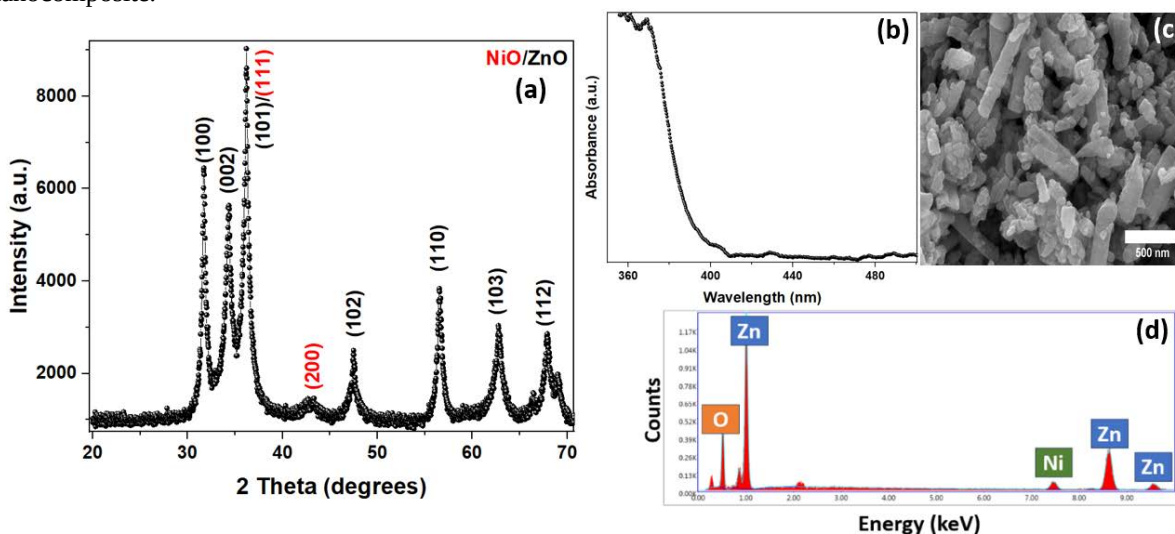


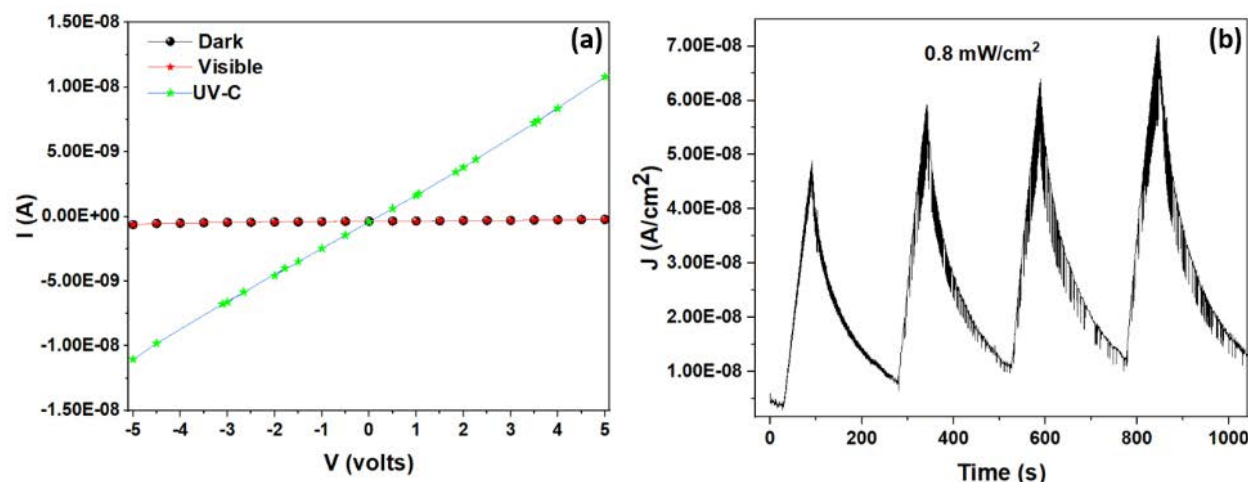
FIGURE 1 a) XRD pattern of NZ nanocomposite, showing distinct peaks corresponding to ZnO and NiO phases b) absorption spectrum of NZ nanocomposite c) FESEM image revealing nanorods decorated with nanoparticles d) EDS spectrum confirming the elemental composition of Zn, Ni and O in the sample.

Photoconductive measurements

The current-voltage (I-V) characteristics of the NZ device were evaluated under both dark and illuminated conditions using a constant bias voltage of 5V. To ensure reproducibility, all measurements were conducted under identical conditions, and the time resolved (I-T) measurements were performed with the sample positioned at a fixed distance of 10 cm from the light source. To isolate the UV-C band, a 260 nm narrow bandpass filter was used, effectively eliminating wavelengths above 260 nm and ensuring that the incident light was confined within the UV-C spectral range (0.8 mW). The I-V measurements were carried out in the dark, under visible light and UV illumination (Figure 2a). The device exhibited negligible dark current. A clear increase in current was observed under UV light, indicating a strong photoresponse. In contrast, there was no noticeable change under visible light, confirming the visible-blind nature of the device. An enhancement in photocurrent was achieved under UV-C illumination. I-T measurements were conducted to assess the dynamic behavior under repeated UV-C on-off illumination cycles (Figure 2b). The results demonstrate a clear and consistent response even to low-intensity UV radiation, indicating the high sensitivity and effective UV-C detection capability of the device. The distinctive morphology comprising one-dimensional ZnO nanorods decorated with NiO QDs enables multiple light reflections within the structure, leading to enhanced UV absorption. Additionally, the favorable band alignment between NiO and ZnO enables a built-in potential that facilitates efficient separation of photogenerated electron-hole pairs, thereby enhancing the overall photodetector response [2, 6].

FIGURE 2A) I-V curve under dark and light (both UV-C and visible) illumination b) photocurrent response of NZ under on/off radiation of UV-C (0.8 mW)

CONCLUSIONS



In summary, we have successfully developed a flexible, visible-blind UV photodetector based on NiO–ZnO nanocomposites synthesized via a simple solution process and characterized through XRD, FESEM, and EDS analyses, confirming their structural integrity and morphological features. This straightforward and scalable synthesis route offers a promising pathway for developing functional nanocomposites for diverse device and energy-related applications. Owing to its wide band gap, the material exhibits excellent potential for visible-blind UV detection, demonstrating a detectable response even at low light intensities (0.8 mW), while remaining inactive under visible light. The combination of 1D ZnO nanorods and NiO quantum dots not only enhanced UV light absorption through multiple scattering effects but also enabled efficient charge separation due to favorable band alignment.

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First-Principles Investigation of Rhodium-Functionalized Cyclo[2n]carbons ($n = 3-9$) for CO₂ Sensing

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Abstract. In this study, first-principles DFT calculations were conducted to investigate the CO₂ sensing performance of Rh-functionalized cyclo[2n]carbons ($n = 3-9$), a series of sp-hybridized carbon nanorings with tunable electronic properties. Although cyclo[8]carbon remains unsynthesized, its negative cohesive energy and absence of imaginary vibrational frequencies indicate thermodynamic stability and synthetic feasibility. CO₂ adsorption energies range from -0.52 to -0.58 eV, suggesting moderate physisorption favorable for reversible sensing, with adsorption distances between 2.28 and 2.31 Å. Upon CO₂ adsorption, notable changes were observed in the HOMO–LUMO gap and Fermi level, particularly for Rh@C₈ ($\Delta E_G = 30.42\%$, $\Delta E_F = 32.22\%$) and Rh@C₁₀ ($\Delta E_F = 41.81\%$), indicating strong electronic sensitivity. Work function values (4.20–4.88 eV) confirm charge redistribution at the sensor interface. Recovery time decreases significantly with ring size, from 4787.07 μ s (Rh@C₈) to 519.38 μ s (Rh@C₁₆), highlighting enhanced desorption kinetics in larger rings. Rh@C₈ exhibited the highest sensing response (354.17), while Rh@C₁₂, Rh@C₁₄, and Rh@C₁₆ offered a balanced combination of adsorption strength and recovery time.

INTRODUCTION

Carbon dioxide (CO₂) is a major greenhouse gas whose continuous accumulation in the atmosphere contributes significantly to global climate change. Monitoring CO₂ levels is therefore essential not only for environmental protection but also for ensuring safety in industrial and confined spaces [1]. However, conventional CO₂ sensors often suffer from limitations such as high-power consumption, slow response, and poor sensitivity at room temperature. Recent advancements in nanostructured materials in particular, cyclo[n]carbons (C_n), a unique class of molecular carbon allotropes, have attracted considerable attention due to their distinct ring structures and potential functional applications. Although their synthesis in condensed phases is limited by high reactivity, on-surface synthesis has enabled the successful fabrication and real-space imaging of various C_n rings (e.g., C₆, C₁₀, C₁₂, C₁₄, C₁₆, and C₁₈) [2-9]. These carbon rings exist in two bonding configurations: cumulenic (with consecutive double bonds) and polyynic (with alternating triple and single bonds). The first successful synthesis of cyclo[18]carbon in its aromatic polyynic form was reported by Kaiser et al. in 2019 [3]. Continued research on cyclo[n]carbons is advancing our understanding of carbon-based nanostructures and paving the way for designing novel materials with tailored electronic and structural properties [2-9]. This study employs first-principles density functional theory (DFT) calculations to investigate the CO₂ adsorption behavior by analyzing key sensing parameters such as adsorption energy, electronic structure changes, recovery time, and sensing response on Rh-functionalized cyclo[2n]carbons.

COMPUTATIONAL METHODOLOGY

In this study, all density functional theory (DFT) calculations were performed using the Gaussian 09 package [15]. Geometry optimizations and vibrational frequency analyses of Rhodium-decorated cyclo[2n]carbon systems were carried out using the long-range corrected hybrid functional ω B97XD combined with the LanL2DZ basis set, a combination known to be reliable for transition metal-functionalized carbon nanomaterials [12-13]. The optimized molecular geometries and frontier molecular orbitals (E_{HOMO} and E_{LUMO}) were visualized using GaussView 6.0. To ensure accurate and stable optimizations, tight convergence criteria were adopted, specifically: a root-mean-square

(RMS) force threshold of 3×10^{-4} Hartree/Bohr, maximum force of 4.5×10^{-4} Hartree/Bohr, RMS displacement of 1.2×10^{-3} radians, and maximum displacement of 1.8×10^{-3} Bohr [10-14]. The HOMO-LUMO energy gap (E_G), the Fermi level (E_F), and adsorption energies (E_{ad}), were computed. The sensing response (S) were estimated from relative changes in E_G at room temperature. Recovery time (τ), a key parameter for sensor reusability, was calculated as well. Additionally, the work function (Φ), has been determined as well [10-14].

RESULT AND DISCUSSION

To investigate the CO₂ sensing capabilities of cyclo[2n]carbons, we first optimized the geometries of pristine nanorings ($n = 3-9$) using the above-discussed DFT methodology. Among these, all structures except cyclo[8]carbon (C_8) have been experimentally synthesized. To evaluate the stability and potential synthesizability of C_8 , we calculated its cohesive energy and IR spectrum. The computed cohesive energy of -6.68 eV per atom and the absence of imaginary frequencies in the vibrational spectrum confirm its dynamical stability. Structural analysis revealed that C_6 , C_{10} , and C_{14} exhibit cumulenic configurations with nearly uniform C=C bond lengths (~ 1.30 Å), while C_8 , C_{12} , C_{16} , and C_{18} exhibit polyyenic structures characterized by alternating C-C (~ 1.37 Å) and C $\equiv$ C (~ 1.23 Å) bonds [2-9]. Bond angles across these systems range from 120° to 161° . Due to the weak interaction of pristine cyclo[n]carbons with CO₂, Rhodium (Rh) atoms were introduced to enhance their reactivity. In all Rh-decorated systems except C_8 , the Rh atom binds externally to the ring with bond lengths around 2.0 Å. In contrast, Rh@ C_8 shows an internal Rh insertion, forming a single bond within the ring. The HOMO-LUMO gap ranges from 7.44 eV (Rh@ C_6) to 5.71 eV (Rh@ C_{16}), while the Fermi energy varies from -5.12 eV (Rh@ C_6) to -4.58 eV (Rh@ C_{14}), indicating tunable electronic properties suitable for gas sensing applications [10]. To further examine the CO₂ sensing behavior, CO₂ molecules were adsorbed on all possible active sites of each Rh@ C_{2n} nanoring. The energetically favorable configurations were selected for further analysis, as illustrated in Figure 1. The optimized CO₂ adsorption distances are 2.3 Å, with adsorption energies ranging from -0.52 eV to -0.58 eV (Table 1), confirming weak physisorption essential for reversible gas sensing. Upon CO₂ adsorption, notable changes were observed in electronic properties, particularly in the HOMO-LUMO gap and Fermi level. The largest HLG reduction occurred in Rh@ C_8 (30.42%), while the smallest was observed in Rh@ C_{16} (2.97%). Similarly, Fermi level shifts were most prominent in Rh@ C_{10} and least in Rh@ C_{18} . The sensing response, which is governed by the variation in electronic structure upon gas adsorption, was highest for Rh@ C_8 (354.17) and lowest for Rh@ C_{16} (0.77). Work function values ranged from 4.20 eV to 4.88 eV. Furthermore, recovery time showed a size-dependent trend, decreasing from 4787.07 μ s (Rh@ C_8) to 519.38 μ s (Rh@ C_{16}). [10-14].

Table 1. Calculated adsorption energy of CO₂(E_{ad}), adsorption distance (d), HLG of System and CO₂ adsorbed system (E_G), absolute change in HLG (ΔE_G), fermi energy of system and CO₂ adsorbed system (E_F), absolute change in fermi energy (ΔE_F), work function of CO₂ adsorbed system (Φ), recovery time of system (τ) and sensing response of systems (s).

System	(E_{ad}) CO ₂ (eV)	d (Å)	(E_G)system (eV)	(E_G)CO ₂ Adsorbed System (eV)	(E_F)system (eV)	(E_F)CO ₂ adsorbed system (eV)	Φ (eV)	τ (μ s)	s
Rh@C ₆	-0.58	2.29	7.44	7.39	-5.12	-4.88	4.88	4722.13	1.33
Rh@C ₈	-0.58	2.28	6.18	6.49	-5.05	-4.72	4.72	4787.07	354.17
Rh@C ₁₀	-0.57	2.31	7.43	7.52	-4.62	-4.20	4.20	3933.18	4.63
Rh@C ₁₂	-0.52	2.30	6.00	5.97	-4.64	-4.46	4.46	626.84	0.81
Rh@C ₁₄	-0.53	2.30	6.93	6.89	-4.58	-4.40	4.40	726.17	1.34
Rh@C ₁₆	-0.52	2.30	5.71	5.68	-4.76	-4.61	4.61	519.38	0.77
Rh@C ₁₈	-0.55	2.31	6.47	6.40	-4.59	-4.55	4.55	1792.44	2.47

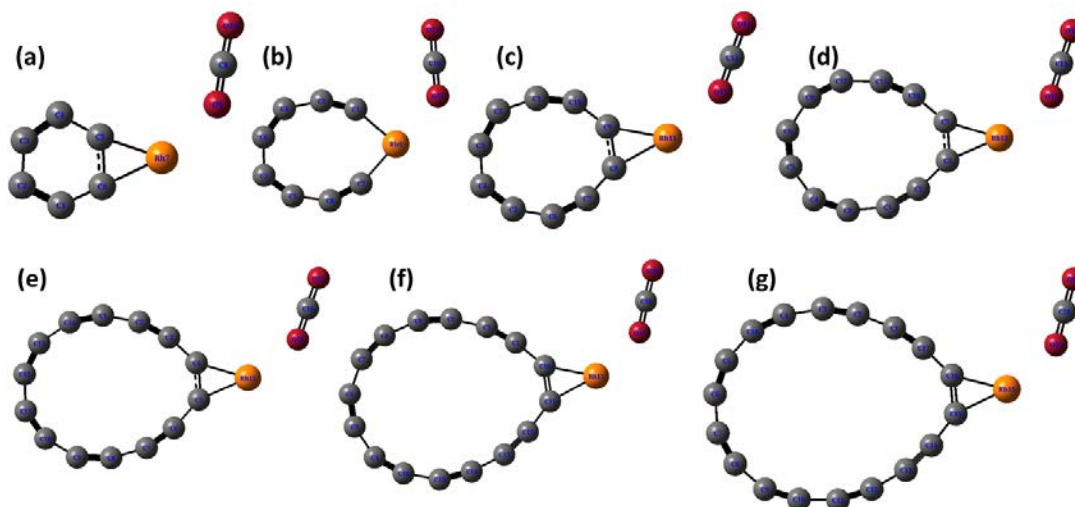


Figure 1. Minimum energy configuration of CO₂ adsorbed Rh-decorated cyclo (a)C₆, (b)C₈, (c)C₁₀, (d)C₁₂, (e)C₁₄, (f)C₁₆ and (g)C₁₈ nanoring.

CONCLUSION

In this study, we investigated the CO₂ sensing potential of Rh-decorated cyclo[2n]carbons (n = 3–9) using first-principles density functional theory. The calculated negative but moderate adsorption energies confirm a physisorption interaction between CO₂ and the Rh-functionalized nanorings, which is desirable for reversible gas sensing. Significant changes in the HOMO–LUMO gap and Fermi energy upon CO₂ adsorption demonstrate the tunable electronic response of these systems, thereby indicating their effective sensing capability. Additionally, the relatively short recovery times observed, particularly for larger ring sizes, suggest excellent sensor reusability and real-time responsiveness. Overall, Rh-decorated cyclo[2n]carbons emerge as promising candidates for CO₂ detection in next-generation nanoscale gas sensing technologies.

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Structural, Photoluminescence And Photocatalytic Properties Of Semiconducting Graphitic Carbon Nitride (g-C₃N₄) Nanosheets

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Abstract. This work presents a comprehensive analysis of the structural, photoluminescent, and photocatalytic properties of semiconducting graphitic carbon nitride (g-C₃N₄). X-ray diffraction (XRD) pattern exhibits a prominent (002) reflection at $2\theta \approx 27.55^\circ$, corresponding to the interlayer stacking of conjugated aromatic systems, and a weaker (100) peak at $2\theta \approx 13.22^\circ$, attributed to in-plane structural repeating units, confirming the graphitic layered structure. Field emission scanning electron microscopy (FESEM) reveals thin, crumpled nanosheets with homogeneous dispersion. Theoretical structural modelling using BioVia corroborates the observed crystallographic features with estimated optical bandgap (~ 3.02 eV) confirming semiconducting behaviour. Photoluminescence (PL) spectrum displays strong visible emission, indicative of effective charge recombination dynamics. Photocatalytic performance was evaluated by visible light induced degradation of Rhodamine B (RhB), monitored through absorption spectra. Kinetic analysis adheres to a pseudo-first-order model, reflecting efficient photocatalytic efficiency, supporting its applicability in environmental remediation.

INTRODUCTION

Semiconducting materials have gained significant attention over the past decades due to their tunable electronic structures, optical activity, and wide range of applications in energy conversion, environmental remediation, sensing, and optoelectronics [1]. Among these materials, metal-free polymeric photocatalysts have emerged as sustainable alternatives owing to their earth-abundant composition, environmental compatibility, and chemical stability [2]. Graphitic carbon nitride (g-C₃N₄) has particularly drawn interest for its unique two-dimensional structure, visible-light activity, and potential in photocatalytic and optoelectronic applications [2, 3]. The intrinsic band gap of g-C₃N₄ lies in the range of 2.6–2.8 eV, enabling efficient absorption in the visible region, which is crucial for harnessing solar energy [2, 3]. This moderate band gap positions g-C₃N₄ as a visible-light-responsive semiconductor, making it highly suitable for photocatalytic processes under UV-visible light, with the generated electron-hole pairs capable of participating in redox reactions. It has been reported that g-C₃N₄ has demonstrated excellent performance in the degradation of various organic pollutants, including dyes like RhB, Methylene Blue, and industrial wastewater constituents [3]. Under UV or visible light irradiation, photoexcited electrons and holes in g-C₃N₄ participate in the generation of reactive oxygen species (ROS), such as hydroxyl and superoxide radicals, which subsequently attack and decompose complex organic molecules into less harmful intermediates like CO₂ and H₂O [2, 3]. The present study focuses on the synthesis and characterization of g-C₃N₄ nanosheets, emphasizing their photocatalytic features, contributing valuable insights into the design of efficient metal-free photocatalysts for environmental applications.

EXPERIMENTAL

Graphitic carbon nitride was synthesized using 10 grams of urea with high-purity (99.999%), sourced from M/s SD Fine Chemicals Ltd. It was transferred into a silica crucible, which was then sealed with aluminum foil to restrict oxygen exposure and promote controlled polymerization. The crucible subsequently underwent thermal treatment at 550 °C for 2.5 hours to get a yellow-coloured g-C₃N₄ powder. XRD measurement was done by a Bruker D8 Advance diffractometer (Cu K α , $\lambda = 1.5406$ Å). FESEM study was conducted with a ZEISS Supra microscope. PL spectrum was recorded by PL LS 55 spectrometer (M/s Perkin Elmer, Xenon Lamp; $\lambda_{\text{ex}} = 350$ nm). Theoretical calculations of the structural parameters and band gap was accomplished using BIOVIA MS software.

RESULTS AND DISCUSSION

The layered, and planar structure of $g\text{-C}_3\text{N}_4$ has been generated through theoretical simulation study by BIOVIA MS which is composed of tri-s-triazine units (heptazine) linked by nitrogen atoms, forming a 2D conjugated network has been depicted in inset of Fig.1a. XRD pattern (Fig.1A) clearly reveals the characteristic crystalline structure. Two prominent diffraction peaks are observed. The first peak at around $2\theta \approx 13.22^\circ$, corresponds to the (100) plane, which is associated with the in-plane structural periodicity of the tri-s-triazine (heptazine) units in $g\text{-C}_3\text{N}_4$ [4]. This peak reflects the periodic arrangement of the conjugated aromatic systems within a single layer and indicates a certain degree of intra-layer ordering [4]. The intense peak observed at $2\theta \approx 27.55^\circ$ is assigned to the (002) plane, which corresponds to the interlayer stacking of the conjugated aromatic layers in a graphite-like structure (Fig.1a).

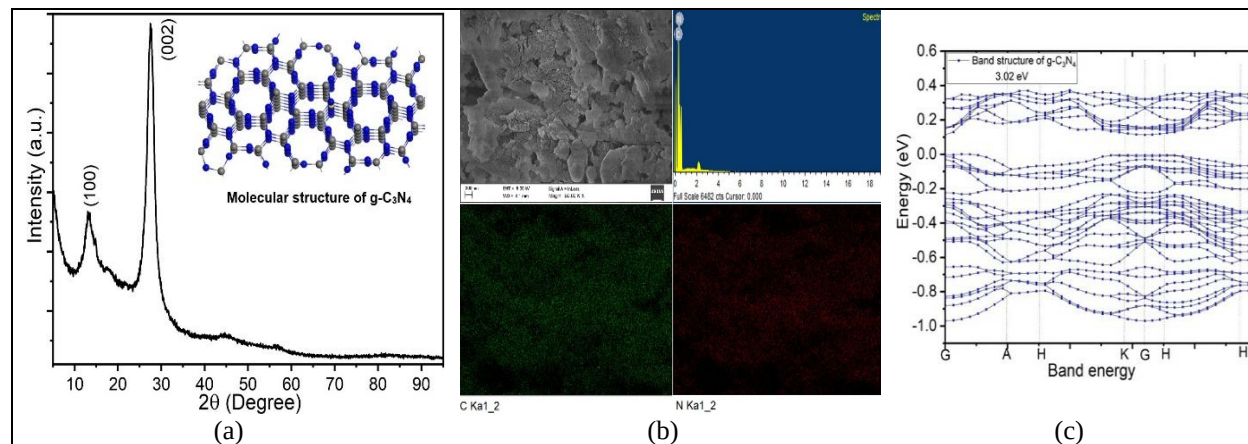


FIGURE 1. (a) XRD pattern, (b) FESEM and elemental mapping images with EDAX spectrum and (c) band diagram of $g\text{-C}_3\text{N}_4$.

This reflection is a hallmark of layered $g\text{-C}_3\text{N}_4$ and shows a significant degree of crystallinity and regular stacking along the c-axis due to van der Waals interactions between layers [4]. The FESEM micrograph (Fig.1b) reveals a crumpled, flaky nanosheet morphology with irregular, layered structures, typical of thermally polymerized $g\text{-C}_3\text{N}_4$. The sheet-like texture is indicative of exfoliated or loosely stacked layers, which significantly increase the surface area [3]. The EDX spectrum (Fig.1b) confirms the elemental composition of the sample, with dominant peaks corresponding to carbon (C) and nitrogen (N) i.e. the principal constituents of $g\text{-C}_3\text{N}_4$. The elemental mapping images (Fig.1b) further validate the homogeneous distribution of carbon and nitrogen atoms across the analyzed area. The band structure of $g\text{-C}_3\text{N}_4$ (Fig.1c), generated through simulation, exhibits an indirect band gap of approximately 3.02 eV, with the valence band maximum and conduction band minimum located at different k-points. This wide band gap confirms its semiconducting nature, suitable for photocatalytic and optoelectronic applications. In the PL spectrum, (Fig.2a), a strong visible emission peak is observed at 447 nm, which is the characteristic of intrinsic band-to-band recombination within $g\text{-C}_3\text{N}_4$ [5]. This emission arises from the radiative recombination of photogenerated electrons in the conduction band with holes in the valence band. The broad emission profile spanning from 400 nm to 600 nm also indicates the presence of multiple recombination pathways, possibly involving surface states, intrinsic structural defects, or sub-bandgap transitions [5]. The UV-Visible absorption spectra (Fig.2b) illustrates the photocatalytic degradation of RhB dye under the irradiation of light in the presence of $g\text{-C}_3\text{N}_4$ nanosheets as the photocatalyst. The characteristic absorption peak of RhB at 591 nm gradually decreases with increasing irradiation time, indicating a time-dependent degradation process [6]. In comparison to the dark spectrum, a continuous reduction in absorbance is observed under light illumination over time intervals of 30, 60, 90, 120, 150, and 180 minutes, with near-complete suppression of the peak at 180 minutes. This clearly demonstrates the photocatalytic efficiency of $g\text{-C}_3\text{N}_4$ under UV-Vis light, attributed to its ability to generate reactive electron-hole pairs upon photoexcitation [4]. The progressive reduction in RhB peak intensity reflects efficient oxidative degradation, facilitated by the photoinduced formation of reactive oxygen species (ROS) such as superoxide ($\cdot\text{O}_2^-$) and hydroxyl radicals ($\cdot\text{OH}$), which attack the dye molecules and break down their chromophoric structure [4, 6]. To evaluate the kinetics of the degradation process, the data were fitted to a pseudo-first-order kinetic model, described by the Langmuir-Hinshelwood equation $\ln(C_0/C_t) = kt$ [4, 7, 8]. The parameters C_0 and C_t correspond to the initial and evolving dye concentrations at time t , respectively, while k signifies the rate constant. A linear fit (Fig.2c) of $\ln(C_0/C_t)$ vs. time yields a straight line, confirming that the reaction

follows pseudo-first-order kinetics. The calculated rate constant (0.0327) demonstrates the high photocatalytic activity of the g-C₃N₄ nanosheets in degrading organic pollutants like RhB under UV-Vis light irradiation. This is due to their favourable electronic structure, high surface area, and strong light absorption capabilities. The degradation study validates the potential application of the material in wastewater treatment and environmental remediation applications.

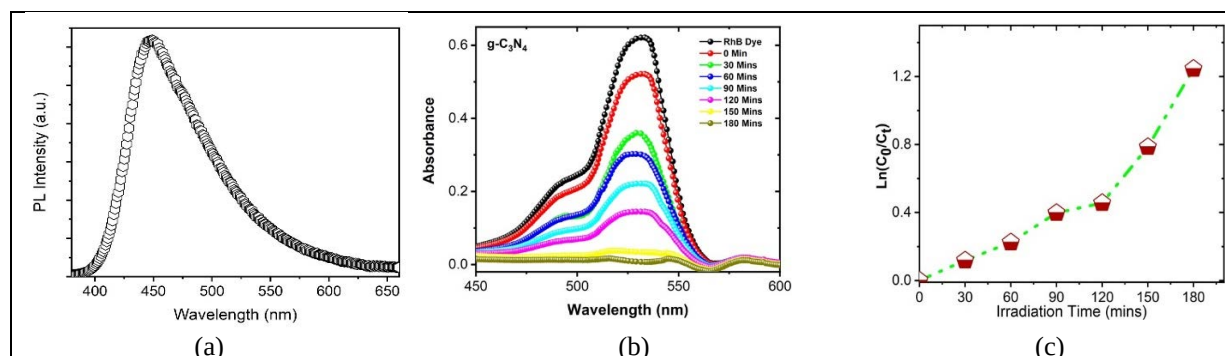


FIGURE 2. (a) PL spectrum, (b) absorption spectra of RhB and (c) chemical kinetics plot for photodegradation of RhB.

CONCLUSION

In summary, graphitic carbon nitride (g-C₃N₄) were successfully synthesized via thermal condensation of urea at 550 °C and systematically characterized to evaluate its structural, optical, and photocatalytic properties. XRD study and theoretical modelling confirmed the formation of a layered graphitic structure, with an estimated band gap of 3.0 eV. FESEM measurement revealed nanosheet like morphology having high surface area suitable for different applications. Strong visible-range photoluminescence indicated active electronic transitions, and the material demonstrated effective photocatalytic degradation of RhB under UV-Vis light irradiation, following pseudo-first-order kinetics. These findings highlight the potential of g-C₃N₄ as a low-cost, metal-free photocatalyst for environmental remediation application.

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Study of the Photo Response of Chemically Prepared Nanocomposite of Reduced Graphene Oxide/Zinc Oxide Nanoparticles at Room Temperature

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Abstract. In this paper, we have synthesized a hybrid nanocomposite of reduced graphene oxide – Zinc oxide (rGO - ZnO). The Raman spectra of rGO – ZnO nanocomposite consists of characteristics peaks. Along with it, FTIR study confirms the characteristics peaks of rGO – ZnO nanocomposite. The SEM micrographs of the prepared samples show that ZnO nanoparticles stick on reduced graphene sheets which embedded in sample S4. The prepared samples tested for photo response measurement. It is observed that sample S4 exhibit a photo response of 7.25 % at 30 Mw/cm². The photo detection response seems to increase with concentration of ZnO. This is may be due to formation of P-N junction.

INTRODUCTION

In recent years, graphene based nanocomposites have received wide attention in device fabrication due to their unique properties. The nanomaterial of reduced graphene oxide incorporated with metal oxide nanoparticles have paved a path for development of various applications such a gas sensor [1], supercapacitor [2], photo catalysis [3] and energy storage [4]. It has also great possibilities towards photo detection and solar cells applications [5]. As the performance of these types of devices are based on the surface to volume ratio of the nanocomposites.

Today, the world is facing crisis of over consumption of energy sources. They are decaying very rapidly and their combustion is responsible for environmental problems. Meanwhile, an alternative and cleaner renewable source of energy is need of hour. Nowadays, a lot of research is going in the field of photo conducting materials as alternate source of renewable energy. In the context of above discussion, the organic, inorganic and their nanocomposite are widely investigated. Kumar et al. [5] have reported the reduced graphene oxide (rGO) based photo conducting material which exhibits a photo response of 6.25 % at 30 mW/cm². The metal oxide nanoparticles based photo sensors are also reported in literature. Rawal et al. have reported the sensing response of 4.1 % at 100 mW/cm². along with it inorganic organic nanocomposite example Polypyrrole-Zinc oxide nanocomposite is also reported with sensing response of 10.7% at 100 mW/cm² [6]. There are some research papers available on the rGO – ZnO composite for improvement in photocurrent due to charge separation. But there is dearth of data in literature which deals with the rGO- ZnO nanocomposite as a promising material for photo response measurement. The reduced graphene oxide (rGO) is an intermediate step between graphene oxide (insulator) and graphene (semi metal) [5]. It is basically a P-type semiconductor [5]. Whereas, Zinc oxide is a n-type semiconductor with a wide band gap of 3.37 eV [6]. In this paper, we have reported rGO-ZnO based photo conducting material at room temperature. It is observed that the rGO- ZnO nanocomposite has exhibit good sensing response of 7.57 % at 30Mw/cm².

SAMPLE PREPARATION AND CHARACTERIZATION

The rGO - ZnO nanocomposite is prepared by adding ZnO nanoparticles (weight %) in Improved Hummer's method. The prepared sample with 5%, 10%, 15% and 20% of ZnO nanoparticles are named as S1, S2, S3 and S4, respectively. The Renishwa In-Via laser Raman microscope is used for the Raman analysis of the prepared samples at monochromatic laser of wavelength of 514.5 nm. The prepared samples are further analysed by RX I spectrometer by Perkin Elmer for FT-IR measurement. The scanning electron microscopy is used for the study of the surface morphologies of the prepared samples (FESEM, Tescan, MIRA3), respectively. The photo response measurements were performed at Keithley's 2000 digital multimeter.

RESULT AND DISCUSSIONS

Raman Studies

The prepared samples are characterized by Raman spectroscopy for structural and chemical information. Figure 1(a) represents the Raman spectra of the samples S1, S2, S3 and S4. The D and G band of the rGO is found to be at 1360 and 1590 cm^{-1} in all the samples along with it band due to ZnO nanoparticles is also present toward lower wave number side.

Fourier Transform Infrared Spectroscopy Studies (FT-IR Studies)

The prepared samples analyzed by FT-IR spectroscopy in Fig. 1(b) and it consist of peaks which attributed to C=C skeletal vibration and vibrations of ketonic species at 1630 cm^{-1} and 1750–1850 cm^{-1} , respectively [5]. Along with it, peaks due to symmetric, asymmetric and deformation vibration of epoxide groups are also present at 1220, 880, and 850 cm^{-1} , respectively.

Scanning Electron Microscopy (SEM) Studies

The SEM micrographs of the prepared samples are recorded as shown in Fig. 2 (a). The SEM micrograph consists of ZnO nanoparticles stick on the rGO sheets planes in S1, S2 and S3 samples. In the sample S4, it is observed that the ZnO nanoparticles are embedded in the graphene sheets.

Photo Response Measurement of Prepared Samples

The photo response of the sample S1, S2, S3 and S4 are reported in the Fig. 2(b). The electrical resistances of the samples were measured in the presence and absence of illuminated intensity of 30 mW/cm^2 . The photo responses of the prepared samples are calculated by:

$$\text{Response (\%)} = \frac{R_d - R_L}{R_d} \times 100 \% \quad (1)$$

Where, R_d and R_L are the resistance of the sample before and after illumination of light, respectively. Fig. shows the response curves of the samples S1, S2, S3 and S4, respectively. The response is found to be highest in S4 with the value of 7.56 %, whereas responses for S1, S2 and S3 are found to be 1.22%, 3.34% and 3.79%, respectively. The increase in photo response of the sample S4 may be due to formation of p-n junction diode [6].

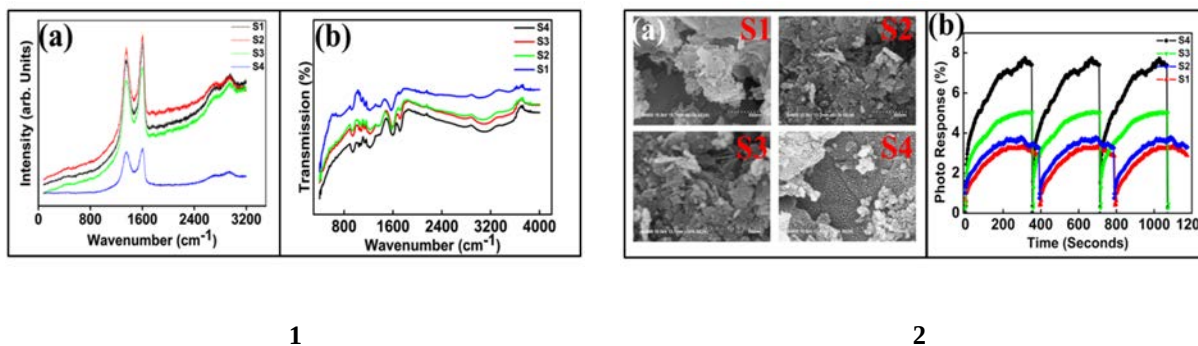


FIGURE 1. (a) Raman spectra of the prepared samples S1, S2, S3 and S4, respectively (b) FT-IR spectra of the prepared samples S1, S2, S3 and S4, respectively. **FIGURE 2.** (a) SEM micrographs of the sample S1, S2, S3 and S4, respectively. (b) The photo response of the prepared samples S1, S2, S3 and S4, respectively recorder at room temperature (30 $^{\circ}\text{C}$).

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Substrate Dependent Growth Study of ZnIn_2S_4 Nanostructures: Single Step Hydrothermal Approach

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Abstract: The unique structural features and fascinating physicochemical properties of 2D nanostructured materials have shown great application in charge storage, optoelectronics and photoconduction device. Zinc Indium Sulfide (ZnIn_2S_4) is the only member of the ternary metal sulfides family with a layered structure. Amongst the methods used for synthesizing ZnIn_2S_4 structures, the hydrothermal technique offers a simple, cost-effective and environmentally friendly route for materials synthesis. To study the effect of substrate on the formation of hydrothermally grown ZnIn_2S_4 on several types of substrates were used. The structures of the ZnIn_2S_4 were systematically studied by scanning electron microscopy (SEM) and XRD. It was demonstrated that the type of substrates used had a great influence on the morphologies, density and alignment of the ZnIn_2S_4 formed. The ordered structure of nanometric dense ZnIn_2S_4 has been prepared on the conductive substrate for practical application in nano electronic devices.

INTRODUCTION

Nanostructured materials have gained colossal attention or attraction because of the new physical and chemical properties and its potential uses in nano devices. In numerous applications the oriented nanostructures are highly desired and it is important to develop effective methods of synthesizing well-defined 2D nanostructured materials with controlled composition and morphology. Two dimensional (2D) nanostructures in a semiconductor array have been widely investigated with regard to their possible use in electro-optical devices. Hence, there is the need of obtaining high quality films containing controlled nanostructures through easy and dependable methods. Densely populated nanostructures in the films have received much attention in various fields of science and industry, including catalysis, optics, electronics, energy, etc. Earlier studies have indicated that morphology of nanostructures plays a crucial role in determining their properties. Processing parameters such as the synthesis method employed, type of substrates, synthesis temperature and others influence these structures. The hydrothermal process is one of the aspired methods in development of nanostructure that demands moderate synthesis temperature, it is cheap, straightforward. It is known that ZnIn_2S_4 is the most efficient ternary metal sulfide due to its high chemical stability, relatively low cost, non-toxic and its small band gap ($E_g = 2.432.70$ eV). We have used in this work a hydrothermal process in order to synthesize ZnIn_2S_4 on various substrates, that is, FTO-coated glass substrates (FTO), Carbon Cloth (CC), stainless steel (SS) wafer, and a systematic study of the morphological evolution of the ZnIn_2S_4 structures on these substrates was performed.

EXPERIMENTAL

All chemicals in the present work were of analytical grade and used as it is without further purification. The synthesis of ZnIn_2S_4 nanostructures by the hydrothermal technique. Zinc nitrate, indium nitrate and thiourea were used as precursors of Zn, In and S. In this work, the substrates used were FTO, CC, SS wafer. All substrates were cut into a dimension measuring $1\text{ cm} \times 2\text{ cm}$. An aqueous solution of zinc nitrate, indium nitrate and thiourea in 1:2:8 mmol ratio, in 80 ml distilled water was prepared than was then transferred to 100 ml Teflon lined stainless steel autoclave. All substrate was suspended vertically in the reaction solution with the help of Teflon tape. The stainless steel autoclave was kept in a muffle furnace. The hydrothermal synthesis was carried out at 150°C for a 15 h duration. After the reaction, all the samples were taken out of the autoclave and rinsed with deionized water several times. [2]

RESULTS AND DISCUSSION

Structures and morphologies:

The purity and crystal structures of the products were analyzed by XRD. Fig. 1. The sample prepared by hydrothermal method on FTO, CC and SS wafer shows the XRD pattern of the typical ZnIn_2S_4 . All of the well distinct diffraction peaks shows that in the XRD pattern of the as-prepared sample of the pure hexagonal phase of ZnIn_2S_4 (JCPDS card No. 72–0773). There is no evidence of peak related to CC, SS which may be due to the growth of dense and uniform ZnIn_2S_4 nanostructures on the entire surface of substrates. There is no other impurities, such as binary sulfides, oxides, or hydroxides were detected by XRD analysis, indicating the phase purity of the ZnIn_2S_4 product.

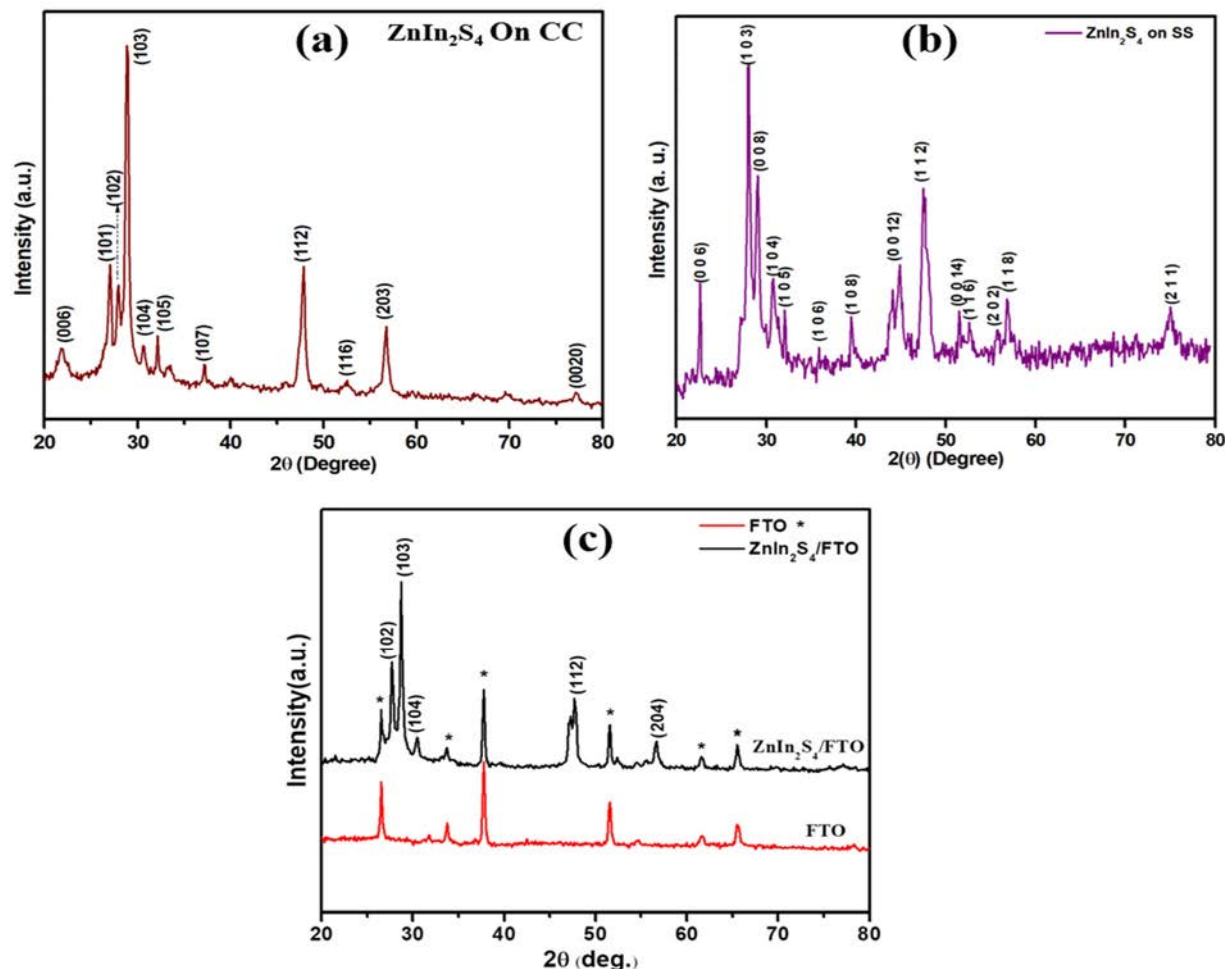


Fig. 1. XRD patterns of the ZnIn_2S_4 film on a) Carbon cloth b) stainless steel c) FTO substrate.

An SEM analysis was performed to investigate the morphology of ZnIn_2S_4 nanostructures which had been grown on the substrate. In Fig. 2(a, d, g), the SEM image of the untouched substrate is presented. These nano-petals are vertically arranged, randomly oriented, making a dense criss-cross network, as seen in the higher magnification SEM image, Fig. 2 (b-c), Fig.2 (e, f), and Fig. (h, i) of the ZnIn_2S_4 nanostructures on the CC, SS and FTO substrate, respectively. SEM images of on-substrate grown hydrothermally, depicted in Fig. 2 reveal that there exists uniform and dense coating of ZnIn_2S_4 nanostructures, nanosheets/nanopetals that cover the whole surface of the substrate. ZnIn_2S_4 nanosheets greatly rely on the substrate to give the desired thickness. Through the study, it is found that the impact of the substrate on ZnIn_2S_4 nanostructures growth.

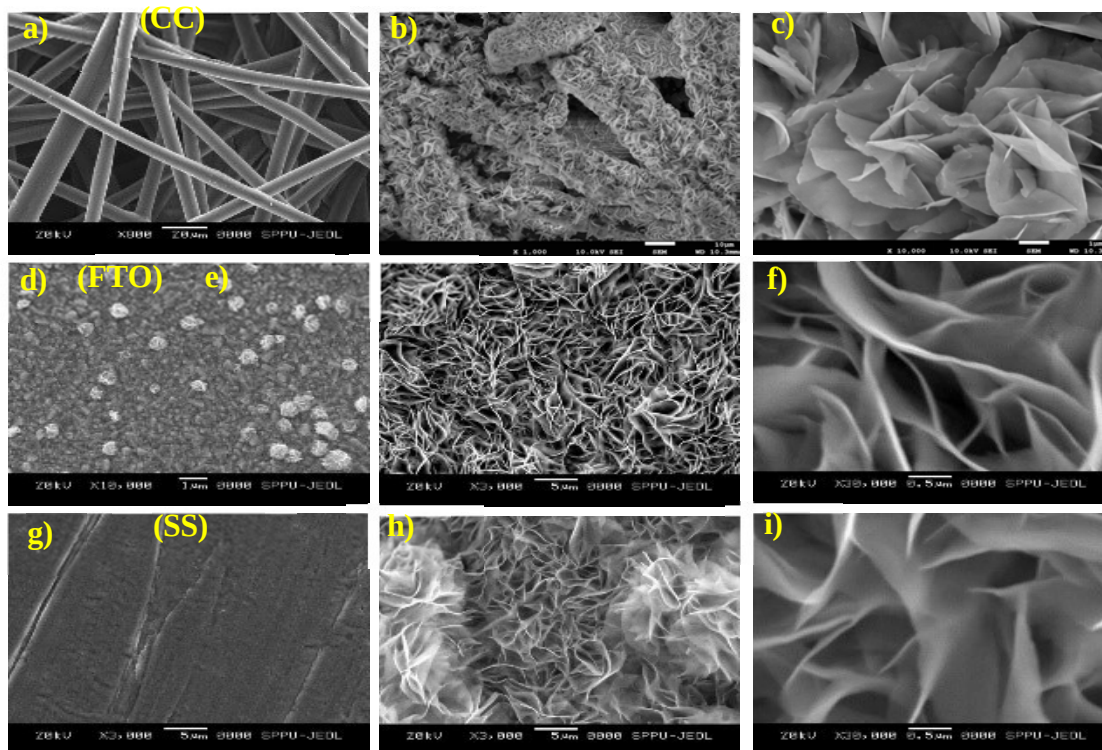


Fig. 2. SEM image of the ZnIn_2S_4 film on (a-c) Carbon cloth (d-f) FTO substrate (g-i) stainless steel.

CONCLUSIONS:

In this paper, nanosheets growth of ZnIn_2S_4 can be supported on various substrates using assisted hydrothermal technique. ZnIn_2S_4 nanosheets nets are well-aligned on substrate. The adjusting reaction created microspheres, porous nanosheets and assembled nanosheets films. Besides, this process enable the formation of coatings on large area can be applied to the production of other films to create hierarchical structures and new characteristics of nanomaterials.

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Characterization of Ni And Cu Doped ZnO Nanoparticles

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Abstract. In this article, exceptionally increase in production of nickel & copper doped zinc oxide nanostructures is reported. The ZnO nanostructures are synthesized with 10% of Ni & Cu doping adopting a Sol-gel method. Further the structural & crystallite size studies were performed by utilizing X-ray diffraction. The identification of wurtzite phase and determination of lattice parameters of Ni & Cu doped ZnO nanocrystallites is ascertained. X-ray diffraction (XRD) results indicate that the crystallite size is in 23-39 nm range, lattice parameters are $a=0.32\text{nm}$ and $c=0.52\text{nm}$ respectively for wurtzite structure of ZnO. Also using UV-VIS spectroscopy of doped ZnO nanoparticles reveal absorbance and reflectance.

INTRODUCTION

Valued for ZnO ultraviolet absorbance, wide chemistry, piezoelectricity and luminescence at high temperatures, ZnO has penetrated far into industry and is one of the critical buildings in today modern society.¹ ZnO is indeed a key element in many industrial manufacturing processes including paints, cosmetics, pharmaceuticals, plastic, batteries, electrical equipment, rubber, soap, textile, floor covering etc. With improvement in growth technology of ZnO nanostructures, single crystal and nanoparticles, ZnO devices will become increasing functional in the near future.² Metal oxide nanoparticles were extensively investigated due to their applications in the field of spintronics,³ photoelectronic,⁴ sensor,⁵ lasing devices⁶ and light emitting diodes,⁷ etc. The properties of the nanomaterials incredibly altered due to quantum confinement and enhanced surface to volume ratio.⁸ ZnO has a quite large band gap of 3.3eV at room temperature and 60meV excitation energy,¹² The advantages of a large band gap include higher values of breakdown voltages, sustaining large electric fields, high-temperature and high-power operations.

METHODOLOGY

Doped Zinc oxide nanostructure was synthesized by using sol-gel method. To prepare a sol, precursor 0.2M of zinc acetate Dihydrate, .02M Nickle acetate (i.e. 10%Doping), reducing agent 0.2 M of sodium hydroxide were weighted using a weighting balance. Then 50ml of distilled water was measured by measuring cylinder for each sample. After that, all the weighting samples were dissolved separately in 50ml of distilled water. All the solutions were stirred with constant stirring for about 30 minutes. After well mixed, .02M Nickle acetate solution was poured to the solution containing zinc acetate with constant stirring by magnetic stirrer for about 30minutes. Then 0.2 M of sodium hydroxide solution as reducing agent was poured to the solution containing zinc acetate & Nickle acetate with constant stirring by magnetic stirrer for about 1hour. Then burette was filled with 100ml of PVA (Poly vinyl alcohol) and titrates dropwise to the solution containing reducing agent, zinc acetate and Nickle acetate. After the constant stirring, precipitates were formed. Dried precipitate was calcined at about 700°C for 24 hours in muffle furnace. So, we have produced Ni Doped ZnO nanoparticles. Similarly, Cu doped ZnO nanoparticles were prepared.

RESULTS AND DISCUSSIONS

X-ray diffraction study confirms that the synthesized material was ZnO with wurtzite phase and the entire diffraction peaks are in agreement with the data available. The X-ray diffraction data were recorded by using Cu K α radiation ($\lambda=1.5406\text{\AA}$). The average grain size was calculated with the help of Scherrer equation using the FWHM of all peaks. Most importantly, all of the XRD peaks were attributed to ZnO and no other undesired peaks were observed due to secondary phases or impurity phases within the detection limit of the X-ray diffractometer.¹⁷ Scherrer equation

is

$$D = 0.89 \frac{\lambda}{\beta \cos \theta}$$

Where D is the grain size, λ is the wavelength of x-ray radiation, β is the full width at the half maximum (FWHM) of the ZnO and θ is the diffraction angle. The c crystallite size is in 23-39 nm range and lattice parameters are $a=0.32\text{nm}$ and $c=0.52\text{nm}$.

Based on the experimental work that has been done, there are series of chemical reaction that takes place. Figure 1, at 10% doping, we are getting, the NiO (200) XRD peak. This is due to the fact that doping of Ni is not completely substituted inside ZnO lattice and therefore, NiO phase is obtained besides ZnNiO phase. On the basis of x-ray diffraction, we infer that Ni doping in ZnO is responsible for transformation of nanoparticles to nanostructure (nanorods). The excess of Ni doping essentially drives the anisotropic growth of ZnNiO nanostructure and hence, nanorods formation takes place.

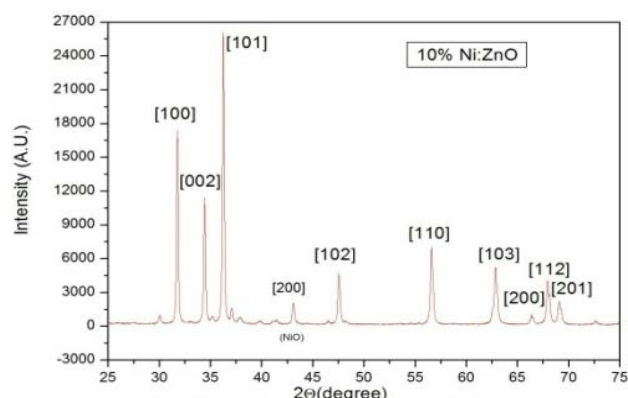


Fig.1 XRD pattern for 10% Ni doped ZnO nanoparticle

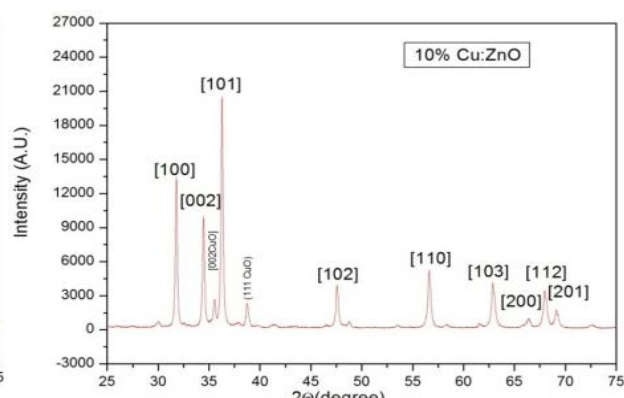


Fig.2 XRD pattern for 10% Cu doped ZnO nanoparticle

In Fig.2, At 10% doping, we are getting, the CuO (002) & (111) XRD peaks. This is due to the fact that doping of Cu is not completely substituted inside ZnO lattice and therefore, CuO phase is obtained besides ZnCuO phase. But overall, there is exceptionally increase in the production of nanostructure.

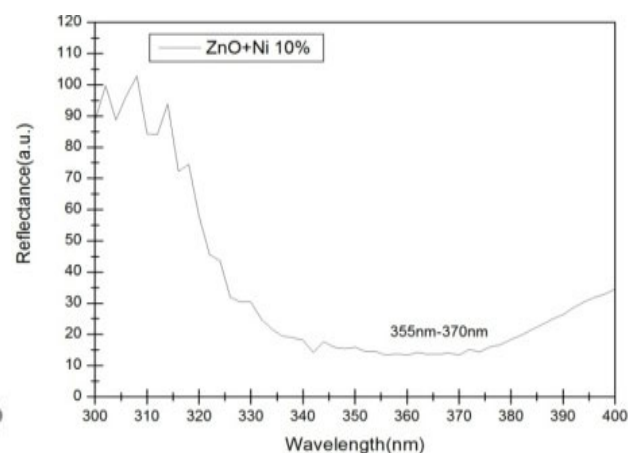
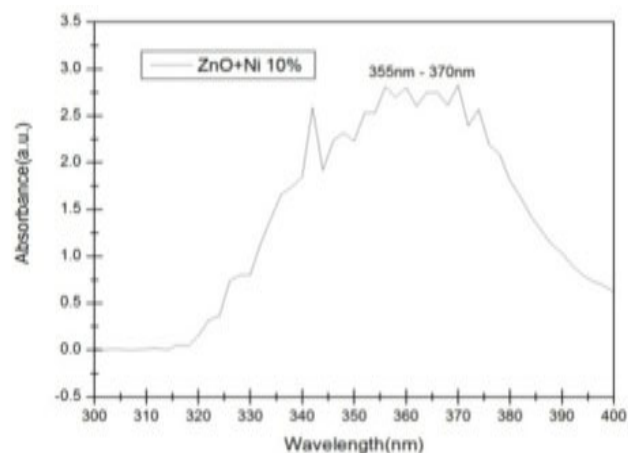


FIGURE 3. UV Spectroscopy Study of Ni doped ZnO Nanoparticles

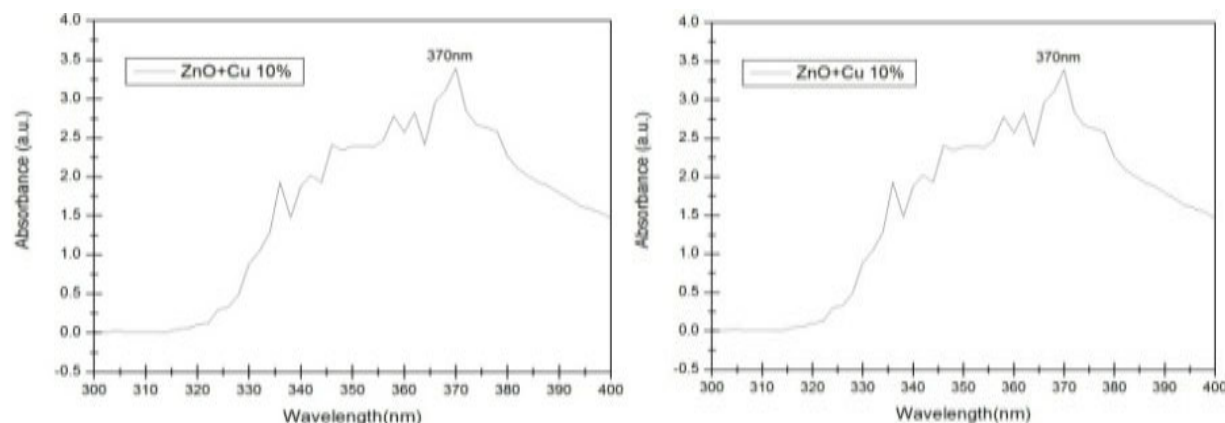


FIGURE 4. UV Spectroscopy Study of Cu doped ZnO Nanoparticles

CONCLUSION

The exceptionally increase in nickel & copper doped ZnO nanostructures can be summarized as follows. At 10% doping of Ni & Cu into ZnO, the Zn-O-Ni or Zn-O-Cu linkages become prominent without any change in phase and size of nanoparticles. Ni or Cu gives rise to weakening of Zn-O bonding and development of Ni-O or Cu-O interactions and Zn-O-Ni or Zn-O-Cu linkages and subsequently favors anisotropic growth in ZnNiO or ZnCuO nanostructures. As a consequence, exceptionally increase of nanostructures takes place. Also, X-ray diffraction (XRD) results indicates that the crystallite size is in 23–39 nm range, lattice parameters are $a=0.32\text{nm}$ and $c=0.52\text{nm}$ respectively for wurtzite structure of ZnO. Also UV-VIS spectroscopy clearly reveals the maxima and minima for absorbance and reflectance.

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Quantification of the Pore Structure in TEOS based Silica Aerogels Doped With Graphene Oxide

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Abstract. Silica aerogels doped with varying concentrations of graphene oxide (GO) were synthesized via a Two-Step Surface Modification method followed by Ambient Pressure Drying. The impact of GO incorporation on the pore morphology and structure of the aerogels was investigated. Pore volume, surface area, pore size, particle size, and radius of gyration were determined. Brunauer-Emmett-Teller (BET) analysis showed a maximum surface area of 541.7 m²/g for the sample containing 0.05 wt% GO. Small-Angle Neutron Scattering (SANS) revealed a highly interconnected porous network, with mass fractal dimensions ranging from 2.72 to 2.90. The results demonstrate that 0.05 wt% GO optimally enhances the structural features of silica aerogels, highlighting their potential for advanced energy storage applications.

INTRODUCTION

Aerogels are highly porous, transparent materials formed by replacing the liquid in a gel with air while maintaining its solid network. First synthesized by Samuel Kistler in 1930 [1], silica aerogels exhibit exceptional properties such as (98%) porosity, low thermal conductivity, high surface area, optical transparency, and low dielectric constant [2–3]. These features make them suitable for applications in thermal insulation, sensing, catalysis, absorption, and cosmic dust collection [4]. While silica aerogels hold great potential, their widespread use is hindered by synthesis challenges. Among various methods, ambient pressure drying (APD) offers a more cost-effective route for their production. Drying wet gels under ambient pressure often causes pore collapse due to their fragile structure. To prevent shrinkage without damaging the nanostructure and preserve properties, a two-step surface modification can be employed, yielding aerogels with enhanced strength, low density, thermal insulation, and hydrophobicity. Incorporating graphene oxide (GO) into silica aerogels may further improve mechanical stability, reduces brittleness, and imparts multifunctionality, making them suitable for energy storage, sensing, and catalysis. Oznur Kaya Cakmak et al. have studied the influence of GO on the physical and mechanical properties of such composite aerogel. In this study, TEOS-based silica aerogels were synthesized incorporating varying wt% of graphene oxide via a two-step surface modification followed by ambient pressure drying. The effects of graphene oxide on the structural, surface, and pore size and shape of the aerogels were investigated. The study is focused on the effects of GO on their structural, surface, and pore characteristics.

EXPERIMENTAL

Graphene Oxide (GO) was synthesized using the Modified Hummers method [5]. For silica aerogel synthesis, TEOS, DMF, deionized water, anhydrous ethanol, and HCl were mixed in different molar ratios and reacted at 60 °C. The resulting solution was then sonicated. GO was added in varying concentrations (0.00, 0.01 wt% , 0.05 wt% , and 0.1 wt%), followed by further sonication for over 15 minutes. The gels were demolded and aged in TEOS and then in *n*-hexane. A two-step surface modification was performed: first in MTMS diluted with *n*-hexane, and second with a TMCS:*n*-hexane mixture at room temperature. The modified alcogels were thoroughly washed with *n*-hexane and dried at 30 °C, 60 °C, and 80 °C, each for 3 hours, to obtain the final aerogels. A RIGAKU SMARTLAB X-ray diffractometer with Cu K α radiation was used for structural analysis with a step size of 0.02° over a 2 θ range of 10°–90°. Surface morphology and particle shape/size were examined using a Carl Zeiss EVO 18 Special Edition Scanning Electron Microscope (SEM). Specific surface area, pore size, and pore volume were determined using a Quantachrome Autosorb IQ QUA 211011 BET surface area analyzer. BET analysis involved nitrogen gas adsorption to evaluate surface area characteristics. Small-angle neutron scattering (SANS) measurements were conducted at Dhruva reactor

Bhabha Atomic Research Centre, Mumbai, using a medium-resolution double crystal based SANS spectrometer. Data were collected at room temperature over a q range of 0.003–0.173 nm⁻¹ with an incident neutron wavelength of 0.312 nm. Scattered intensities were measured as a function of the momentum transfer vector (q) and corrected for background, transmission, and resolution broadening [5].

RESULTS AND DISCUSSION

X-ray Diffraction showed sharp diffraction peaks at $2\theta = 10^\circ$ and $2\theta = 43^\circ$, which are the characteristic peaks of pristine GO, confirming the formation of GO. The XRD pattern of Silica aerogel with and without of GO exhibited a diffuse hump at around 22° confirming its amorphous nature. Notably, the characteristic peak of GO at $2\theta = 10^\circ$ and $2\theta = 43^\circ$ disappeared and were replaced by diffused feature, suggesting the uniform dispersion and possible exfoliation of GO within the silica matrix. The surface morphology of the aerogel composite obtained by SEM showed particles of spherical shape and their sizes varies from 78.96 nm to 54.28 nm. An increase in GO concentration from 0.01 to 0.1 wt% resulted in decrease in particle size. The surface morphology became increasingly rougher with higher GO content indicating enhanced surface texturing due to GO incorporation.

Adsorption desorption Study by BET

The nitrogen adsorption–desorption isotherms for both monolithic and composite aerogels are presented in Figure 1 (a). The Si/GO composite aerogels exhibit isotherms characteristic of IUPAC Type IV with H2-type hysteresis loops, indicating the presence of mesoporous structures. Table 1 shows the pore properties of Si/GO aerogels. The specific surface area of the pure silica aerogel without GO was 528.9 m²/g. The composite aerogel containing 0.05 wt% GO exhibited the highest specific surface area, of 541.7 m²/g. This enhancement can be attributed to a relatively higher total pore volume, which is likely resulting from an increase in mesoporous volume. However, at a GO content of 0.1 wt%, the specific surface area dropped to its lowest value. This decline is likely due to poor dispersion of GO within the silica matrix, leading to restacking or agglomeration of GO sheets, which can reduce accessible surface area.

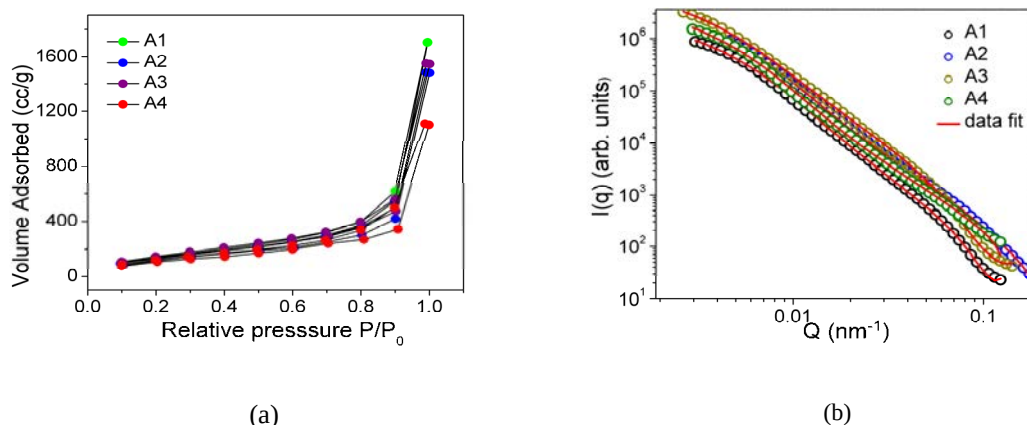


FIGURE 1. (a) Nitrogen adsorption-desorption isotherms of silica aerogel with and without GO (b) SANS profile of silica aerogel with and without GO with the data Fit

TABLE 1. Textural parameters of GO-doped silica aerogels obtained from BET analysis

Sample	Wt (%) of GO	Specific Surface Area (m ² /g)	Pore Size (Å)	Pore volume (CC/g)	Mesopore Surface Area (m ² /g)
A1	0	528.90	18.06	2.54	401.13
A2	0.01	496.03	18.09	2.29	496.03
A4	0.05	541.7	18.13	2.39	380.05

A5	0.1	440.71	18.05	1.7	327.65
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SANS profile for sample A1, A2, A3 and A4 are shown in Fig.1(b). The scattering profile typically shows three regions: Guinier, Fractal, and Porod. At low-Q, the Guinier region appears where intensity flattens or curves, reflecting the size of large aggregates. In the mid-Q range, the fractal region exhibits the linear trend on a logarithmic scale, indicating fractal behavior whereas in the higher Q range, the Porod region displays a sharp decrease in intensity consistent with Porod's law. The mass fractal dimensions of the composite aerogels were determined from the profile fitting using the mass fractal model and were found to be 2.72, 2.80, 2.78 and 2.84 respectively. For aerogels the fractal dimensions are usually in the range 2-3. Since A1 has the lowest fractal dimension it is expected have a simpler surface morphology, with comparatively larger pores and moderate porosity, while A2, A3 and A4 will have more complex, finely interconnected pores, leading to a higher surface area which increases as fractal dimensions increases. During the gelation stage of aerogel synthesis, sol transforms into gel, the silica particles starts to interact with each other, resulting into formation of smaller cluster which then grow into larger aggregates. These aggregates are a result of the attractive inter particle attractions in the gel network. The aggregate size from the profile is found to be 94 nm, 97 nm, 104 nm, 112 nm and 125 nm respectively for A1, A2, A3, A4 samples.

CONCLUSION

Graphene oxide was synthesized using a modified Hummers method and incorporated into silica aerogels at concentrations of 0, 0.01, 0.05, and 0.1 wt%. The aerogels were prepared via ambient pressure drying (APD) with a two-step surface modification using methyltrimethoxysilane (MTMS) and trimethylchlorosilane (TMCS). MTMS reduced residual pore water and prevented structural collapse, while TMCS replaced surface -OH groups with -CH₃, enhancing hydrophobicity and stability. X-ray diffraction study confirmed amorphous nature of the GO composite. Brunauer–Emmett–Teller (BET) analysis showed the 0.05 wt% GO composite had the highest surface area (541.7 m²/g), pore size (1.83 nm), and pore volume (2.393 cc/g). Small Angle Neutron Scattering (MSANS) indicated a highly branched microstructure with mass fractal dimensions of 2.72 - 2.90. It also exhibited the highest particle size and radius of gyration. These findings suggest that GO-doped silica aerogels, particularly at 0.05 wt%, possess excellent properties for energy storage application.

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Rare-Earth (Er, Tb) Doping-Induced Structural and Optical Modulation in Beta-Gallium Oxide Nanoparticles for Enhanced Blue Luminescence

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Abstract. This study explores the structural and optical evolution of β -Ga₂O₃ nanoparticles doped with 1 wt.% of Er³⁺ and Tb³⁺, synthesized via solid-state combustion method. X-ray diffraction (XRD) and Williamson-Hall (W-H) analysis confirm preservation of the monoclinic phase, along with a reduction in crystallite size and increased lattice strain upon doping. Raman spectroscopy reveals enhanced phonon damping and lattice disorder while retaining structural integrity. UV-Vis absorption spectra show an increase in band gap energy, which can be attributed to dopant-induced strain, lattice distortion, and associated modifications in the electronic structure. Photoluminescence (PL) studies demonstrate notable enhancement in blue emission, with all samples exhibiting a dominant peak at 428 nm, attributed to intrinsic defect states such as oxygen vacancies (V_O), gallium vacancies (V_{Ga}), or vacancy complexes (V_O-V_{Ga}). The Er³⁺ doped sample shows enhanced PL intensity compared to the undoped sample due to additional 4f transitions, while the Tb³⁺ doped sample displays the most intense and well-resolved emission peaks among all three, including a distinct green emission at 544 nm corresponding to the ⁵D₄→⁷F₅ transition. These findings underline the potential of rare-earth doped β -Ga₂O₃ for next-generation optoelectronic and photonic applications.

INTRODUCTION

β -Ga₂O₃ is an emerging ultra-wide bandgap (UWBG) semiconductor (~4.8 eV) known for its high breakdown electric field, thermal stability, and transparency in the deep-UV region, making it highly suitable for advanced optoelectronic and power device applications [1]. Despite its advantages, the optical response of pristine β -Ga₂O₃ remains limited by intrinsic defects and suboptimal emission efficiency. Doping with rare-earth (RE) elements has proven effective in modulating the crystal lattice, minimizing structural imperfections, and tailoring the optical bandgap [2]. Such modifications enhance light absorption and emission characteristics, often through strain engineering and carrier concentration effects. In this study, we systematically investigate the influence of Erbium (Er³⁺) and Terbium (Tb³⁺), each introduced at 1 weight %, on the structural and optical properties of β -Ga₂O₃ nanoparticles.

METHODOLOGY

β -Ga₂O₃ nanoparticles were synthesized via solid-state combustion using gallium nitrate octahydrate [Ga(NO₃)₃·8H₂O] as the gallium source and urea as the fuel. Erbium nitrate pentahydrate [Er(NO₃)₃·5H₂O] and terbium nitrate pentahydrate [Tb(NO₃)₃·5H₂O] were added at 1 weight % for rare-earth doping. The samples labeled Er-1 and Tb-1 represent β -Ga₂O₃ nanoparticles doped with 1 wt.% of Er³⁺ and Tb³⁺ ions, respectively. The precursors were thoroughly ground to ensure homogeneity and then combusted at ~500 °C in a muffle furnace, initiating a self-sustained redox reaction. The as-combusted powders obtained at this temperature are presumed to be in the metastable γ -Ga₂O₃ phase. These intermediate-phase samples were subsequently annealed at 900 °C for 3 hours in air to induce

complete transformation into the thermodynamically stable monoclinic β -Ga₂O₃ phase. The synthesized materials were then subjected to detailed structural and optical evaluation.

RESULTS AND DISCUSSIONS

X-ray diffraction patterns for undoped β -Ga₂O₃ and rare-earth doped variants (Er-1 and Tb-1) are presented in **Fig.1**. All observed peaks match well with the standard monoclinic β -phase of Ga₂O₃ (JCPDS No. 41-1103, space group C2/m), with no secondary phases detected, confirming the phase purity and successful incorporation of Er³⁺ and Tb³⁺ ions into the Ga₂O₃ lattice. Doping leads to a notable reduction in the intensity of the (-202) peak and increased peak broadening, indicative of deteriorated long-range crystallinity and the introduction of point defects and lattice strain.

Table 1. Structural features of pure and Er and Tb doped β -Ga₂O₃ samples with the highest intensity (-202) peak

Sample	2 θ (Degree)	FWHM (Degree)	Crystallite Size (nm)	Strain ($\epsilon \times 10^{-3}$)	Intensity (cps)
β -Ga ₂ O ₃	31.65	0.2864 $\pm$ 0.0013	26.67	-2.34 $\pm$ 0.64	2930
β -Ga ₂ O ₃ : Er-1	31.65	0.3767 $\pm$ 0.0018	20.28	-2.99 $\pm$ 0.62	1732
β -Ga ₂ O ₃ : Tb-1	31.67	0.3573 $\pm$ 0.0026	21.39	-2.83 $\pm$ 0.58	1807

The average crystallite size (D) was estimated using the Debye–Scherrer equation, $D = (K\lambda) / (\beta \cos \theta)$, and the lattice strain (ϵ) was extracted using the Williamson–Hall (W-H) relation, $\beta \cos \theta = (K\lambda / D) + 4\epsilon \sin \theta$, where β is the FWHM in radians, θ is the Bragg angle, λ is the X-ray wavelength (0.154 nm for Cu K α), K is the shape factor (0.89), and ϵ is the microstrain. The corresponding W-H plots are shown in **Fig.2**, and detailed structural parameters are tabulated in **Table 1**. Interestingly, crystallite size decreases significantly for Er-1 and then slightly increases for Tb-1. This non-monotonic trend correlates with the strain values; the higher strain in Er-1 more severely hinders crystallite growth, while the relatively lower strain in Tb-1 permits limited crystallite coarsening.

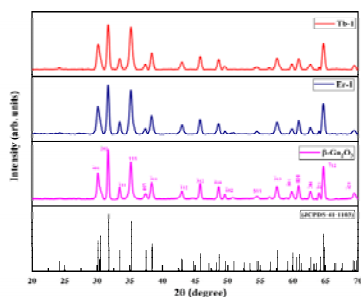


Fig.1 XRD pattern of β -Ga₂O₃, Er-1 and Tb-1 samples

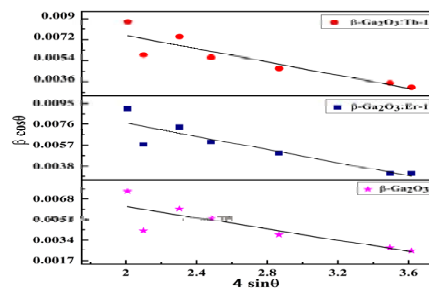


Fig.2 W-H plot of β -Ga₂O₃, Er-1 and Tb-1 samples

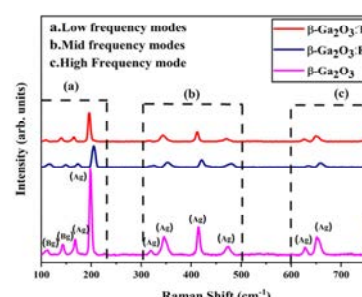


Fig.3 Raman Spectra of β -Ga₂O₃, Er-1 and Tb-1 samples

Raman spectra (**Fig. 3**) of undoped and RE-doped β -Ga₂O₃ samples further affirm the retention of the monoclinic structure, showing no major shifts in peak positions across all samples. However, rare-earth doping—particularly with Er³⁺—induces noticeable broadening, intensity suppression, and a slight blueshift in certain modes, signaling enhanced lattice disorder. These changes stem from dopant-induced strain and local symmetry disruption, consistent with the structural distortion observed in XRD. **Fig.4** shows the UV–Vis absorbance spectra of all samples, with the inset displaying the corresponding Tauc plots used to estimate the optical bandgap. A noticeable blue shift in the absorption edge is observed upon rare-earth doping, indicating modifications in the electronic structure of β -Ga₂O₃. The Er-doped sample exhibits a bandgap of $\sim$ 4.70 eV, which can be attributed to reduced crystallite size and increased lattice strain, leading to lattice distortion and defect-induced changes in the electronic structure. The Tb-doped sample shows a slightly higher bandgap ($\sim$ 4.73 eV), likely resulting from a combination of moderate strain, restricted grain growth,

and ionic size mismatch. In contrast, the undoped β -Ga₂O₃ sample, characterized by larger crystallite size and lower lattice strain, exhibits the lowest bandgap (~ 4.61 eV). These results suggest that bandgap variation is primarily governed by microstructural changes and dopant-induced lattice perturbations.

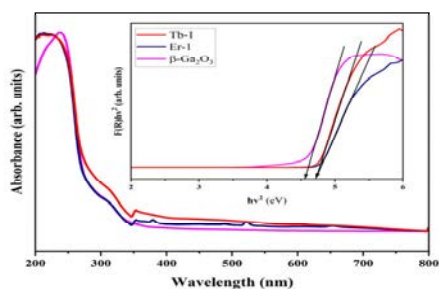


Fig.4 UV-vis absorbance spectra of β -Ga₂O₃, Er-1 and Tb-1 samples [inset: Tauc's plot]

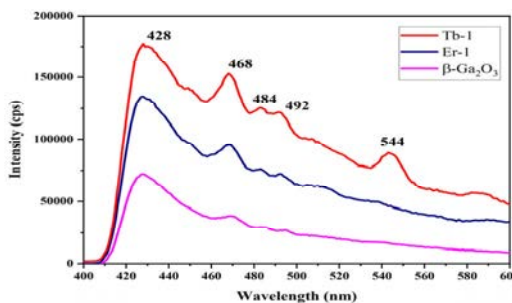


Fig.5 Photoluminescence Spectra of β -Ga₂O₃, Er-1 and Tb-1 samples [$\lambda_{\text{exc}} = 264$ nm]

Fig.5 presents the photoluminescence (PL) spectra of undoped and rare-earth (Er³⁺ and Tb³⁺) doped β -Ga₂O₃ nanoparticles, showing a clear enhancement in emission intensity upon doping [3]. All samples exhibit a dominant blue emission peak at 428 nm, attributed to intrinsic defect states such as oxygen vacancies (V_{O}), gallium vacancies (V_{Ga}), or vacancy complexes ($V_{\text{O}} - V_{\text{Ga}}$). Additional emission bands observed at 468 nm, 484 nm, and 492 nm across all samples are also associated with defect-related radiative transitions within the host lattice. The Er³⁺ doped sample shows moderate enhancement, arising from the combined contribution of host defect emission and overlapping 4f–4f transitions of Er³⁺ ions. In contrast, the Tb³⁺ doped sample exhibits significantly higher emission intensity along with sharper and well-resolved peaks, including a distinct green emission at 544 nm corresponding to the characteristic $^3\text{D}_4 \rightarrow ^7\text{F}_5$ transition of Tb³⁺.

CONCLUSION

In summary, rare-earth (Er³⁺ and Tb³⁺) doping in β -Ga₂O₃ nanoparticles effectively modulates their structural and optical properties. The monoclinic β -phase is preserved across all samples, while doping leads to a reduction in crystallite size and an increase in lattice strain. Raman analysis confirms enhanced lattice disorder, particularly in the Er³⁺-doped sample, arising from ionic size mismatch-induced lattice distortion. UV–Vis studies reveal a widening of the optical bandgap, primarily attributed to strain effects and dopant-induced modifications in the electronic structure. Photoluminescence results demonstrate enhanced blue emission upon doping, with the Tb³⁺-doped sample exhibiting the highest emission intensity along with characteristic green emission due to 4f–4f transitions. These findings highlight the potential of rare-earth doped β -Ga₂O₃ for advanced optoelectronic and photonic applications.

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Temperature-Dependent PL and Optical Study of CIZS Nanoparticles Functionalized with 5-Fluorouracil

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Abstract. In this work, we have successfully conjugated the drug 5-Fluorouracil (5-FU) to Cu–In–Zn–S nanoparticles (CIZS NPs), thereby developing a nanocarrier system with enhanced optical properties and potential for targeted drug delivery. The 5-FU-conjugated CIZS NPs were synthesized at room temperature and characterized using UV-Visible absorption, photoluminescence (PL), and Fourier-transform infrared (FTIR) spectroscopy, and temperature-dependent PL studies. Conjugation with 5-FU was confirmed by a red shift in UV-Visible spectra and the appearance of characteristic vibrational peaks in FTIR, which indicates the successful binding through hydrogen bonding and electrostatic interactions. PL intensity showed a moderate quenching upon drug attachment, attributed to charge transfer and surface interaction effects. Temperature-dependent PL studies revealed thermally induced quenching with partial reversibility, suggesting stable binding without compromising the NP's core optical features. These results support the potential of CIZS NPs as a multifunctional platform for simultaneous drug delivery and optical monitoring.

INTRODUCTION

5-Fluorouracil (5-FU), which is a well-known and widely used anti-cancer drug, has been commonly prescribed as a treatment option for a range of cancer-related diseases. Even though the efficacy of 5-FU in cancer therapy has been well established, its practical use is limited by its short half-life, nonspecific distribution, and dose-dependent systemic toxicity [1]. Moreover, a major part of 5-FU is metabolized or excreted before reaching the target site, resulting in poor therapeutic efficiency along with unwanted side effects [2].

To overcome the limitation of the aforementioned approaches, nanocarriers-assisted delivery system have gained significant attention in recent years. Among nanocarriers, quantum dots (QDs) are particularly advantageous owing to their photoluminescent properties, high surface-to-volume ratio, and surface biochemistry. Among all QDs, CuInZnS nanoparticles (CIZS NPs) are found to be more efficient than others, including CdTe and CdSe QDs, because of their low toxicity, good optical properties, and capability of being synthesized in aqueous media [3].

In the following study, we have used 5-FU as a drug and conjugated it with CIZS NPs, focusing on the binding interaction, structural characterization, and optoelectronic properties of the nanoconjugates prepared by us. The novelty of the study lies in the fact that it utilizes biocompatible CIZS NPs as drug carriers as well as optoelectronic probes for 5-FU, making it more efficient than others in the context of drug delivery in cancer treatment.

EXPERIMENTAL SECTION

Characterization details

For the characterization of 5-FU conjugated CIZS NPs, several techniques were applied. The Fourier-transform infrared (FTIR) spectra of 5-FU conjugated CIZS NPs were recorded by a Perkin-Elmer Spectrum 400 FTIR Spectrometer by preparing a pellet of the sample in KBr and pressing it in the sample holder. The UV-Visible absorption spectra were recorded by a LABINDIA UV-Vis Spectrophotometer in the range 200 to 800 nm, and the fluorescence emission spectra were recorded by a Shimadzu RF-5301 PC Spectrofluorophotometer at room temperature. The temperature-dependent photoluminescence (PL) spectra was also recorded by a Shimadzu RF-5301 PC Spectrofluorophotometer

Materials and Methods

To prepare the drug solution, a known quantity of 5-Fluorouracil (5-FU, SRL) was accurately weighed and dissolved in deionized water. For the conjugation process, 5 mL of freshly synthesized CIZS NPs solution was taken reported by Swati et al. [4], and 15 μ L of the 5-FU solution was added dropwise into it under continuous stirring. The mixture was stirred for 4 hours using a magnetic stirrer at room temperature. This drug loading process was carried out under ambient conditions, without the need for any specialized atmosphere, allowing the drug molecules to effectively interact and bind with the surface of the CIZS NPs.

RESULTS AND DISCUSSION

Absorption and Emission Spectroscopy

The UV-Vis absorption spectra of CIZS NPs and 5-FU loaded CIZS NPs as shown in Fig. 1 (a) were recorded in the range of 200–800 nm to study their optical behavior and confirm drug conjugation. Bare CIZS NPs showed no distinct peak in the visible range (200–800 nm) and free 5-FU exhibited a characteristic absorbance peak near 260 nm, corresponding to its $n \rightarrow \pi^*$ electronic transition [4, 5]. After conjugation with CIZS NPs, there is a slight red shift in peak position with a reduction in intensity. Importantly, no new absorbance peak appeared in the 300–800 nm region after drug loading, which suggests that the interaction between 5-FU and CIZS NPs did not induce any aggregation or chemical transformation of the core NPs structure [6]. The preservation of 5-FU's peak around 267 nm and the absence of any additional peaks indicate a successful and stable conjugation of 5-FU with CIZS NPs.

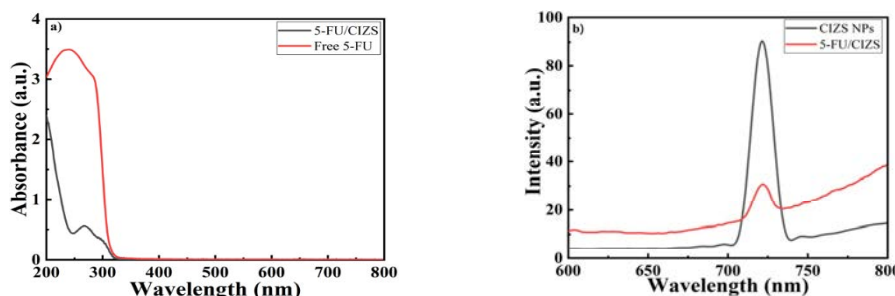


Figure 5. Represents the (a) UV-Vis spectra of free 5-FU and 5-FU/CIZS NPs and (b) PL spectra of 5-FU/CIZS NPs.

PL spectroscopy shown in Fig. 1 (b) shows the emission behavior of the 5-FU conjugated CIZS NPs. When excited at 480 nm, the CIZS NPs exhibited a strong and broad emission peak centered around 720 nm, confirming their fluorescent nature. However, after the successful conjugation of 5-FU, a noticeable quenching in the PL intensity was observed, while the peak position remained unchanged [7]. The quenching can be attributed to the formation of non-radiative pathways introduced by the 5-FU molecules, which likely interfere with the surface states responsible for light emission. Additionally, the binding of 5-FU to the NPs surface may block active emissive sites or alter surface defect states, further contributing to the decreased PL signal [8]. The electronic interaction between the CIZS NPs and the drug 5-FU creates alternative decay routes for excited electrons, diverting them from radiative recombination.

Temperature-Dependent PL Spectroscopy and FTIR Spectroscopy

The temperature-dependent PL of drug-conjugated CIZS NPs is shown in Fig. 2(a) and (b), as the temperature increases and when it cools down. In temperature-dependent PL studies of 5-FU conjugated CIZS NPs, the PL intensity decreases with rising temperature as shown in Fig. 2(a) due to enhanced non-radiative recombination caused by increased lattice vibrations and activated surface defects. Drug molecules on the CIZS NPs surface may further promote quenching by disrupting surface passivation [9,10]. However, upon cooling, the PL intensity gradually recovers as thermal vibrations subside, reducing non-radiative pathways and favouring radiative emission as shown in Fig. 2(b) [9]. The unchanged position of the emission peak during this cycle typically indicates that the electronic structure of the CIZS NP core remains stable, and the drug-NP interface has not been disrupted by the thermal cycle. This reversible behaviour indicates stable 5-FU/CIZS NPs conjugation throughout the thermal cycle.

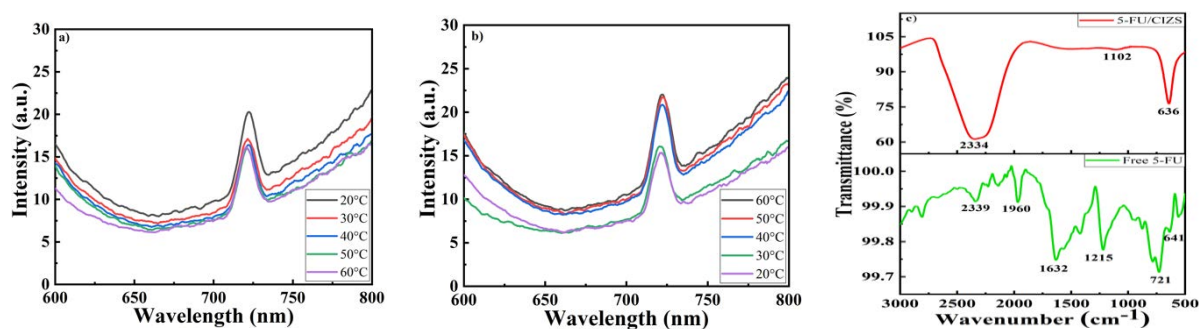


Figure 6. Represents the temperature-dependent PL spectra of 5-FU/CIZS NPs (a) increasing temperature from 20°C to 60°C, (b) decreasing temperature from 60°C to 20°C, and (c) FTIR spectra of free 5-FU and 5-FU/CIZS NPs.

The FTIR spectra of 5-FU/CIZS NPs and free 5-FU are shown in Fig. 2(c). The peak at 2334 cm^{-1} and 1102 cm^{-1} is due to the O-H (water) present in the solution of 5-FU/CIZS NPs and C-F stretching [2]. 5-FU (powder) exhibits distinct infrared absorption peaks. A peak around 721 cm^{-1} corresponds to C-H stretching vibrations, and 1632 cm^{-1} is attributed to C=O (carbonyl) stretching [1]. Additionally, the band near 1215 cm^{-1} is associated with C-H in-plane bending. Moreover, the characteristic peak observed at 641 cm^{-1} in pure 5-FU, which corresponds to aromatic ring vibrations, was found to shift slightly to 636 cm^{-1} in the 5-FU/CIZS NPs [2]. This shift, along with a noticeable change in intensity, suggests a strong interaction between 5-FU and the CIZS NPs.

CONCLUSION

In this study, we have successfully synthesized a drug-loaded nanocarrier system for the drug -FU using CIZS NPs. The results have confirmed that the drug has been effectively conjugated to the surface of the NPs without affecting their core structure or optical properties. UV-Vis and FTIR studies have confirmed the conjugation of the drug to the surface of NPs, whereas the PL studies have confirmed a significant quenching in the emission spectra of CIZS NPs upon conjugation with the drug, indicating their interaction with the drug. Therefore, the CIZS NPs have proven to be a stable drug carrier for the drug 5-FU, showing promising results for future biomedical applications.

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Mechanical Stability and Elastic Anisotropy in 2D Group III Nitride Monolayers

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Abstract. The mechanical properties of two-dimensional (2D) materials play a pivotal role in determining their reliability and performance in nanoscale devices, especially under strain-induced conditions. Using density functional theory (DFT), we systematically investigate the elastic constants, Young's modulus, and Poisson's ratio of group III nitride monolayers (BN, AlN, GaN, InN) in the hexagonal phase. Our results reveal their mechanical stability, anisotropic nature, and tunable stiffness, with BN exhibiting the highest rigidity and InN showing maximum incompressibility. These findings provide valuable insights for designing flexible and strain-engineered nanoelectronic applications.

INTRODUCTION

Mechanical qualities are very important for 2D materials¹⁻³ because they affect how strong, flexible, and stable they are in nanoelectronic and optoelectronic devices. High mechanical resilience makes it possible to tune electrical and transport features through strain engineering without changing the composition of the material. Due to their broad bandgaps, chemical stability, and promise for high-performance applications in sensors, transistors, and flexible electronics, group III nitrides have recently drawn a lot of attention among the many 2D systems. Therefore, improving their incorporation into next-generation strain-adaptive devices requires an understanding of their elastic behavior. Using first-principles calculations, we have methodically examined the elastic constants, Young's modulus, Poisson's ratio, and deformation potentials of hexagonal group III nitride monolayers in this work, as well as their anisotropic mechanical response under applied strain.

THEORY AND COMPUTATION

Density functional theory (DFT) with projector augmented wave (PAW) pseudopotentials was used in the Vienna Ab initio Simulation Package (VASP)⁴⁻⁶ to determine the mechanical characteristics of hexagonal phase XN monolayers (X = B, Al, Ga, and In). For exchange-correlation⁷ the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form was utilized. We used a k-point grid of 20×20×1 for the self-consistent field (SCF) computation⁸ with a 20 Å vacuum along the z-axis to prevent interlayer interactions, and a cutoff energy of 500 eV for our comprehensive analysis. Up till the energy and force convergence reached 10⁻¹ eV and 0.001 eV/Å, respectively, geometry optimization was carried out. Using a 7×7×1 k-point mesh, elastic constants, Young's modulus, and Poisson's ratio were derived from strain-stress relations⁹.

RESULTS AND DISCUSSION

The ability of 2D materials to withstand operating strain during manufacture, device integration, or external loading in real-world applications is largely dependent on their mechanical performance. In this work, we use density functional theory (DFT) to comprehensively study the elastic and strain-dependent characteristics of monolayer hexagonal XN (X = B, Al, Ga, and In) compounds.

The 2D elastic constants (C_{2D}) for both electron and hole carriers in the armchair and zigzag crystallographic directions were used to assess the materials' in-plane stiffness (Table 1). According to the calculated C_{2D} values, BN has the maximum in-plane stiffness (≈ 246.3 - 246.6 N/m) for both carrier types in both directions, whereas InN has the lowest stiffness (≈ 94.8 - 94.9 N/m). It's interesting to note that for a given material, the C_{2D} values for electrons

and holes are the same, suggesting that carrier type has no bearing on mechanical stiffness. When taking charge carrier conveyance into account, this feature implies isotropy in the elastic response.

Significant variation is observed as well in the deformation potential constants (E_1) across the series, with InN exhibiting significantly larger E_1 values for holes (~6.83-7.84 eV) and BN having the weakest E_1 for electrons (~0.22-0.35 eV). Potential benefits in high-mobility applications under mechanical deformation are implied by lower deformation potential values, which correlate to a weaker link between electronic states and strain.

TABLE 1. The 2D elastic constants (C_{2D}) for both electron and hole carriers in the armchair and zigzag directions of XP compounds and deformation potential constant (E_1) of XN compounds.

Carriers	Materials	Phase	Direction	C_{2D} (Nm ⁻¹)	E_1 (eV)
Electron	BN	<i>h</i>	Armchair	246.33	0.22
		<i>h</i>	Zigzag	246.61	0.35
	AlN	<i>h</i>	Armchair	143.44	0.04
		<i>h</i>	Zigzag	143.68	0.10
	GaN	<i>h</i>	Armchair	112.21	0.15
		<i>h</i>	Zigzag	112.35	0.03
	InN	<i>h</i>	Armchair	94.84	0.15
		<i>h</i>	Zigzag	94.92	0.41
Hole	BN	<i>h</i>	Armchair	246.33	0.79
		<i>h</i>	Zigzag	246.61	0.81
	AlN	<i>h</i>	Armchair	143.44	4.23
		<i>h</i>	Zigzag	143.68	3.90
	GaN	<i>h</i>	Armchair	112.21	0.19
		<i>h</i>	Zigzag	112.35	0.03
	InN	<i>h</i>	Armchair	94.84	6.83
		<i>h</i>	Zigzag	94.92	7.84

Stress-strain relations under limited homogeneous deformations were used to generate the elastic tensors C_{11} , C_{22} , C_{12} and C_{66} for the h-XN systems (Table 2). Born's mechanical stability criterion are met by all compounds: $C_{11} > 0$, $C_{11}-C_{12} > 0$ and $C_{66} > 0$. This demonstrates that in their relaxed states, all h-XN monolayers are mechanically stable. Strong in-plane covalent bonding is demonstrated by BN's greatest C_{11} and C_{22} values (~290.47 N/m), whereas InN's values are the lowest (~95 N/m).

To further measure stiffness and transverse strain response, Young's modulus (Y) and Poisson's ratio (ν) were calculated along both the x and y axes. BN has the lowest Poisson's ratio (~0.22) and the maximum Young's modulus (~276 N/m), suggesting excellent stiffness with little lateral expansion. In contrast, InN exhibits the biggest Poisson's ratio (~0.58) and the lowest Young's modulus (~62-63 N/m), indicating significant lateral displacement under uniaxial load and increased incompressibility. The divergence from perfect circular symmetry in the polar plots of Y and ν (Figure 1) shows that anisotropy is evident for all compounds. The hexagonal crystal structure and directional bonding differences are the sources of this anisotropy, which can be used to create mechanical or electromechanical devices that are direction-specific.

TABLE 2. The elastic-tensors, namely C_{11} , C_{22} , C_{12} , and C_{66} , expressed in units of Nm⁻¹, the Young's modulus and Poisson's ratio in the x and y axes for all h-XN materials are as shown in the below table.

Compounds	C_{11}	C_{22}	C_{12}	C_{66}	Young's modulus		Poisson's ratio	
					Y_x	Y_y	ν_x	ν_y
BN	290.47	290.48	64.21	112.88	276.27	276.29	0.22	0.22
AlN	143.93	143.86	65.28	39.37	114.32	114.25	0.45	0.45
GaN	137.82	137.93	65.76	36.00	106.44	106.58	0.48	0.48
InN	95.38	95.71	55.76	19.63	62.78	63.23	0.58	0.58

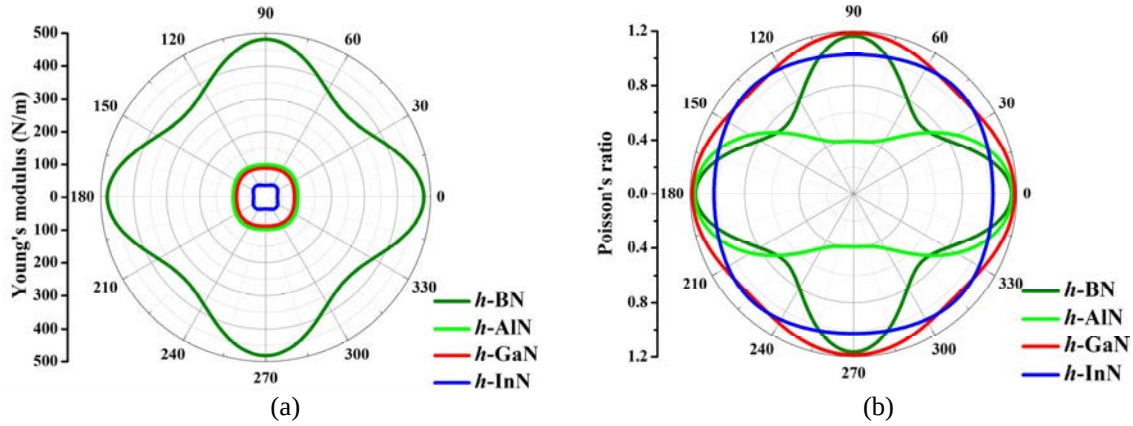


FIGURE 1: Polar diagrams of the ascertained (a) Young's modulus and (b) Poisson's ratio of the hexagonal monolayer 2D XN materials.

CONCLUSION

The mechanical properties of 2D group III nitride monolayers in hexagonal phase are thoroughly analyzed using first-principles calculations. Directional anisotropy and mechanical stability are present in all systems, with BN exhibiting the highest stiffness and InN the highest Poisson's ratio. Because of these unique elastic properties, h-XN compounds are attractive options for strain-engineered nanoelectronic and optoelectronic applications. The design of flexible, robust, and high-performing 2D nitride-based devices is made possible by our discoveries.

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Tailoring Optical and Structural Properties of Polycarbazole–TiO₂ Nanocomposites as an Emissive Layer for OLED Applications

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Abstract. The demand for high-performance Organic light emitting devices (OLEDs) has intensified in recent years, prompting significant research efforts towards the development of advanced emissive materials. Here we report the synthesis and characterization of a novel nanocomposite comprised of polycarbazole (PCZ) and titanium dioxide (TiO₂) for application as an emissive material in OLEDs. The resulting nanocomposite exhibits enhanced structural and optical performance, combining the high conductivity of PCZ with the superior electrical properties of TiO₂. The formation of PCZ with the correlative change in the nanostructure with the embodiment of TiO₂ was confirmed by X-ray diffraction technique (XRD). Irregular tetragonal bipyramidal arrangement of TiO₂ was formed over the agglomerated nanospheres of PCZ as confirmed by FESM images. The PL emission spectrum of PCZ-TiO₂ nanocomposite showed four emission peaks in the visible spectrum 391 nm, 414 nm, and 440 nm. The reinforcement of TiO₂ into PCZ matrix greatly enhanced the PL intensity that refers the more radiative electron-hole recombination which suggested the PCZ-TiO₂ nanocomposite could be a potential candidate as emissive layer for OLEDs.

INTRODUCTION

Organic light-emitting devices (OLEDs) have emerged as a promising display and lighting technology due to their inherent advantages such as flexibility, lightweight form, low power consumption, and wide viewing angles [1]. The continued evolution of OLED performance, however, relies heavily on the discovery and engineering of advanced emissive materials that can deliver enhanced optical and electrical properties. In particular, the incorporation of nanostructured materials into polymeric systems has opened up new avenues for tailoring the emission characteristics and charge transport behavior of OLED active layers. Among various organic semiconductors, polycarbazole (PCZ) has attracted attention due to its excellent film-forming ability, thermal stability, and high hole-transport efficiency. However, the relatively limited luminescence efficiency of pristine PCZ has motivated efforts to modify or reinforce its optical functionality. In this context, the integration of inorganic nanomaterials such as titanium dioxide (TiO₂) renowned for its high dielectric constant, wide band gap, and excellent electron-accepting properties offers a strategic approach to create hybrid systems with synergistically improved optoelectronic performance [2]. This study presents the synthesis and comprehensive characterization of a PCZ–TiO₂ nanocomposite tailored for OLED applications. The work demonstrates a cost-effective and facile method to develop a homogeneous hybrid material, where the inclusion of TiO₂ not only modulates the structural morphology of the polymer matrix but also significantly enhances its photoluminescent properties. Through detailed morphological and spectroscopic analyses, we evaluate the potential of the PCZ–TiO₂ nanocomposite as an emissive layer in next-generation OLEDs.

EXPERIMENTAL SECTION

Synthesis of Polycarbazole (PCZ)

Polycarbazole was synthesized via oxidative polymerization of 1.504 g carbazole (0.3 M) in 30 mL acetonitrile, stirred at room temperature. A solution of 1.622 g FeCl_3 in 20 mL acetonitrile was added dropwise over 30 min, turning the solution light green. Stirring continued for 6 h, followed by 2 days of freezing. The product was filtered with DI water/methanol, dried at 65 °C overnight, and ground into fine powder.

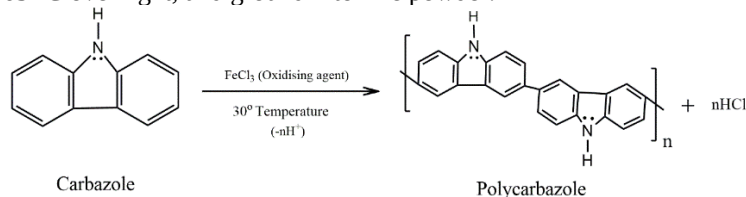


FIGURE 1. Polymerization mechanism from carbazole to polycarbazole

Synthesis of PCZ-TiO₂ nanocomposite

During the synthesis, 1.504 g of carbazole monomer was dissolved in 30 mL of acetonitrile with magnetic stirring. TiO₂ powder (50 wt.% of monomer) was added and stirred for 30 minutes. Then, 20 mL of ferric chloride solution (1.622 g FeCl_3 in acetonitrile) was added dropwise over 30 minutes while stirring, turning the solution light green, indicating oxidation. The mixture was stirred for 6 hours and stored in a freezer for 48 hours to complete polymerization. A dark green precipitate was formed, filtered repeatedly with DI water and methanol, and dried at 65 °C overnight. The final dried product was crushed into fine powder using a mortar and pestle.

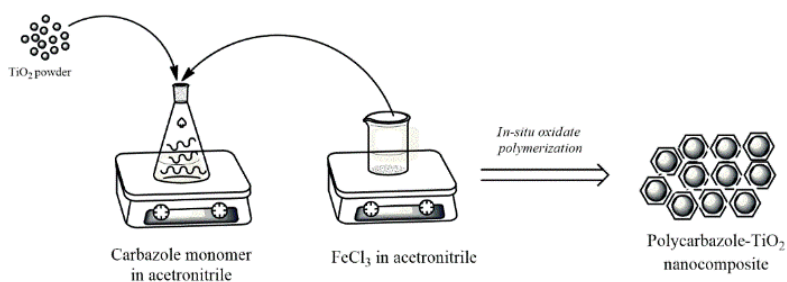


FIGURE 2. Schematic diagram for the synthesis route for PCZ-TiO₂ nanocomposite

RESULTS AND DISCUSSION

XRD Analysis, Surface Morphological Studies and Photoluminescence Analysis

The XRD profiles provided detailed insights into the phase purity, chain conformation, and particle size of both the pristine materials and as synthesized nanocomposites. XRD of pristine PCZ, TiO₂, and PCZ-TiO₂ nanocomposite have been shown in Figure 3. (A). PCZ showed prominent peaks at $2\theta = 9^\circ, 19^\circ, 23^\circ$ and 27° which corresponds to (020), (040), (200) and (201) planes, respectively as well matched with JCPDS card no. - 32-1556 [3]. The XRD spectra of TiO₂ indicated characteristic peaks at $2\theta = 25^\circ, 37^\circ, 47^\circ, 53^\circ, 55^\circ, 62^\circ, 74^\circ$ corresponding to (101), (004), (200), (105), (211), (220) and (215), respectively and well matched with JCPDS card no. – 015-0875 [4]. In case of PCZ-TiO₂ nanocomposite the mutual peaks at $2\theta = 9^\circ, 25^\circ$, and 47° confirmed its formation. The average crystallite size for PCZ-TiO₂ nanocomposite was calculated using Debye Scherrer's formula and found it was 45 nm. The surface morphological images of PCZ, TiO₂ and nanocomposite have been shown in Figure 3. (B-D). PCZ clearly showed the nanospheres like structures where as TiO₂ showed the irregular tetragonal nanoparticle structure. Figure 3. (D) showed the FESEM image of PCZ-TiO₂ nanocomposite and it depicted the agglomeration of TiO₂ nanoparticles over the PCZ

nanospheres matrix. Thus, reinforcement of TiO_2 increases the crystallinity of PCZ. The PL spectra of PCZ, TiO_2 and PCZ- TiO_2 nanocomposite were recorded using micro-PL with laser excitation wavelength 325 nm as shown in Figure 3. (E). It was observed that there were four distinct band emission peaks in the visible spectrum at 391 nm, 414 nm, 440 nm, and 440 nm due to $\sigma^* \rightarrow \pi$, $\pi^* \rightarrow \pi$ and $\pi^* \rightarrow \pi$ transitions respectively [3]. The rate of exciton recombination, efficiency and nature of emitted light could be understood directly from the PL emission intensity. The PL emission intensity rate of PCZ- TiO_2 nanocomposite is much greater than pristine PCZ and TiO_2 confirmed having potential to aimed as an emissive layer for OLEDs. The color purity and CCT value for PCZ- TiO_2 nanocomposite is 72.90% and 1933 K which corresponds the blue light in the warm emission.

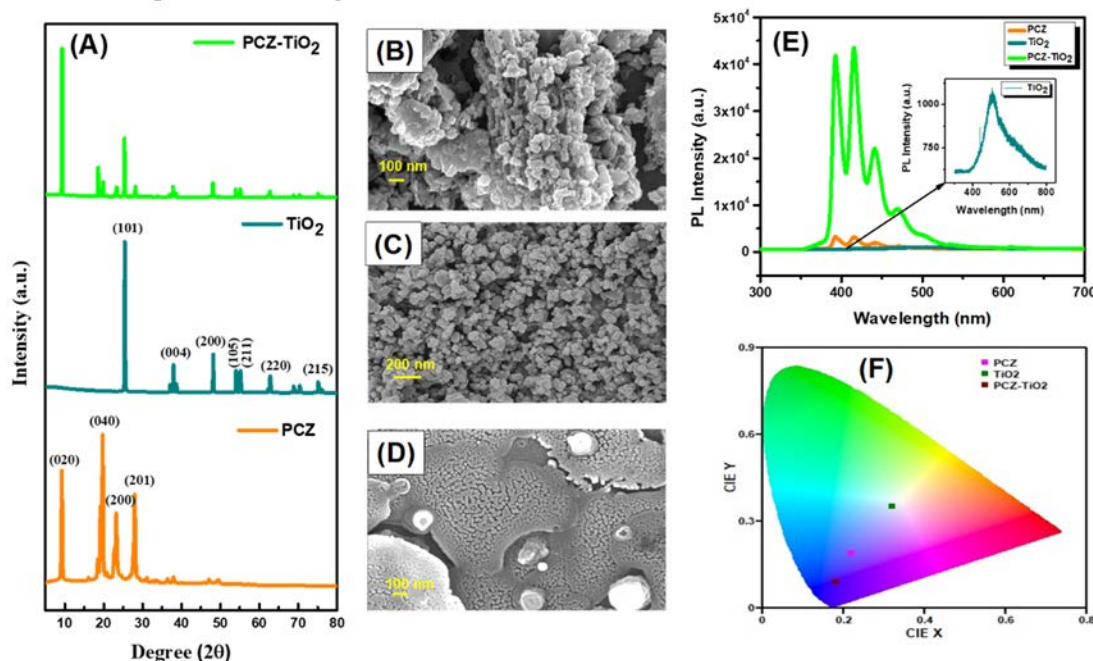


FIGURE 3. (A) XRD of PCZ, TiO_2 and PCZ- TiO_2 nanocomposite, (B-D) FESEM images of PCZ, TiO_2 and PCZ- TiO_2 nanocomposite (E & F) PL spectra & CIE of PCZ, TiO_2 and PCZ- TiO_2 nanocomposite

CONCLUSION

The pristine PCZ, TiO_2 and PCZ- TiO_2 nanocomposite was synthesized via in-situ polymerization method. The average crystallite size for PCZ- TiO_2 nanocomposite was evaluated as 45 nm. The agglomerated TiO_2 nanoparticles was found over polycarbazole nanospheres as found in FESEM images which confirmed the formation of PCZ- TiO_2 nanocomposite. The PL emission spectrum of PCZ- TiO_2 nanocomposite showed four emission peaks in the visible spectrum 391 nm, 414 nm, and 440 nm. The reinforcement of TiO_2 into PCZ matrix greatly enhanced the PL intensity that refers the emission in blue region which suggested the PCZ- TiO_2 nanocomposite could be a potential candidate as emissive layer for OLEDs.

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Controlled Pattern Formation on a Ferrofluid Surface

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Abstract. Rosensweig instability is the formation of spikes and valleys on a ferrofluid surface under an application of external magnetic field, perpendicular (normal) to the surface of ferrofluid. In this work, the instability was examined by changing the properties of ferrofluid with varying magnetic field. The experiments were conducted using a custom-built experimental setup, comprising a camera, light source, and a sample stage. Beyond a critical magnetic field (B_c), applied vertically to a ferrofluid drop, a principal spike form. An increment in the magnetic field results in a rise in its height to a maximum. On further increase of the field, secondary and tertiary spikes are formed around the central spike, conserving the volume of the fluid. The height of the spikes is observed to be dependent on the initial droplet volume and the concentration of magnetic nanoparticles in ferrofluid.

INTRODUCTION

Ferrofluid is a liquid in which nanoparticles, generally superparamagnetic in nature, are dispersed homogeneously. The surface of this fluid develops regular patterns, such as spikes and valleys under an applied vertical magnetic field. This surface instability is known as ‘Rosenweig instability’ or ‘normal field instability’. In addition to this well-known instability, ferrofluids may display additional surface instabilities under varying magnetic fields. These includes fingering instability¹, Rayleigh-Taylor instability², and normal-field instability³. Furthermore, ferrofluids may experience interfacial instabilities due to electric fields. In these instabilities, the applied external magnetic field pulls the nanoparticles with the base fluid along the field lines, while the surface tension and the gravity try to flatten the surface. In the present study, the instabilities are studied with varying experimental conditions such as field strength and particle concentrations.

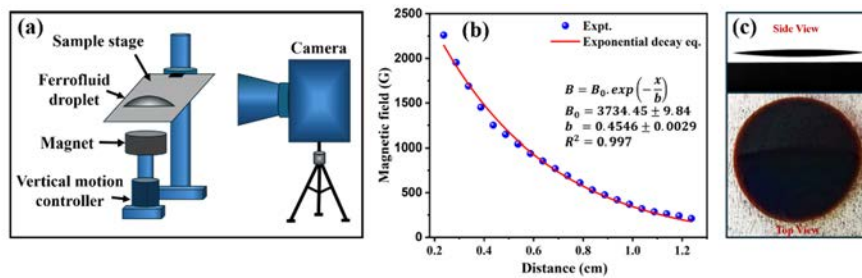


FIGURE 1. (a) Schematic diagram of homemade experimental setup and (b) strength of magnetic field at the center spot of the ferrofluid droplet as a function of distance between the surface of the magnet and the droplet spot. (c) Side and top views of a ferrofluid droplet in equilibrium (without magnetic field).

MATERIALS AND METHODS

The ferrofluid composed of iron oxide (3-15% v), oil-soluble dispersant (6-30 % v), and distillates (petroleum) hydrotreated light (55-91 % v) was purchased from Ferrotec (USA) Corporation. The magnetic field was applied using neodymium magnets with a diameter 20 mm and thickness of 10 mm.

As schematically described in Fig. 1 (a), a custom-made experimental arrangement was used in the present study. Before starting the experiment, the magnetic field was calibrated with a Gauss meter by changing the distance between

the magnet and the glass slide. By varying the magnetic field, the instability at the ferrofluid surface was generated, which was video graphed with the digital microscope. To see the effect of nanoparticle concentration, the carrier fluid was evaporated by placing the ferrofluid on a hot plate (Scilogex, MS-H-Pro) at $\sim 70^\circ\text{C}$. During this heat treatment, only the carrier fluid was evaporated, enhancing the concentration of particles. The final concentration (C_f) was represented as a factor of initial one (C_i) using the relation

$$C_i V_i = C_f V_f \text{ or } C_f = C_i \left(\frac{V_i}{V_f} \right) \quad (1)$$

where V_i and V_f are the initial and final volume of the ferrofluid.

RESULTS AND DISCUSSION

The field strength was modified by varying the distance (x) between the spot and the top surface of the magnet. Data shown in Fig. 1(b) exhibits the field strength (B) to decrease exponentially following a phenomenological expression,

$$B(x) = B_0 \cdot \exp\left(-\frac{x}{b}\right) \quad (2)$$

where, B_0 is a magnetic field at distance $x = 0$ and b is the characteristic distance at which the magnetic field strength is reduced to $\left(\frac{1}{e}\right)$ of B_0 . The values of these parameters were found to be $B_0 = 3734.45 \pm 9.84$ G and $b = 0.4546 \pm 0.0029$ cm, respectively, obtained from the fit shown in Fig. 1 (b). In the subsequent part of the investigation, this calibration curve was utilized to predict the strength of the field at the fluid spot at different positions of the magnet. A volume of $30\ \mu\text{L}$ ferrofluid forms a stable sessile droplet exhibiting a static contact angle of $4.22 \pm 1.30^\circ$ manifesting the fluid to spread well on the glass surface (Fig. 1(c)). The drop reaches equilibrium quickly (~ 15 seconds). The side and top views of the droplet at its equilibrium state are shown in Fig. 1 (c).

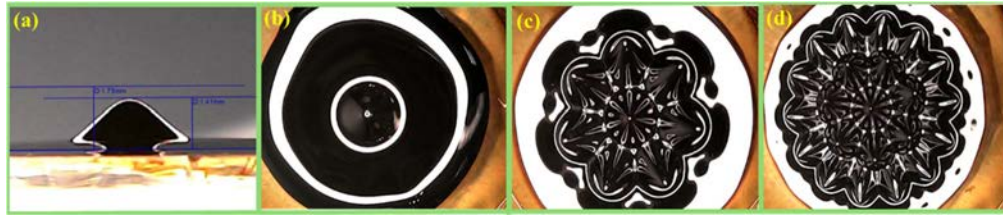


FIGURE 2. Principal spike with maximum height (a) side and (b) top view at 400 G magnetic field and its splitting into (c) secondary and (d) tertiary spikes at 690 and 1250 G field, respectively for $30\ \mu\text{L}$.

At a critical field strength (B_c) of ~ 250 G, the ferrofluid droplet starts forming a single spike, which is termed as the initial ‘principal spike’ as shown in Fig. 2(a, b). For the present case, the principal spike height increases with the field intensity reaching a maximum value at a field strength of 400 G. This value of the field is close to the magnetic field saturation value (440 G) of the used ferrofluid. The maximum height of the spike remains unaltered on further increase of the field. However, beyond a field of ~ 690 G, the spike starts expanding its base with a decrease in the height, resulting formation of ‘secondary spikes’ as shown in Fig. 2 (c). When the magnet is brought closer to the glass slide, more magnetic lines of force pass through the neighboring area of the principal spike, which induces such a splitting of the spike. Bringing the magnet very close to the glass slide causes further splitting of the secondary spikes into ‘tertiary ones’ (Fig. 2(d)).

The spikes have a shape of elliptical cone with the volume (V) given by,

$$V = \frac{\pi d^2 h}{6} \quad (3)$$

where, d and h are the diameter of the base and height of the elliptical cone, respectively which were obtained from the analysis of images. The calculated volume of spikes is provided in Table 1.

TABLE 1. A comparison between the volume of principal and sum of all spikes after splitting.

Volume of initial principal spike	Sum of the volume of central and secondary spikes	Sum of the volume of central, secondary and tertiary spikes
$6.89 \pm 0.23\ \mu\text{L}$	$7.45 \pm 0.45\ \mu\text{L}$	$7.25 \pm 0.52\ \mu\text{L}$

Table 1 shows that the volume of the initial principal spike is nearly equal to the sum of the volume of central spike and the secondary spikes. As the total volume of the fluid remains almost constant, the splitting causes the spikes to reduce their height systematically from the initial principal one to secondary and tertiary ones.

Fig. 3 (a) shows the spike height of the principal spike, which achieves its maximum height at around 400 G. Interestingly, this critical value of the field is observed to be independent of the initial droplet volume. However, the maximum height depends on the volume as depicted with a bar graph in Fig. 3(b). The increased droplet volume facilitates more magnetic nanoparticles to accumulate following the field lines, which helps to increase the spike height. For the concentration dependent study, the pure system concentration is denoted as 1, which is increased to 1.08 and 1.16 times of initial one as defined by equation 1. The increased concentration of nanoparticles enhances the initial principal spike height, as shown in Fig. 3(c) at the low magnetic field region. At a higher magnetic field, the spike height becomes independent of the concentration. The value of critical magnetic field, forming the initial principal spike, decreases with higher particle concentration. This is readily understood as the high concentration fluid expected to be more responsive to the field. On increasing concentration, more nanoparticles are available, and their self-alignment along the field increases the spike height.

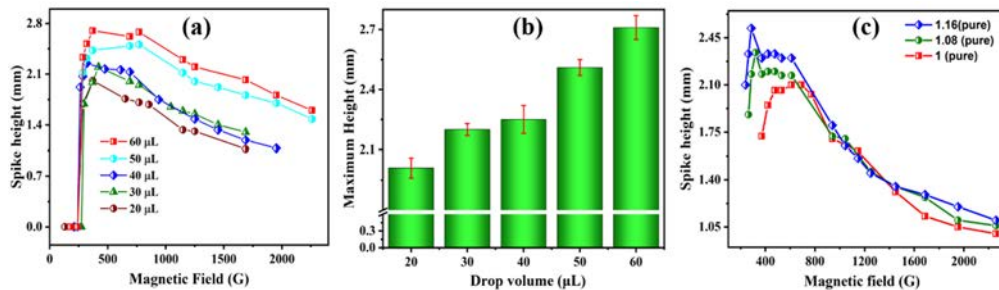


FIGURE 3. (a) Variation of spike height as a function of the magnetic. (b) A comparison of the maximum height of the spike at $\sim 400 \pm 20$ G. (c) Changes in spike height as a function of the magnetic field.

CONCLUSION

In this work, the formation of spikes in ferrofluid under a vertical magnetic field has been examined. The spike formation starts with a principal spike whose height attains a maximum value at a critical field. Beyond this field, the height reduces to form secondary and tertiary spikes, keeping the net volume of fluid constant. The increased volume of ferrofluid droplet and the particle concentration facilitates an increased number of nanoparticles to follow the field direction, resulting in an enhanced height of the principal spike.

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Phase Evolution, Morphology and Photoluminescence Properties of Cr Doped K_3AlF_6 Nanophosphors: Role of Calcination Temperature

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Abstract. This work investigates $K_3AlF_6:xCr^{3+}$ ($x = 0.005$) (KAF:Cr³⁺) for the evolution of structure, morphology, and photoluminescence (PL) properties. KAF is a polymorph possessing monoclinic (α), tetragonal (β), orthorhombic (γ) and cubic (δ) phase. KAF:Cr³⁺ have been synthesized using coprecipitation method. The as prepared (AP) KAF exhibits δ -cubic phase which remains the same up to 300 °C and interestingly transform to β -tetragonal at 500 and 600 °C. The morphological study reveals octahedral shaped particles which gets larger as the calcination temperature increases. Under excitation wavelength of 442 nm, photoluminescence (PL) study shows the enhanced PL intensity peaking around 730 nm in the red region of visible spectrum in case of 300 °C calcined sample compared to AP sample. Thus, the novel calcined KAF: 0.5at% Cr³⁺ offers promising optical features useful in anti-counterfeiting and other applications like LED fabrication.

INTRODUCTION

Counterfeiting remains a global challenge to overcome. This includes fake currencies, fake products, and even fake passports and medicines. To tackle this, one promising solution is using fluorescent anti-counterfeiting technology due to cost-effective and ease of production. The material used depends on the appearance and properties of the luminescent material, substance that glows, making it useful for security applications.[1-2] The Rare earth (RE) doped luminescent materials like NaYF₄: Er, Yb, YBO₃:Eu etc., are used frequently and can emit light across a wide range of spectrum from UV to near-infrared.[3-5] On the contrary, there are quantum dots being used for this purpose but suffer due to their toxicity.[6-7] The emission mechanisms include downconversion and upconversion. However, RE precursors are costly and increase the overall production cost of security features being developed. The non-rare earth elements like Mn, Cr, and Cu doped in a suitable host appear as an appropriate and alternate system for low-cost and superior luminescent pigments in anti-counterfeiting. [8-10] In this context, this work reports the preparation of non-rare earth, Cr doped K_3AlF_6 nanophosphors and their structural, morphological and photoluminescence evolution as a function of calcination temperature.

MATERIALS AND METHODS

2.1 Synthesis

K_3AlF_6 (KAF) and $K_3Al_{1-x}F_6:xCr^{3+}$ ($x = 0.005$) (K-Cr) phosphors were prepared using the co-precipitation method [9]. The starting materials were used as received with high-purity $Al(NO_3)_3 \cdot 9H_2O$ (99%), $Cr(NO_3)_3 \cdot 9H_2O$ (99.95%), and KF ($\geq 99.5\%$). The undoped KAF sample was stirred and left to settle for 24 hours, then filtered, washed with water, acetone, and ethanol, and dried at 80 °C. For Cr³⁺-doped KAF samples, solutions of aluminium and chromium nitrates were mixed, KF was slowly added, and the solution was aged for 2 hours before filtration, washing, and drying at 65 °C. pH of the solution and synthesized samples was maintained at 5. The powders were finally dried and calcined at 300 °C, 500 °C, and 600 °C to investigate the effects of heat treatment.

2.2 Characterizations

The phase of the samples was identified by X-ray Diffraction (XRD), RIGAKU, Model: Smart lab 3KW with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) operating at 40 kV and 40 mA with a step size 0.02°. The field-emission scanning

electron microscopy (FESEM) images were taken with JSM-IT800 of JEOL make. The Photoluminescence properties were measured using a fluorescence spectrometer, Make Horiba Fluoromax.

RESULTS & DISCUSSION

The structure of the synthesized samples has been determined using XRD. Fig.1 shows the XRD patterns of KAF:Cr³⁺ samples calcined at different temperatures. AP sample exhibits δ -cubic phase of KAF matching with ICSD#01-080-7929. [9-10] At 300 °C, the diffraction peaks remain essentially unchanged, indicating that the crystal structure i.e., cubic phase of KAF is almost the same as AP sample. At 500 °C and 600 °C, the noticeable shifts in peak positions and emergence of new peaks are seen. These changes point to partial breakdown of the original phase and the formation of secondary phases corresponding to tetragonal KAF.

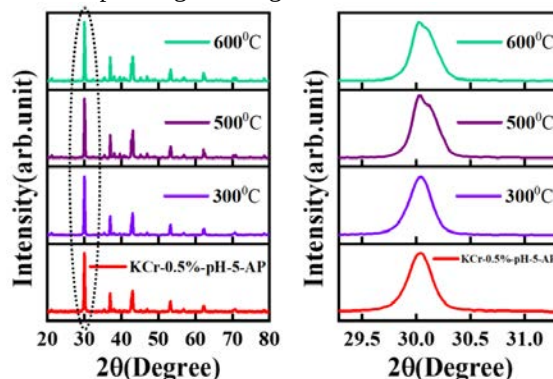


FIGURE. 1 XRD pattern of 0.5 at% Cr doped KAF calcined at different temperature. AP sample diffraction peaks are matched with ICSD#01-080-7929.

Fig. 2 depicts the FESEM images of 0.5 at% Cr doped KAF calcined at 300 and 500 °C. The morphology of synthesized KAF:Cr³⁺ and calcined at 300 °C reveal octahedral shaped particles. However, when the samples calcined at higher temperature at 500 °C, the particle morphology transform to more or less similar to the dodecahedrons and cuboids primarily due to the coalescence phenomenon.

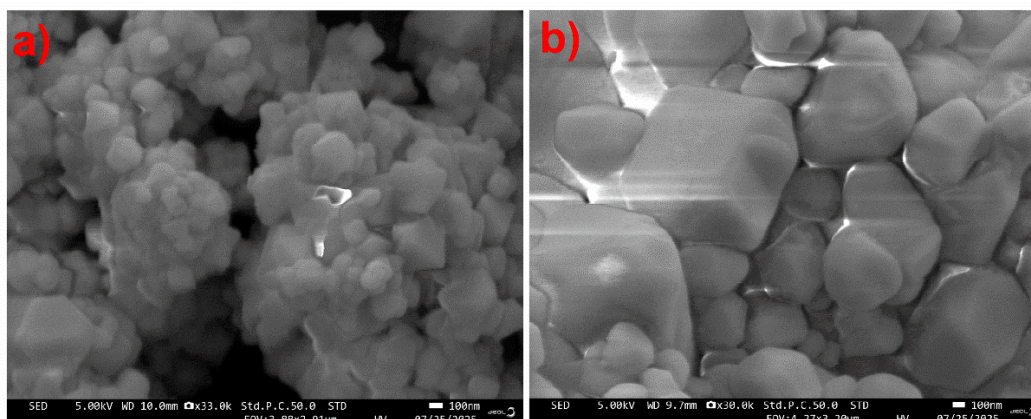


FIGURE 2. FESEM images of KAF:Cr³⁺ samples calcined at a) 300 °C and b) 500 °C

The PL emission spectra of 0.5% Cr³⁺ doped K₃AlF₆ samples calcined at different temperatures and recorded under an excitation wavelength of 442 nm are shown in fig.3. The PL emission band ranging from 650-850 nm peaking at around 730 nm originated due to ${}^4T_2 \rightarrow {}^4A_2$ transition of Cr³⁺. [9-10] In case of sample calcined at 300 °C, a noticeable increase in PL intensity was observed about 1.6 times higher than that of AP sample. This drastic improvement in PL emission is due to better crystallinity offering favorable crystal field strength and the removal of some surface or structural defects inherited at lower temperatures. However, when the calcination temperature is raised to 500 °C and 600 °C, the PL intensity decreased abruptly. The diminished intensity at higher calcined temperature samples

exhibiting tetragonal phase of KAF is because of thermal quenching or generation of new defects with poor crystal field strength which can reduce the efficiency of luminescence.

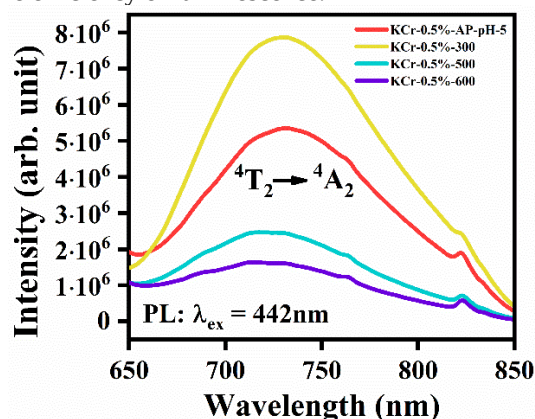


FIGURE 3. PL emission spectra of 0.5% Cr doped KAF at different calcination temperatures.

CONCLUSIONS

This work demonstrated the phase transformation from cubic to tetragonal in 0.5% Cr doped KAF as the calcination temperature is increased from 300 to 500 °C. The sample that exhibited octahedron shaped particles evolved with the dodecahedron and cuboid shaped particles. PL study revealed broad emission band ranging from 650-850 nm peaking at ~730 nm within visible and near-infrared (NIR) region when excited at 442 nm. The PL emission was strongest for the 300 °C calcined sample due to favourable crystal field strength offered by the cubic phase of KAF with minimal structural defects. The calcined 0.5% Cr doped KAF appears the potential candidate for anti-counterfeiting applications in harsh environments.

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Study of Optical, Magnetic and Dielectric Properties of ZnCo-ferrite Nanoparticles

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Abstract. $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles were prepared by the sol-gel auto-combustion method and were annealed at 900 °C. A single-phase cubic spinel structure was confirmed by XRD, with a crystallite size of **36.3 nm**. FTIR analysis established metal–oxygen vibration corresponding to the spinel structure in the sample. UV–Vis spectroscopy showed a direct band gap of 1.38 eV. The spontaneous magnetization value of 77.62 emu/g was observed at 300 K, and it was enhanced to 91.8 emu/g at 10K with a very high coercivity of 1.64kOe. Dielectric properties were studied at different frequencies and temperatures for the possible application of the nanomaterial at high frequency devices.

INTRODUCTION

Spinel ferrites have garnered significant interest for numerous technological applications, ranging from magnetic data storage to sensors, magnetic refrigeration, MRI contrast agents, magneto-optical devices, and biomedical as well as environmental applications due to their outstanding physical, chemical, electrical, magnetic, and biocompatible characteristics^{1,2}. Zinc-substituted cobalt ferrite has found notable interest among the research fraternity with its outstanding properties, i.e., high saturation magnetization and magnetic permeability, high magneto-crystalline anisotropy, intrinsic coercivity, and Curie temperature compared to other spinel ferrites. The interesting properties of these magnetic nanocrystals with inverse spinel structure are dependent on many factors, such as the method of synthesis, concentration of the dopant, sintering temperature, and cation distribution³. The cation distribution among different lattice sites influence the magnetic, optical, thermal, structural, and electrical properties of these nanomaterials⁴. To facilitate their use across different domains, several synthesis techniques have been used, which include the ceramic method, coprecipitation method, hydrothermal method, and sol-gel method⁵. In this work, the sol-gel auto combustion method was used for the synthesis of $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles, and their structural, optical, magnetic and dielectric properties were studied.

EXPERIMENTAL METHOD

For the synthesis of $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles, stoichiometric quantities of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 25 mL of ethylene glycol. The detailed synthesis procedure is discussed in our previous work⁵. The salt solution was stirred at 60 °C for 15 minutes at 650 rpm to produce a viscous gel, and subsequently it was heated to 200 °C for solvent evaporation and self-ignition. After cooling to room temperature, it was ground and annealed at 900 °C in air for 2 hours, followed by furnace cooling to room temperature⁶.

The structural property of the sample was studied by a Rigaku Miniflex600 X-ray diffractometer. Fourier transformed infrared (FTIR) spectra were collected at room temperature in the 400–4000 cm^{-1} range by Perkin Elmer FTIR Spectrum Two spectrometer. Optical properties were studied using an Agilent Cary UV-Vis NIR Spectrometer. Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) attachment of Quantum Design PPMS. Dielectric properties were studied by Wayne Kerr WK 6500B Precision Impedance Analyzer.

RESULTS AND DISCUSSION

Figure 1(a) shows the XRD pattern of the sample. The XRD spectra was analyzed with the help of ICDD PDF card no: 221086 for CoFe_2O_4 . The lattice constant and crystallite size were calculated considering the most intense (311) peak. The lattice constant was found to be 0.842 nm compared to the standard 0.839 nm for Co-ferrite. The crystallite size calculated using the Scherrer equation⁷ was found to be 36.3 nm.

FTIR spectra recorded for the sample in the range of 400 - 4000 cm^{-1} are shown in Fig.1(b). The absorption peak around 562 cm^{-1} corresponds to intrinsic metal–oxygen (M–O) vibrations in the tetrahedral sites. A lower frequency band between 450–380 cm^{-1} is generally observed due to M–O vibration in the octahedral sites, which was not detected in our study due to the experimental limitations. The band at 1385 cm^{-1} corresponds to residual nitrate ion (NO_3^-) on the surface of the nanoparticles⁸. The weak bands at 2887 cm^{-1} and 2980 cm^{-1} may be due to the CH_2 group⁵.

The optical band gap energy was estimated using the Tauc plot method, as shown in Fig.1(c). The UV-Vis spectra recorded for the sample is shown as an inset in Fig.1(c). The energy band gap was determined by implementing the Kubelka-Munk method⁹. The band gap (E_g) of a material can be calculated by the relation:

$$\alpha h\nu \propto (h\nu - E_g)^n, \quad (1)$$

where $n = 1/2$ for direct electronic transition and 2 for an indirect electronic transition. In the present study, a direct bandgap of 1.38 eV was obtained, which is nearly equal to the value reported for CoFe_2O_4 ¹⁰.

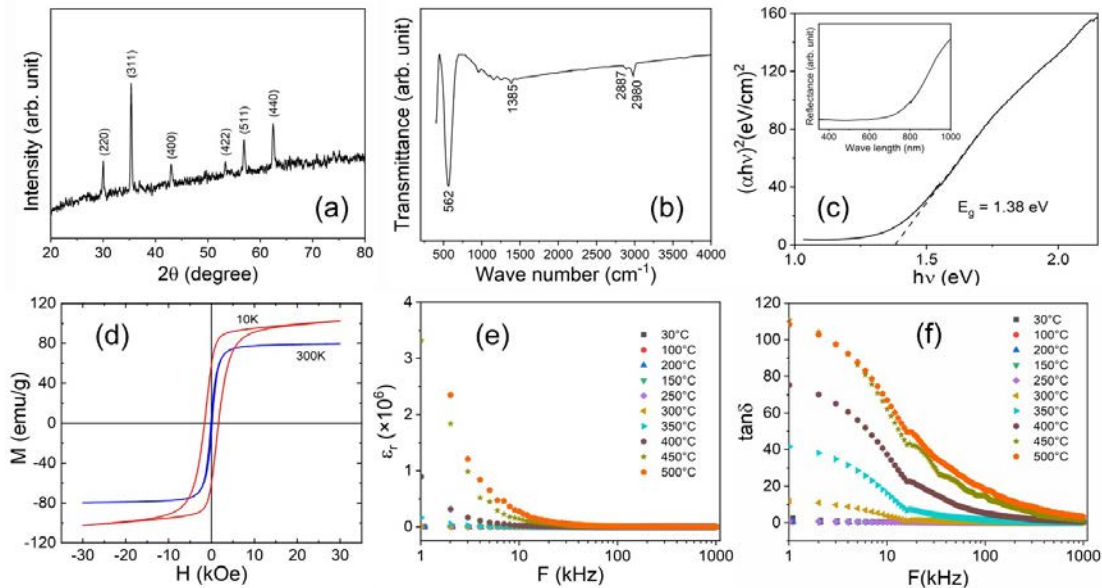


FIGURE 1. (a) XRD pattern, (b) FTIR spectra, (c) Tauc plot, (d) M-H loops, Variation of (e) dielectric constant and (f) $\tan\delta$ with frequency of the sample. The inset in Fig.(c) shows the UV-Vis reflection spectra of the sample.

Magnetic hysteresis (M-H) loops for the sample, measured at 300K and 10K, are presented in Fig.1(d). As seen in Fig.1(d), the loops are not saturating. The magnetic parameters, such as spontaneous magnetization (M_s), remanence (M_r), and coercivity (H_c), were obtained from the loops and are listed in Table 1. At 300 K, the observed M_s value is 77.62 emu/g with very low M_r and H_c values as seen in Table 1. With the decreasing temperature to 10 K, all the magnetic parameters were enhanced. Moreover, the H_c value is one order higher in magnitude, and the M_r/M_s ratio was observed to be 0.64. At low temperature, greater magnetic ordering and higher anisotropy enhance the magnetic properties¹¹.

TABLE 1. Magnetic properties of the sample.

M_s (emu/g)	M_r (emu/g)	M_r/M_s	H_c (kOe)

300K	10K	300K	10K	300K	10K	300K	10K
77.62	91.8	6.96	59.06	0.09	0.64	0.14	1.64

The dielectric constant (ϵ_r) was observed to diminish with increasing frequency, as observed in Fig.1(e). This is due to Maxwell–Wagner interfacial polarization¹² and Koop's phenomenological theory¹³. At low frequencies, space charge polarization is dominant because of charging at grain boundaries. At higher frequencies, polarization cannot keep pace with the fast-changing field, and a lower dielectric constant was observed. Moreover, the ϵ_r increased with the increase in temperature, indicating the increased dipolar polarization and thermal activation of charge carriers. The loss tangent ($\tan \delta$), depicted in Fig.1(f), decreases with increasing frequency. According to Iwauchi¹⁴, there exists a strong correlation between the conduction mechanism and the dielectric behavior of ferrites¹⁵. Moreover, at higher frequencies, the ϵ_r is relatively constant with very low value, indicating that it can be a potential candidate for high-frequency applications.

CONCLUSIONS

The sol-gel auto-combustion method was used to prepare single-phase cubic spinel $\text{Co}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ nanoparticles. FTIR spectroscopy substantiated metal–oxygen bonding, whereas UV–Vis showed a direct band gap of 1.38 eV in the sample. The magnetization value of 77.62 emu/g was observed at 300K, and increased to 91.8 emu/g at 10K. Dielectric measurements indicated Maxwell–Wagner type interfacial polarization in the nanoparticle sample, and temperature-dependent behavior may be understood based on Koop's phenomenological theory.

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Energy Levels of Polaron in Metal Halide Perovskite Quantum Dots with Parabolic and Gaussian Potentials

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Abstract. This study presents a theoretical investigation of metal halide perovskite quantum dots (MAPbBr₃) with both parabolic and Gaussian confinement potentials. Using a unitary transformation and a variational method based on the Pekar model, the ground- and first-excited-state polaron energies arising from electron–phonon interactions are determined. Transition energies are also evaluated. The results reveal that Gaussian confinement leads to stronger localization and lower energy states. The type of potential has a significant influence on polaron characteristics. This work contributes to the understanding of polarons in perovskite nanostructures for optoelectronic applications.

INTRODUCTION

Organic–inorganic hybrid perovskites (OIHPs), which are part of the metal halide perovskite (MHP) family [1–2], with the formula, CH₃NH₃PbX₃ (MAPbX₃, where X = Br/Cl/I), are widely studied for their applications in solar cells [3], LEDs [4], lasers [5], photodetectors, and magneto-optical data storage [6]. These hybrid crystalline materials, when synthesized as nanostructures like quantum dots (QDs) [7], nanowires [8], and quantum wells [9], exhibit unique properties due to quantum confinement effects, distinguishing them from bulk counterparts [10, 11]. MHP QDs are particularly promising for studying quasiparticles like polarons [12–14], which arise from electron-phonon coupling and significantly influence nanostructure transport properties [15–19].

Recent research on polarons in MHP QDs includes Kim et al. [20], who showed that inter-QD interactions enable large polaron formation with enhanced spatial scattering and longer lifetimes compared to small polarons. Li et al. [21] observed multi-phonon sidebands in the optical absorption characteristics of Fröhlich polarons in metal halide perovskite quantum dots with spherical geometry. Nuber et al. [22] identified a polaron stabilization time constant, while Buizza et al. [23] noted diverse polaronic effects influenced by potential barriers and enhanced lattice relaxation at interfaces. This study investigates strong-coupling polaron energy levels in MAPbBr₃ QDs by applying a variational approach based on the Pekar model to determine the ground- and first-excited-state energies together with the corresponding transition energies under parabolic and Gaussian confinement potentials [24–31], addressing a gap in theoretical studies on this topic

MODEL AND FORMULATION

We consider a system in which an electron moves within a crystalline environment under parabolic and Gaussian confinement potentials and interacts with longitudinal optical (LO) phonons. The resulting electron–phonon system is described by the following Hamiltonian.

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_h^2 r^2 + \lambda \left(V_0 - \frac{1}{2}m\omega_h^2 r^2 - V_0 e^{-\frac{r^2}{2R^2}} \right) + \sum_q \hbar\omega_{LO} a_q^\dagger a_q + \sum_q [V_q a_q \exp(iq \cdot r) + h.c.], \quad (1)$$

If $\lambda = 0$ then the QD is modelled with parabolic potential that is $V(r) = \frac{1}{2}m\omega_h^2 r^2$ and if $\lambda = 1$ then the QD is modelled with Gaussian potential that is $V(r) = V_0(1 - e^{-\frac{r^2}{2R^2}})$. Here $\omega_h^2 = \frac{V_0}{mR^2}$ and $V_q = i \left(\frac{\eta\omega_{LO}}{q} \right) \left(\frac{\eta}{2m\omega_{LO}} \right)^{\frac{1}{4}} \left(\frac{4\pi\alpha}{V} \right)^{\frac{1}{2}}$, V_q is the Fröhlich electron–phonon interaction potential. $\alpha = \left(\frac{e^2}{2m\omega_{LO}} \right) \left(\frac{2m\omega_{LO}}{\eta} \right)^{\frac{1}{2}} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right)$, α is the Fröhlich coupling constant. $\frac{p^2}{2m}$ denotes the kinetic energy of the electron, where m is the electron mass, second term represents the harmonic oscillator potential energy, third term is the confining potential including parabolic and Gaussian

terms. The phonon energy is given by $\sum_q \hbar \omega_{LO} a_q^\dagger a_q$ while the term $\sum_q [V_q a_q \exp(iq \cdot r) + h.c.]$ represents the electron–phonon interaction energy. Here, V_0 denotes the potential depth, r is the position of the electron, and R is the radius of the quantum dot, λ is the switching parameter, ω_h^2 is the harmonic oscillator frequency, $\hbar$ is the reduced plank constant, $h.c$ is the Hermitian conjugate, A unitary transformation is employed.

$$H' = U^{-1} H U \text{ where } U = \exp [\sum_q a_q^\dagger f_q - a_q f_q^*], \text{ and } U^{-1} = \exp [\sum_q f_q^* a_q - f_q a_q^\dagger], \quad (2)$$

here f_q and f_q^* are treated as variational functions. Following the unitary transformation, the Hamiltonian is expressed in a transformed representation.

$$H' = \frac{p^2}{2m} + \frac{1}{2} m \omega_h^2 r^2 + \lambda \left(V_0 - \frac{1}{2} m \omega_h^2 r^2 - V_0 e^{-\frac{r^2}{2R^2}} \right) + \sum_q \hbar \omega_{LO} (a_q^\dagger + f_q^*) (a_q + f_q) + \sum_q [V_q (f_q + a_q) \exp(iq \cdot r) + h.c.], \quad (3)$$

Throughout this paper, we shall use as the energy in *meV*, Quantum dot radius in *nm*. By minimizing expectation value in Lee-Low- Pines transformation we will get the ground state and first excited state energies. To employ variational method choosing the trial wave functions are.

$$|\psi_0\rangle = \pi^{-\frac{3}{4}} \mu_0^{\frac{3}{2}} \exp\left(-\frac{\mu_0^2 r^2}{2}\right), \quad |\psi_1\rangle = \left(\frac{\pi^3}{4}\right)^{-\frac{1}{4}} \mu_1^{\frac{5}{2}} r \cos\theta \exp\left(-\frac{\mu_1^2 r^2}{2}\right), \quad (4)$$

The wave functions ψ_0 and ψ_1 correspond to the ground-state (GS) and first-excited-state (FES) energy levels, respectively. Here, μ_0, μ_1 are the variational parameters. the transition energy between two states is defined as ΔE .

$$\Delta E = E_1 - E_0. \quad (6)$$

Where E_0 and E_1 correspond to the ground-state and first-excited-state energies, respectively.

RESULTS AND DISCUSSION

The theory developed in the previous section is working for any QD system. However, we shall apply our theory to a metal halide perovskite (MAPbBr₃) QD, which has plenty of applications. We have taken the metal halide perovskite materials' phonon energy (15.3meV), coupling constant (1.69), Active mass (0.117 m), and polaron radius (364.01nm).

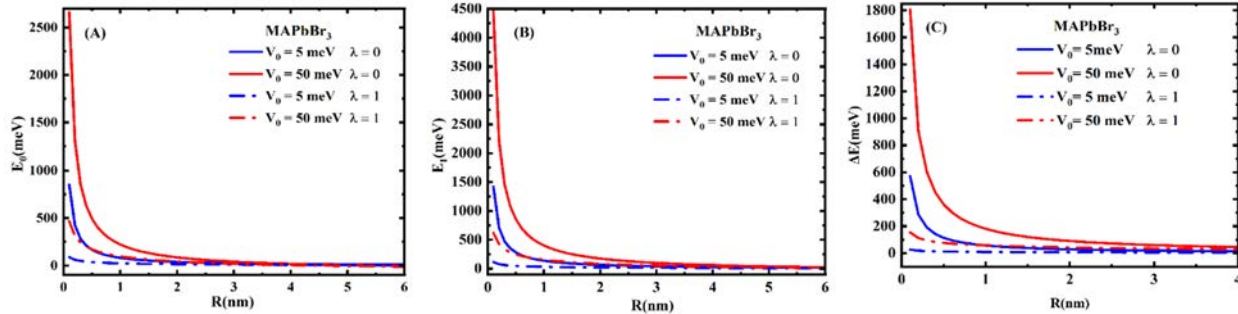


FIGURE 1. (A) The ground state energy(E_0), (B) The first excited state energy(E_1), and (C) The transition energy (ΔE) as function of QD radius.

In Figs.1(A), (B), (C) we show the intermediate coupling polaron ground state (E_0), the first excited state (E_1), and the transition energies (ΔE) variation with quantum dot radius for two distinct confinement potentials: parabolic and Gaussian, respectively. The comparison is made for the same values of potential depths in MHP QD. The results reveal that the energies ($E_0, E_1, \Delta E$) increase due to enhanced confinement. We also observe that the energies ($E_0, E_1, \Delta E$) The energy decreases with increasing quantum dot radius. This behavior can be attributed to the reduction in confinement as the dot size increases, which allows greater spatial freedom for the electron and lowers the

confinement energy. Consequently, the total energy of the system decreases. In contrast, an increase in the confinement potential V_0 or a reduction in the dot radius R leads to stronger confinement and higher energy.

CONCLUSION

In this work, we present a theoretical study of polarons in metal halide perovskite quantum dots. A variational method using a Pekar-type trial wavefunction was employed. Both parabolic and Gaussian confinement potentials were considered. Polaron energy levels were computed for MAPbBr₃ quantum dot. The results reveal that the nature of the confinement potential plays a crucial role in determining the ground-state (GS) and first-excited-state (FES) energies. Specifically, the energy levels increase with the confinement strength V_0 , indicating that stronger confinement raises the system's energy. Conversely, as the quantum dot radius increases, the energies decrease. The Gaussian potential results in higher energy shifts compared to the parabolic potential, due to stronger carrier localization. These results provide insight into polaron behavior in confined perovskite systems.

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Electrochemical Performance of $\text{CH}_5\text{N}_2\text{PbI}_3$: A Potential Electrode for Energy Storage

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Abstract. In the current research on energy storage devices, like supercapacitors, excellent electrode materials are being explored. With the goal of designing electrode material with high specific capacitance, formamidineium lead iodide ($\text{CH}_5\text{N}_2\text{PbI}_3$) hence named as FAPbI₃ has been synthesized. This study involves with the synthesis, structural characterization and investigation of electrochemical performance of formamidineium lead iodide ($\text{CH}_5\text{N}_2\text{PbI}_3$) hence named as FAPbI₃ and highlights its charge storage mechanisms. Electrochemical analysis using cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) in a three-electrode setup revealed excellent specific capacitances of 127 F/g at 5 mV s⁻¹ and 121 F/g at 4 A g⁻¹ respectively. Detail analysis of the experimental results distinguishes the capacitive and diffusive contribution towards the charge storage mechanism.

INTRODUCTION

Efficient energy storage systems are evolving as an urgent need to meet the ever-increasing energy demands. Among them, supercapacitors in particular are attracting unparalleled attention because of their light weight, high power density, rapid charge discharge and extended cyclic ability. [1] Based on the nature of the electrode material and the underlying energy storage mechanism, supercapacitors are generally classified into three main categories: electric double-layer capacitors (EDLCs), pseudocapacitors (PCs), and hybrid capacitors. In EDLC, no charge transfer occurs between the electrode and electrolyte; instead, charge storage arises from the electrostatic accumulation of ions at the electrode-electrolyte interface (non-faradaic process). [2] In pseudo capacitors charge storage arises from reversible faradaic reactions occurring at the electrode-electrolyte interface. Charge storage in hybrid capacitors arises from a combination of both faradaic and non-faradaic processes. Over the years, a wide range of materials have been investigated for their supercapacitive properties; however, the pursuit of new, improved, and more stable electrode materials remains an ongoing challenge. Electrochemical performance studies of the electrode materials are crucial for evaluating stability under bias, redox activity, and ion migration that directly affect device durability and functionality. This study reports on the investigation of the electrochemical performance of a hybrid halide viz. the δ -phase of formamidineium lead iodide ($\text{CH}_5\text{N}_2\text{PbI}_3$) which is a thermodynamically stable phase. The electrochemical performance of FAPbI₃ was investigated using cyclic voltammetry and galvanostatic charge–discharge measurements in a three-electrode system with Na_2SO_4 as the liquid electrolyte. The results provide deeper insight into the underlying charge transport mechanisms.

EXPERIMENTAL

Synthesis of FAPbI₃ Nanoparticles: To synthesize FAPbI₃, Formamidineium acetate was mixed with hydroiodic acid (HI) in stoichiometric ratio followed by continuous stirring for 2 h in an ice bath. Prepared solution was then dried and cleaned with diethyl ether thrice to pull out unreacted acid if any. The resultant mixture was then dried overnight at 60 °C to yield Formamidineium iodide salt ($\text{CH}_5\text{N}_2\text{I}$). Formamidineium iodide and lead iodide (PbI_2) were taken in stoichiometric ratio and dissolved in DMF and stirred for 10 h at 60 °C. The solution was then filtered and dried at 65 °C to obtain the required yellow FAPbI₃.

RESULTS AND DISCUSSIONS

Structural and Morphological Analysis: The X-ray diffraction pattern of as-synthesized FAPbI₃ using $\text{CuK}\alpha$ radiation is shown in Fig. 1a. The XRD pattern is found to be similar as reported in the literature [3] suggesting the

formation of hexagonal δ -FAPbI₃ (yellow polymorph) with P6₃mc space group. The absence of any detectable impurity phase suggests the formation of pure δ -phase. The particle size using Williamson Hall plot (Fig.1a inset) is estimated as ~ 23 nm. The FTIR spectra of FAPbI₃ in transmission mode demonstrate the prominent absorption bands at 3150 cm⁻¹, 3223 cm⁻¹, 1700 cm⁻¹, 1600 cm⁻¹ and 1120 cm⁻¹ which are assigned to C–H stretching, N–H stretching, C=N stretching, N–H bending and scissoring of NH₂ group, respectively.

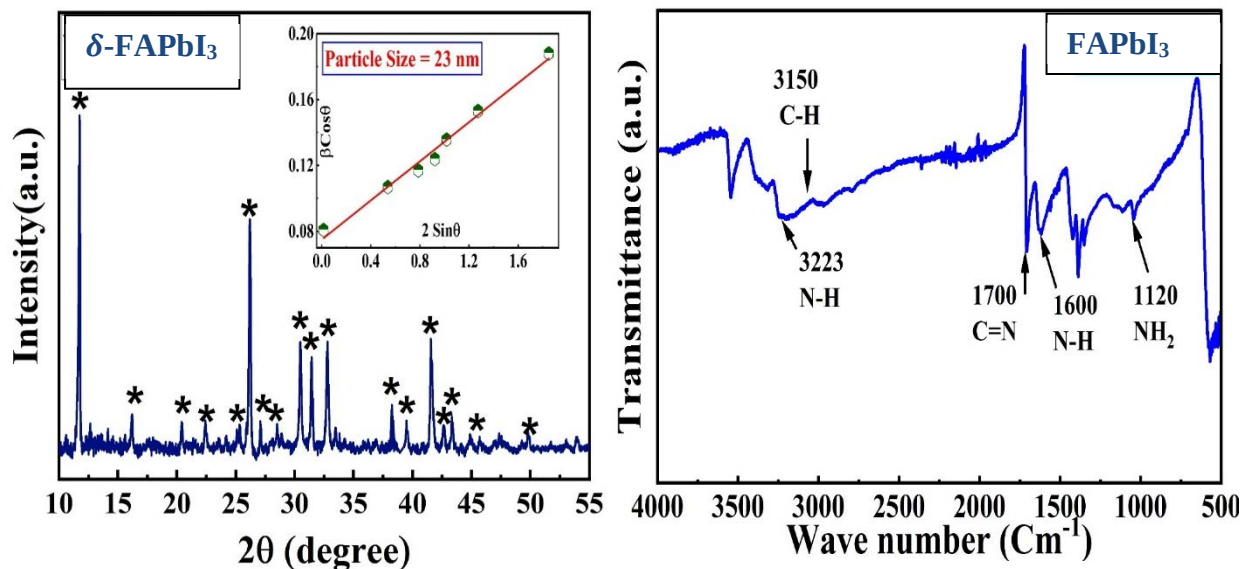


FIGURE 1: (a) XRD, and (b) FTIR images of FAPbI₃. Inset of (a) W-H plot of FAPbI₃

Electrochemical analysis: Electrochemical energy storage property FAPbI₃ using cyclic voltammetry (CV) analysis and Galvano static charging discharging (GCD) in three electrode system within the potential range of -0.2 V to 1.2 V were performed. The quasi-rectangular CV curves scanned at different scan rate as shown in Fig. 2a are attributed to the pseudo capacitance which is responsible for the charge storage at the electrode. The oxidation and reduction curves observed in the CV curves of hybrid halide materials are primarily due to the reversible redox reactions of the halide ions. Variation of the specific capacitances calculated by using this equation is illustrated in Fig. 2 b

$$C_A = \frac{\oint I dV}{m \nu \Delta V} \quad (1)$$

C_A denotes the specific capacitance of the device, $\oint I dV$ represents the integral area of the curve, ν refers to the scan rate and ΔV is the working potential window. The maximum specific capacitance obtained from CV was 127 F/g at 5 mV s⁻¹ scan rate. Gradual decrease of specific capacitance with increasing scan rate is a typical characteristic of pseudo capacitor. GCD measured at different discharging current (I) as shown in Fig. 2c are analyzed by using the relation

$$C_A = \frac{I \Delta t}{m (\Delta V)} \quad (2)$$

where, Δt refers to the discharge time. The specific capacitance (C) obtained from GCD data at different discharge current (I) is shown in Fig. 2d. From GCD, a maximum specific capacitance value of 121 F/g is recorded at 4 A/g. To investigate the charge storage mechanism in FAPbI₃, the power-law relationship $i_p = av^b$ was used, where i_p and v represent peak current and scan rate, respectively. The value of b ($= 0.76$) obtained from the slope of the $\log(i_p)$ vs. $\log(v)$ plot (Fig. 2d) may suggest the dominance of pseudocapacitive behavior of FAPbI₃ over EDLC.

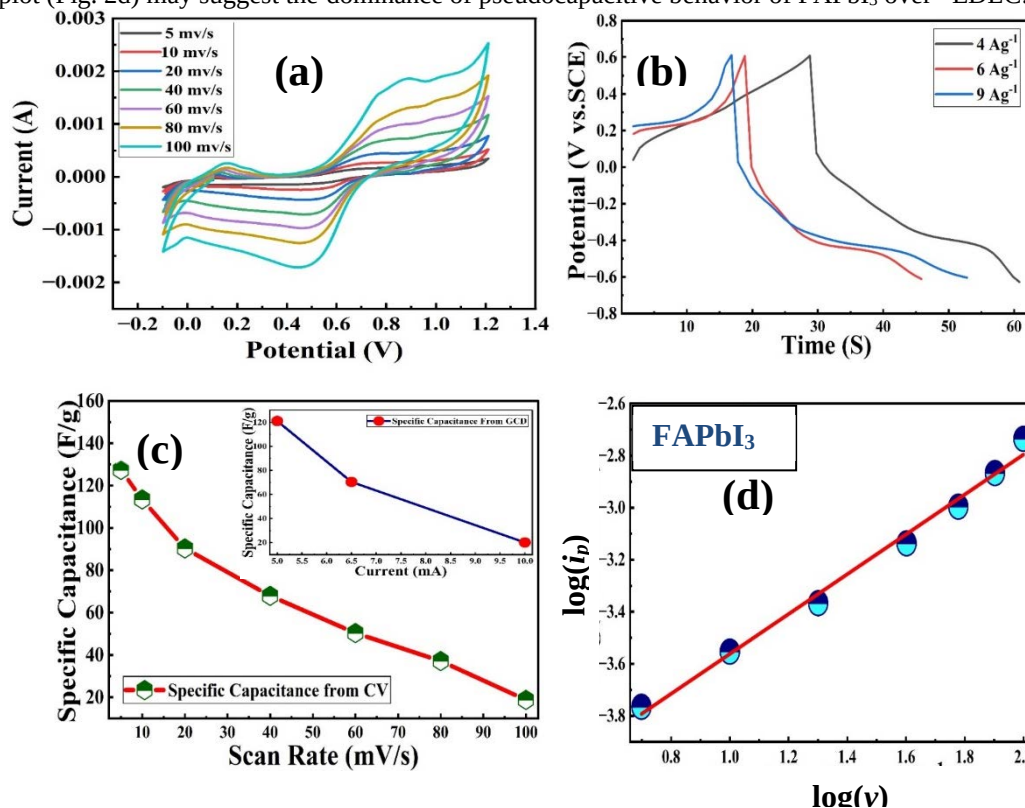


FIGURE 2: (a) CV curves, (b) GCD Curves (c) specific capacitance from CV plot (Inset: from GCD plot) d) $\log(i_p)$ vs $\log(v)$ plot,

CONCLUSION

In this study, FAPbI₃ demonstrated specific capacitance values of 127 F/g (CV) and 121 F/g (GCD) in a three-electrode system using sodium sulphate electrolyte. These values are comparable to or slightly superior to those reported for other hybrid perovskites like MAPbI₃, MAPbI₃ indicating enhanced electrochemical performance. Using power law, we get the slope value is 0.76 which clearly indicate that FAPbI₃ can be used as pseudocapacitive electrode material, making it a promising candidate for future energy storage and electrochemical device applications.

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Synthesis and Characterization of Various Size Gold Nanoparticles for Catalytic Activity in Sealed-off CO₂ Laser

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Abstract. Commercial glass tube sealed off CO₂ laser use gold nanoparticles (Au NPs) coating as catalyst for maintaining constant CO₂ lasing molecules by recombining CO and O₂, which are produced due to dissociation of CO₂ under discharge conditions. In this study, Au NPs of various sizes were synthesized and characterized by UV-Visible spectroscopy. These nanoparticles were subsequently deposited on to silicon substrate via drop casting and thoroughly characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD) to evaluate their morphology and crystallinity. Based on these characterizations, Au NPs with sizes below 30 nm was then deposited onto glass substrate and annealed at 200°C. Characterization of Au NPs deposited on glass substrate revealed that the deposited Au NPs were approximately five times smaller than those used in commercial tubes. A reduction in size is expected to enhance catalytic efficiency and extend the operational lifetime of the laser. Hence, these sub-30 nm Au NPs were subsequently coated onto the inner surface of glass tubes for potential application in sealed-off CO₂ laser.

INTRODUCTION

Sealed off CO₂ lasers are widely used in industrial, medical and scientific applications, but their long-term performance is limited by gradual CO₂ dissociation under discharge, leading to reduced laser output [1-2]. To resolve this issue, various catalytic method have been explored to enhance gas recombination process with in laser cavity. Au NPs have attracted significant interest as potential catalyst for CO oxidation due to their unique surface properties and chemical stability. Catalytic efficiency in CO oxidation is strongly dependent on nanoparticle size, morphology and various literature also reported that small Au NPs exhibit high activity in CO oxidation reaction [3-4]. In this study, colloidal solution of Au NPs with various sizes were synthesized via citrate reduction [5]. The resulting colloidal solutions of Au NPs were characterized optically using UV-visible spectroscopy and then deposited on silicon substrates (Si (100)) via drop cast method. These substrates were then analyzed using SEM and XRD for assessing particle morphology and crystalline structure. Based on these analyses, the colloidal solution of Au NPs with sizes below 30 nm was deposited on glass substrates and then annealed in furnace at 200°C. Au NPs deposited on glass substrate was further characterized for morphology and crystallinity and then coated on inner surface of a glass tube for sealed-off CO₂ laser applications.

EXPERIMENTAL DETAILS

Gold (III) chloride trihydrate (HAuCl₄·3H₂O) and sodium citrate dihydrate (Na₃C₆H₅O₇) were procured from Sigma Aldrich. 0.1 ml of gold solution was dissolved in 25 ml of deionized water and heated to 100°C under constant stirring. For preparation of various sizes of colloidal Au NPs solution, the concentration of citrate was varied while keeping the gold precursor concentration constant. Citrate quantities of 15, 20, 25, 30 and 60 mg were used to prepare five distinct sample labeled from (a) to (e), as shown in Fig. 1(A).

The optical properties of colloidal Au NPs solution were analyzed using an UV-visible spectroscopy (Avantes, Netherlands). Surface morphology of Au NPs deposited on various substrate was examined using a scanning electron microscope (SEM, Carl Zeiss, Germany) and structural analysis was carried out using X-ray diffraction technique (Bruker GmbH Germany). Annealing of the Au NPs deposited on glass substrate and on the inner surface of glass tube was done in muffle furnace (Yamato, Japan). The colloidal solution of Au NPs with sizes below 30 nm was introduced into a glass tube (15 cm length, 5 mm inner diameter) and left to coat on the inner surface over a period of two days.

RESULTS AND DISCUSSIONS

Figure 1(A) shows the colloidal Au NPs solutions and their UV-Visible absorption spectra in Fig. 1(B), exhibiting surface plasmon resonance peaks in the 520–550 nm range. Peak broadening and shoulder formation in samples (a) and (b) indicate irregular nanoparticle morphology due to insufficient citrate concentration and incomplete reduction of Au ions [6]. XRD analysis confirmed the crystalline face-centered cubic (fcc) structure of the Au NPs through their characteristic diffraction peaks [7]. Additionally, a diffraction peak corresponding to the Si substrate was observed at $2\theta = 69.1^\circ$, as shown in Fig. 1(C). The increased peak broadening at higher citrate concentrations indicates a decrease in the size of the Au NPs.

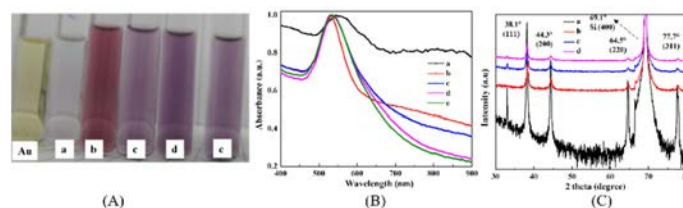


FIGURE 1. (A) Colloidal Au NPs Solution, (B) UV-Visible Absorption Spectra, (C) XRD Pattern of Colloidal Au NPs Solution (a-d) Deposited on Si Substrate.

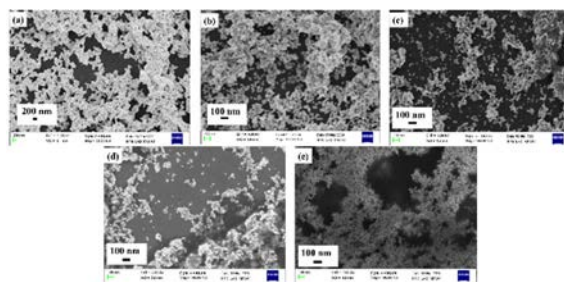


FIGURE 2. (a-e) Shows the SEM Images of Colloidal Au NPs Solution (a-e) Deposited on Silicon Substrate via Drop Cast.

Figure 2 (a-e) shows the SEM images of drop-cast Au NPs on silicon substrates which showed that increasing citrate concentration reduced Au NPs size, consistent with XRD results. Samples (c–e) mainly contained spherical nanoparticles, while samples (a) and (b) showed a mixture of spherical and irregular elongated particles, in agreement with UV-Visible spectroscopy. The particle size ranges are summarized in Table 1.

TABLE 1. Particle Size (nm) Distribution obtained from SEM Measurements for Colloidal Au NPs Solution

Sample	a	b	c	d	e
Size range	150-200	35-50	17-30	15-25	Less than 15

The colloidal Au NPs solution with particle sizes below 30 nm (c) was used for uniform coating, as the other samples contained larger and irregular nanoparticles. Glass substrates were coated by immersing them in the solution for 10 and 120 min, as presented in Fig. 3(a). The air-dried films appeared blue and turned pink after annealing at 200°C as shown in Fig. 3(b) and 3(c) respectively. Glass tubes were also successfully coated on the inner surface by prolonged immersion followed by annealing as shown in Fig. 3(d). XRD analysis of the 10 min deposited sample showed improved crystallinity after annealing as shown in Fig. 3(e).

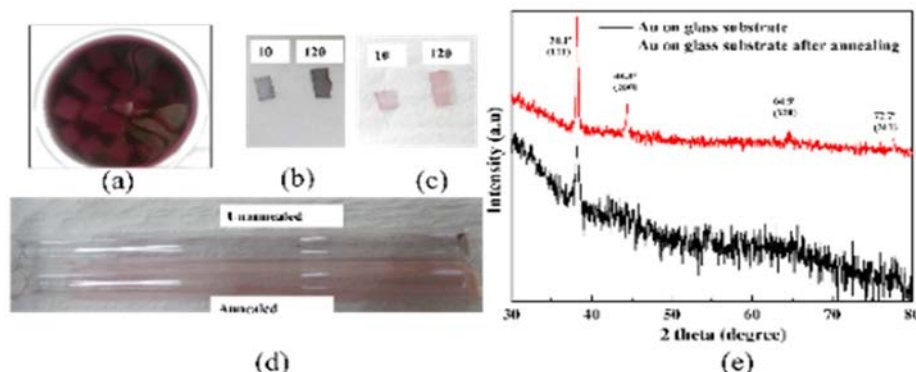


FIGURE 3. (a) Glass Substrate Immersed in Colloidal Au NPs (size below 30 nm) Solution, (b) Air Dried Films for 10- and 120-Minute Deposition, (c) Annealed at 200°C for 10- and 120-Minute Deposition, (d) Coating of Au NPs on Inner Surface of Glass Tube in Air Dried and Annealed Conditions, (e) XRD Pattern of 10 min Deposition of Colloidal Au NPs Solution Deposited on Glass Substrate in Air Dried and Annealed Conditions.

SEM analysis showed that increasing the deposition time from 10 to 120 min increased the density of deposited Au NPs as shown in Fig. 4(a, b). After annealing, the 10 min deposition sample as shown in Fig. 4c it exhibited more uniform and spherical nanoparticles. Size analysis confirmed that the deposited Au nanoparticles were about five times smaller than those used in commercial glass tubes as shown in Fig. 4(d).

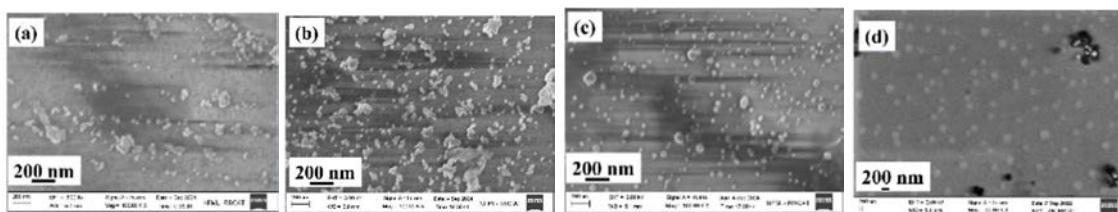


FIGURE 4. SEM of (a) Colloidal Au NPs Solution Deposited on Glass Substrate for 10 min, (b) 120 min, (c) After Annealing for 10 min Deposition, (d) Commercial Glass Tube.

CONCLUSIONS

Colloidal Au NPs of different sizes were synthesized using the citrate reduction method. UV–Visible spectroscopy confirmed size-controlled nanoparticle formation, while SEM and XRD analyses revealed their morphology and crystallinity. Au NPs smaller than 30 nm were successfully deposited on glass substrates and inside glass tubes. These particles are about five times smaller than those used in commercial CO₂ laser tubes, which is expected to improve catalytic activity for sealed-off CO₂ laser applications.

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Nanoengineering Portland Cement Mortars With Borophene Quantum Dots: A Route To Enhanced Strength and Microstructural Optimization

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Abstract. Borophene, a monolayer of boron atoms and the lightest elements Dirac material, has developed as a highly promising two-dimensional (2D) nanomaterial due to its exceptional structural, mechanical and electrical properties. Among its derivatives, borophene quantum dots (BQDs) have gained attention as a novel zero-dimensional material with significant potential in advanced composite applications. This study investigates the impact of BQDs on the mechanical and microstructural properties of cement mortar composites. Results demonstrate a notable enhancement in compressive strength at 28 days with the incorporation of BQDs. Microstructural analysis further reveals the development of a denser cement matrix, attributed to the presence of BQDs. These findings suggest that BQDs are a promising nanomaterial for reinforcing cementitious systems, offering improved performance and durability.

INTRODUCTION

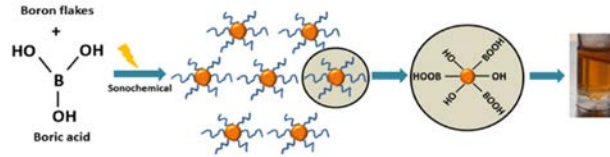
Ordinary Portland Cement (OPC) is a fundamental construction material used worldwide. However, its inherent limitations such as low tensile strength, brittleness, and heat generation during hydration-restrict its performance in structural applications. These deficiencies are largely due to flaws within the cement matrix, including microcracks, internal voids, and weak interfacial zones. To overcome these limitations, conventional reinforcements like steel fibers have been employed. More recently, nanotechnology has emerged as a transformative approach for modifying the properties of cement-based systems[1].

The integration of nanomaterials including nanoparticles, nanorods, nanotubes, and various nano-oxides has shown the ability to accelerate hydration kinetics, densify the matrix, and improve durability. However, challenges remain, particularly in achieving uniform dispersion and maintaining workability in fresh mixes.

Among nanomaterials, carbon-based nanostructures like carbon quantum dots (CQDs), carbon nanotubes (CNTs), graphene oxide (GO), and graphene nanosheets have been widely studied. These materials improve strength, durability, and microcrack control in cementitious composites. However, dispersion issues and high cost limit their scalability. In contrast, boron-based nanomaterials, especially borophene a 2D allotrope of boron—have emerged as low-cost, high-performance alternatives due to their electronic versatility, chemical stability, and unique structural properties[2].

Over the past decade, low-dimensional boron nanostructures such as nanowires, clusters, nanosheets, and borophene quantum dots (BQDs) have been investigated for their mechanical, catalytic, and electronic applications. BQDs, in particular, exhibit outstanding dispersion, surface activity, and electron mobility, making them ideal candidates for nano-reinforcement in cement matrices [3].

To date, no comprehensive studies have examined the role of BQDs in cement systems. This work presents the first investigation of BQDs incorporated into cement mortar composites, focusing on their effects on compressive strength and microstructural refinement. The findings demonstrate that BQDs enhance hydration kinetics, reduce microcracking, and improve the mechanical integrity of cement mortars.



SCHEME 1. Schematic representation synthesis of BQDs by sonochemical assisted method

EXPERIMENTAL SECTION

Materials

Boric acid, boron powder (99.99%), isopropyl alcohol (IPA), and Ordinary Portland Cement (OPC) were used as received. All chemicals were of analytical grade and purchased from Sigma-Aldrich. Double-distilled water was used throughout the study.

Synthesis of Borophene Quantum Dots (BQDs)

BQDs were synthesized via a sonochemical-assisted method (Scheme 1). Boron powder and boric acid were dispersed in IPA and ultrasonicated, followed by treatment with hydrogen peroxide to promote oxidation and exfoliation. The suspension was probe-sonicated at 5 °C, purified by centrifugation and dialysis, and dried at 70 °C to obtain BQDs powder [4].

Preparation of BQD-Reinforced Cement Composites (BQDRC)

BQDRC samples containing 0.005–0.030 wt% BQDs were prepared with a water-to-cement ratio of 0.45 and a sand-to-cement ratio of 3:1. The BQD suspension was mixed with cement using a mechanical mixer at 2000 rpm for 5 min. The mortar was cast into 70.5 × 70.5 × 70.5 mm molds, vibrated to remove air voids, and cured in water for 7, 14, and 28 days. Before testing, the specimens were air-dried for 12 h.

RESULTS AND DISCUSSIONS

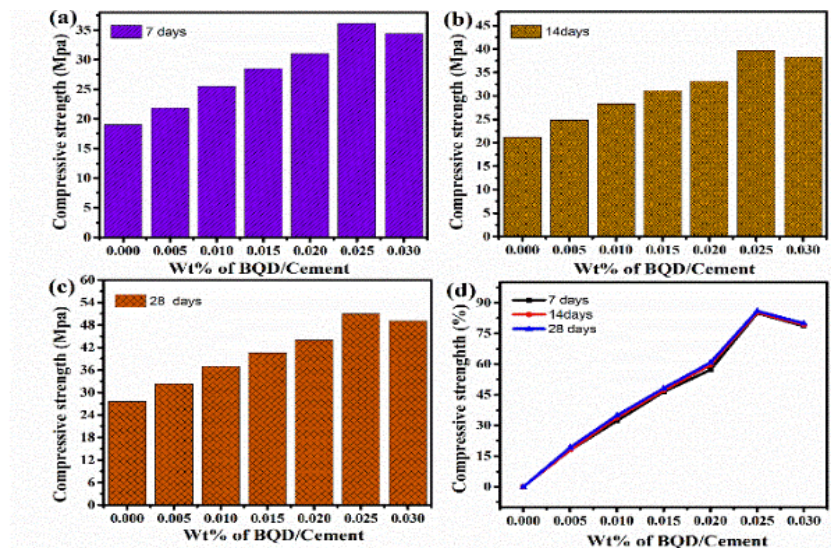


FIGURE 1. Compressive strength results BQDs/cement mortar (a) 7-Days (b) 14-Days (c) 28-Days of curing period and (d) standard deviation of compressive strength results measured at various ages for different wt% of BQDs.

Compressive strength was evaluated after 7, 14, and 28 days of curing (Fig. 1). Mortars containing 0.025 wt% BQDs exhibited the highest compressive strength an enhancement of 88% (7 days), 87% (14 days), and 86% (28 days), compared to control samples. Further addition (0.030 wt%) resulted in a decline, likely due to agglomeration [4]. This strength gain is attributed to the **seeding effect** of BQDs on hydration products (e.g., C–S–H, portlandite, ettringite), which form a dense matrix. Their hydrophilicity and high surface area promote nucleation and pore refinement.

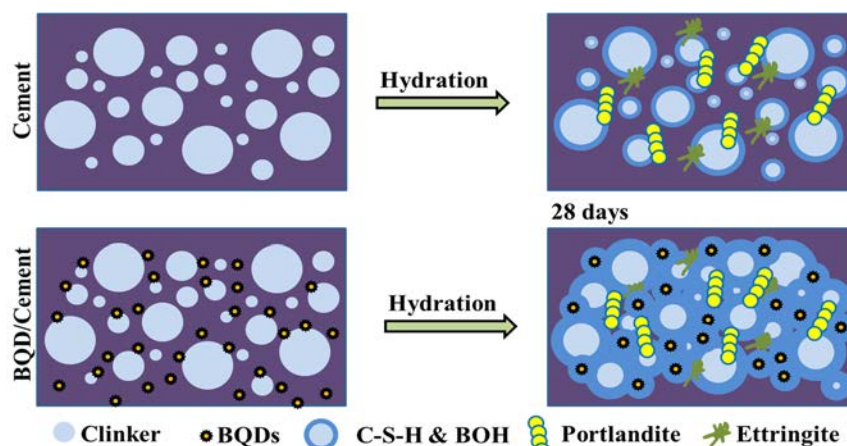


FIGURE 2. Mechanism of effect of BQDs on cement hydration.

As illustrated in Fig. 2, BQDs serve as active nucleation centers and nano-fillers, encouraging simultaneous growth of hydration products on BQDs and cement particles. This improves interfacial bonding, reduces permeability, and leads to microstructural densification. The synergy of chemical activity and filler effect explains the superior mechanical performance [5].

CONCLUSIONS

The enhancement in mechanical strength of borophene quantum dot-reinforced cement nanocomposites (BQDRC) can be attributed to a synergistic mechanism involving nucleation promotion, pore refinement, and microstructural densification. During cement hydration in the presence of BQDs, key hydration products—such as calcium silicate hydrate (C–S–H), boron hydroxide (B–OH), portlandite, and ettringite—are formed. BQDs serve as effective nucleation sites due to their high surface area and hydrophilic functional groups, facilitating the growth of C–S–H on both their surfaces and adjacent cement particles. This interaction accelerates hydration and promotes a more uniform microstructure.

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Hot-injection Based Synthesis and Characterization of Lead-free Cu-Ag-Bi-I Pnictohalide Nanocrystals (NCs)

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Abstract: Solution-processed lead halide perovskites have garnered attention in recent years. Nowadays, research is being conducted to find a suitable alternative for lead, which is poisonous, unstable, and harmful to the environment. Due to their low toxicity and diverse structural dimensions, Pb-free perovskite-inspired materials (PIM) like copper or silver pnictohalides ($A_x B_y X_{x+3y}$) like $CuBiI_4$, Cu_2BiI_5 , Cu_2AgBiI_6 , and Ag_3BiI_6 , are becoming popular for optoelectronic and photocatalytic applications. Hot Injection synthesis of Cu-Ag-Bi-I nanocrystals (CABI-NCs) is described here. As synthesised, the CABI-NCs crystal structure and characteristics were examined. The trigonal structure of CABI-NCs, whose space group $R\bar{3}m$ was disclosed by X-ray diffraction. Raman vibrational spectroscopy is also used for CABI-NCs. A detailed investigation of CABI-NCs' composition and chemical states is also provided. According to UV-Vis spectroscopy, the CABI perovskite NCs have a direct band gap. The study on CABI-NCs discloses potential as a lead-replacement material for various Optoelectronics, RRAM (Resistive random access memory), photodetectors, and solar energy harvesting applications.

INTRODUCTION

In recent decades, the optoelectronic area has transformed the world. Lead perovskite hybrids are created for optoelectronic applications due to their unique characteristics, featuring Vis-NIR optical absorbance coefficients, configurable band gaps, long carrier recombination lifetimes, strong electron/hole mobilities, and low effective masses¹. The extreme toxicity and instability of lead halide perovskite materials in ambient air, heat, humidity, and light limit their commercialization². Pb-free perovskite-inspired materials (PIM) like copper or silver pnictohalides ($A_x B_y X_{x+3y}$), where ($A=Cu^+$, Ag^+ ; $B=Bi^{3+}$, Sb^{3+} ; $X=I^-$), such as $CuBiI_4$, Cu_2AgBiI_6 , Cu_2BiI_5 , and Ag_3BiI_6 , are gaining popularity for optoelectronic and photocatalytic applications due to their low toxicity and diverse structural dimensions³. Research on the CABI system, namely Cu_2AgBiI_6 , has shown an adjustable direct band gap and a very good absorption coefficient ($>1 \times 10^5 \text{ cm}^{-1}$) similar to Liquid halide perovskites (LHPs), addressing phase stability concerns⁴. We present the colloidal Hot Injection-based synthesis of lead-free CABI-NCs. XRD, Raman, TEM, SEM, EDS, FESEM, XPS, and UV-vis-NIR spectroscopy were used to analyze the structure, surface morphology, chemical state, and optical properties of synthesized CABI-NCs. The material synthesis, composition, structure, and optoelectronic properties are detailed in this paper. We found a straight bandgap of 2.89 for CABI-NCs. This study highlights the potential of lead-free perovskite CABI-NCs for future optoelectronic device production and applications.

EXPERIMENTAL SECTION

The following chemicals were bought from Sigma Aldrich and were used without further purification; copper (I) acetate ($CuOAc$, 99%), silver (I) acetate ($AgOAc$, 99.99%), bismuth (III) acetate ($Bi(OAc)_3$, 99.99%), oleic acid (OA, technical grade, 90%), oleylamine (OAm, technical grade, 70%), 1-octadecene (ODE, technical grade, 90%), iodotrimethylsilane (TMS-I, $\geq 97\%$), ethyl acetate ($\geq 99.5\%$), and hexane ($\geq 95\%$). Colloidal Cu_2AgBiI_6 nanocrystals were produced using a modified hot injection technique as described earlier⁵.

RESULTS AND DISCUSSIONS

The X-ray diffraction (XRD) pattern (Figure 1a) of the as-synthesized CABI-NCs shows that they have a trigonal structure, which is expected based on the known pattern of Cu_2BiI_5 single and bulk crystals⁶. This suggests that the CABI-NCs have the characteristics of a defect spinel-type $\text{A}_2\text{B}_1\text{X}_5$ material with Ag^+ partially filling the A site. The adjacent characteristic peaks at $2\theta = 42.1^\circ$ and 41.7° in the reference pattern of Cu_2BiI_5 SCs converge into a broader peak at $2\theta = 42.0^\circ$ in the pattern of CABI-NCs. This phenomenon has also been observed in Cu_2BiI_5 bulk crystals, likely due to reduced crystallinity in both nanocrystal and bulk forms relative to their single-crystal counterparts. The XRD pattern of CABI-NCs shows a distinct peak at 25.4° , which is thought to be caused by BiI_3 impurities that have broken down or stayed the same⁶. Furthermore, there is no significant alteration in the Bragg angles of CABI-NCs relative to the reference pattern (i.e., Cu_2BiI_5 single crystals), indicating that the incorporation of Ag^+ with Cu^+ at the A site has a minimal effect on the lattice constants, attributed to the comparable ionic radii of Ag^+ (0.6 Å) and Cu^+ (0.5 Å).

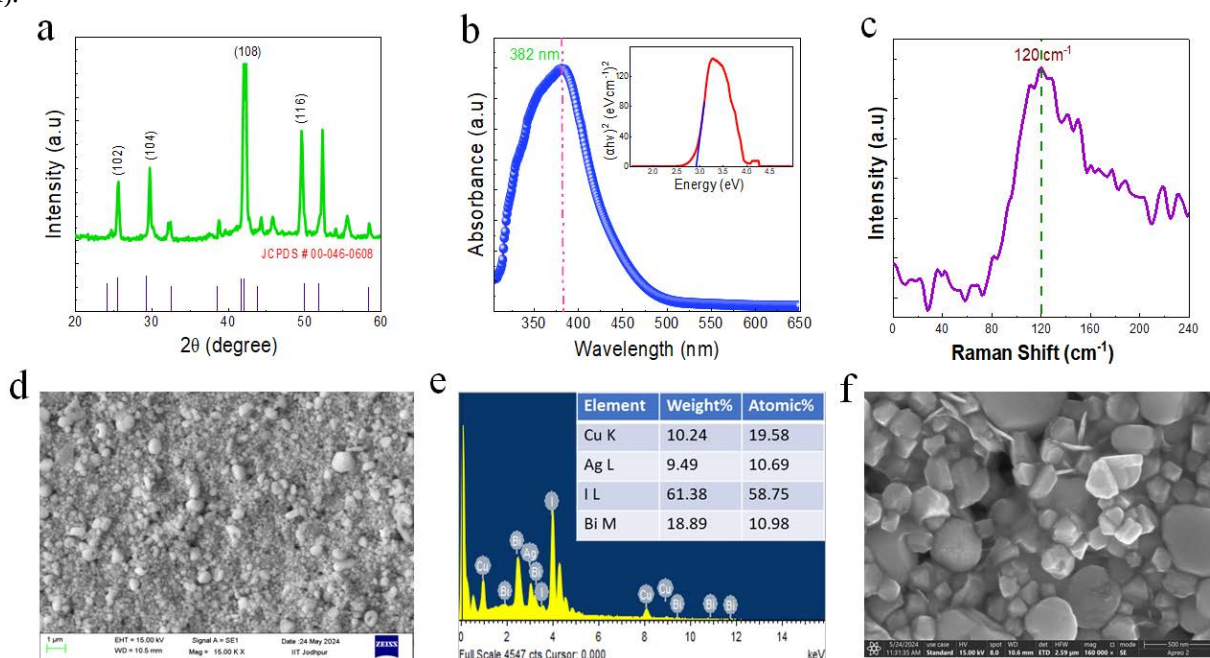


FIGURE 1. (a) XRD pattern of synthesized CABI-NCs. (b) UV-Vis absorption spectroscopy, with an absorbance peak at 382 nm. The inset shows Tauc's plot for material band gap calculation. (c) Raman spectra of as-prepared CABI-NCs thin films. (d) SEM image of CABI-NCs film on a glass substrate. (e) Measurement of the film's EDX to determine its atomic composition. (f) FESEM image of CABI-NCs film on a glass substrate.

We conducted a detailed examination of the optical properties, the bandgap value of a material is a crucial determinant that affects both the efficiency and applicability in optoelectronic and solar applications. A distinct peak was observed in UV-Vis spectroscopy (Figure 1b) for the NCs suspended in Hexane, indicating that the NCs are monodispersed. The NCs exhibited absorption maxima at 382 nm. We evaluated the band gap of the NCs using the Kubelka-Munk function. We utilized the subsequent equation: $(\alpha h\nu)^2 = (h\nu) + E_g$ (1), where E_g , ν , h , and α are the bandgap of the material, frequency of wavelength, Planck's constant, and absorption coefficient, respectively. The Tauc analysis of the absorption spectra (Inset of Figure 1b) reveals a direct band gap for CABI-NCs. The determined band gap of CABI-NCs has the value 2.89 eV. The phases derived from the vibrational modes in the CABI-NCs thin films were identified and validated using their corresponding Raman spectra. Figure 1c illustrates the Raman spectra of the CABI thin films. Five prominent peaks are identified in the Raman spectra with their wavenumbers of 42, 81, 120, 141, and 150 cm^{-1} . The peak at 120 cm^{-1} is the most significant. The Raman peak at 150 cm^{-1} may arise from the second-order Raman line of BiI_3 ⁷. The morphological analysis of the sample was performed utilizing SEM and FESEM. Figure 1(d) illustrates the surface morphology of the CABI-NCs film deposited on a glass substrate via drop-casting, as observed using a SEM, with a scale bar of 1 μm . Using energy-dispersive X-ray spectroscopy (EDX), the film's atomic composition was analyzed. The atomic percentages of Cu, Ag, Bi, and I are 19.58%, 10.69%, 10.98%, and 58.75%, respectively (Figure 1e). Figure 1f illustrates the morphology of the CABI-NCs film, which was analyzed using FESEM in secondary electron mode at an acceleration voltage of 15 kV and with a scale bar of 500 nm. The SAED (Selected Area Electron Diffraction) pattern (Figure 2a) exhibits bright spots corresponding to several planes (102, 104, 108, etc.), signifying the development of a highly crystalline material,

which is compatible with our XRD pattern. The TEM image in Figure 2(b) indicates that the CABI-NCs films exhibit a prism-like morphology with an average diameter of 15.6 nm (inset shows the particle size distribution).

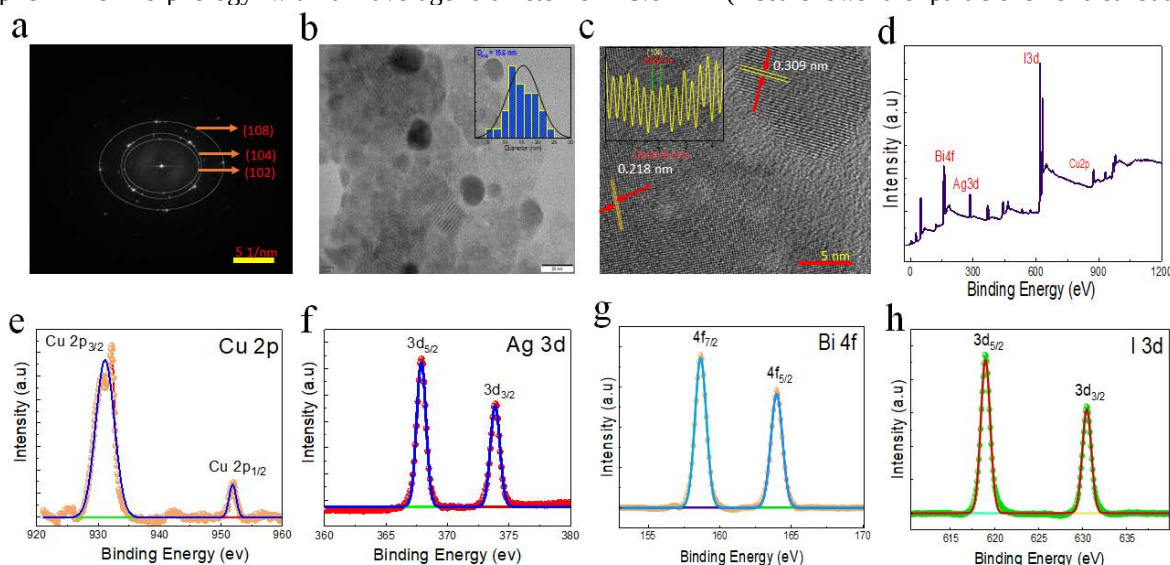


FIGURE 2. (a) SAED pattern of CABI-NCs. (b) The TEM image shows that the CABI-NCs (c) HRTEM image of a CABI-NCs with clearly visible lattice fringes, and the inset shows the line profile of the HRTEM image. (d) The full XPS spectra of CABI-NCs range from 0 to 1200 eV. The intensity vs. binding energy shows the XPS peaks for (e) Cu 2p, (f) Ag 3d, (g) Bi 4f, and (h) I 3d orbitals.

The HRTEM pictures of the materials have been acquired, revealing crystal fringes as depicted in Figure 2c. The interlayer distance was quantified utilizing ImageJ software. The interlayer distances are 0.309 nm for the (104) crystal plane and 0.218 nm for the (102) crystal plane. The line scan of 15 crystal planes of (104) is shown in the inset of Figure 2c, where the total distance is 4.45 nm, and the average interplanar spacing is 0.309 nm. To elucidate the surface chemistry of CABI-NCs, we performed XPS (X-ray photoelectron spectroscopy) experiments, as depicted in Figure 2(d-h). The XPS spectra demonstrate the presence of all components in the CABI-NCs. Figure 2(d) illustrates the complete spectrum of binding energy, ranging from 0 eV to 1200 eV, with peaks for all elements. The XPS spectra were calibrated using the carbon peak at 284.80 eV. The maxima of the Cu 2p orbital occur at binding energies of 931.12 eV and 952 eV, corresponding to $2p_{3/2}$ and $2p_{1/2}$, respectively (Figure 2e). Correspondingly, the orbital peaks for Ag $3d_{5/2}$, $3d_{3/2}$, Bi $4f_{7/2}$, $4f_{5/2}$, I $3d_{5/2}$, and $3d_{3/2}$ are observed at 367.88 eV, 373.88 eV, 158.88 eV, 164 eV, 619.1 eV, and 630.5 eV, respectively (Figure 2f, g, and h).

ACKNOWLEDGEMENTS

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ZnS-Bi₂O₃ Nanocomposite: An Efficient Material For Environmental Remediation

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Abstract. ZnS-Bi₂O₃ nanocomposite was successfully synthesized using an ultrasound-assisted wet chemical method, aiming to explore its potential for environmental remediation. Detailed insights into the phase structure and molecular interactions of the composite were obtained using X-ray diffraction (XRD) and FTIR spectroscopy. XRD findings evidenced the formation of a heterostructured nanocomposite with good crystallinity revealing the co-existence of ZnS and Bi₂O₃ phases without any detectable impurity. FESEM analysis indicates a heterogeneous morphology, where ZnS appears as fine particles while Bi₂O₃ is distributed in a rod-like form across the composite. Vibrational properties involving Zn-S and Bi-O bonding features were verified from FTIR study. The degradation of methylene blue (MB) under UV-visible light was used to evaluate the photocatalytic capability of the material. UV-Vis absorption studies of the dye solutions revealed significant reduction in absorbance, indicating efficient degradation of 84.01%. The degradation process was governed by pseudo-first-order kinetics, with the improved catalytic activity resulting from the combined effect of ZnS and Bi₂O₃ that enhances charge separation and surface active centers. These findings demonstrate that ZnS-Bi₂O₃ nanocomposite is a promising material for wastewater treatment applications involving organic dye pollutants.

INTRODUCTION

The rapid expansion of industrial activities has led to the discharge of hazardous organic pollutants like dyes into aquatic ecosystems [1]. These dyes are highly toxic, non-biodegradable, and pose serious environmental and health risks even at low concentrations [1]. A major limitation of traditional wastewater treatment lies in its inability to remove these enduring pollutants. Among various advanced treatment strategies, semiconductor-based photocatalysis has emerged as a sustainable and cost-effective approach for degrading organic dyes under light irradiation [2]. However, the inability to efficiently absorb light, coupled with rapid recombination of charge carriers, constrains the functionality of single-component photocatalysts. To overcome these challenges, binary nanocomposites combining two semiconductors have shown great promise [2]. Such systems can form heterojunctions that facilitate efficient charge carrier separation and broaden the light absorption range, significantly enhancing photocatalytic activity. ZnS, known for its strong oxidation ability and stability, suffers from poor visible-light absorption [3]. In contrast, Bi₂O₃ is active under visible light but has limited redox potential [4]. Their combination in a nanocomposite structure provides effective solution to the above challenges offering improved performance through synergistic interaction. The development of such hybrid materials holds immense potential for practical applications in environmental remediation, especially in the degradation of persistent organic dyes in wastewater. The present work focuses the preparation and environmental remediation application of ZnS-Bi₂O₃ nanocomposites.

EXPERIMENTAL

A precursor solution was prepared using AR-grade zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O), bismuth(III) nitrate pentahydrate (Bi(NO₃)₃·5H₂O), thiourea (CS(NH₂)₂), and ammonia (NH₃). First, 0.5 M Bi(NO₃)₃·5H₂O was dissolved in 20 mL of double-distilled water (DDW) and stirred for 15 min at room temperature (28 °C) to form solution A. Separately, 0.5 M each of zinc acetate dihydrate and thiourea were dissolved in 20 mL DDW to form solution B. Ammonia (25%) was added dropwise to both solutions under constant stirring to adjust pH. Solutions A and B were then combined and ultrasonicated (VC-375, Sonic & Materials Inc.) for 60 min. The resulting grey-white precipitate was collected via centrifugation and washed with acetone and distilled water.

RESULTS AND DISCUSSION

The synthesized ZnS-Bi₂O₃ nanocomposite was characterized by XRD to determine its crystal structure and phase composition. The diffraction pattern (Fig.1a) of the composite demonstrated the peaks corresponding to ZnS at 2θ values of approximately 28.9°, 33.1°, 48.2°, and 56.3° linked with (111), (200), (220), and (311) planes respectively. These are characteristic of the cubic zinc blende structure (JCPDS card no. 005-0566) [3]. The monoclinic α -Bi₂O₃ component present in the binary nanocomposite was verified by the appearance of major diffraction peaks at 2θ values around 25.7°, 26.8°, 27.7°, 33.9°, 37.2°, and 53.9°, indexed to the (002), (111), (120), (200), (130), and (231) planes (File No. 00-041-1449, JCPDS) [4]. So, the nanocomposite sample shows all the major peaks from both ZnS and Bi₂O₃ phases indicating its successful formation without any structural degradation and impurity phases. The sharpness and intensity of the peaks suggest good crystallinity. Using the Scherrer formula, the crystallite size was estimated to be around 35 nm, falling within the nanometer range. The FESEM image (Fig.1b) of the ZnS-Bi₂O₃ nanocomposite reveals two distinct morphological features, indicating successful composite formation. Rod-like structures observed throughout the image are attributed to Bi₂O₃, while the surrounding spherical and granular nanoparticles are associated with ZnS. The Bi₂O₃ rods are uniformly distributed and embedded within a dense network of ZnS particles, ensuring close interfacial contact. The FTIR profile (Fig. 1c) indicates the existence of hydroxyl-related species through a broad O–H stretching band around 3400 cm⁻¹ [3, 4]. Peaks positioned near 1380 cm⁻¹ and 1630 cm⁻¹ are attributed to NO₃⁻ and water bending vibrations, respectively. Evidence of Bi–O and Zn–S interactions is provided by the metal–oxygen and metal–sulfur stretching bands observed in the 500–700 cm⁻¹ range [3, 4]. The XRD and FTIR analyses collectively confirm the successful formation of the ZnS–Bi₂O₃ nanocomposite, with well-defined crystalline phases and the presence of characteristic functional bonds.

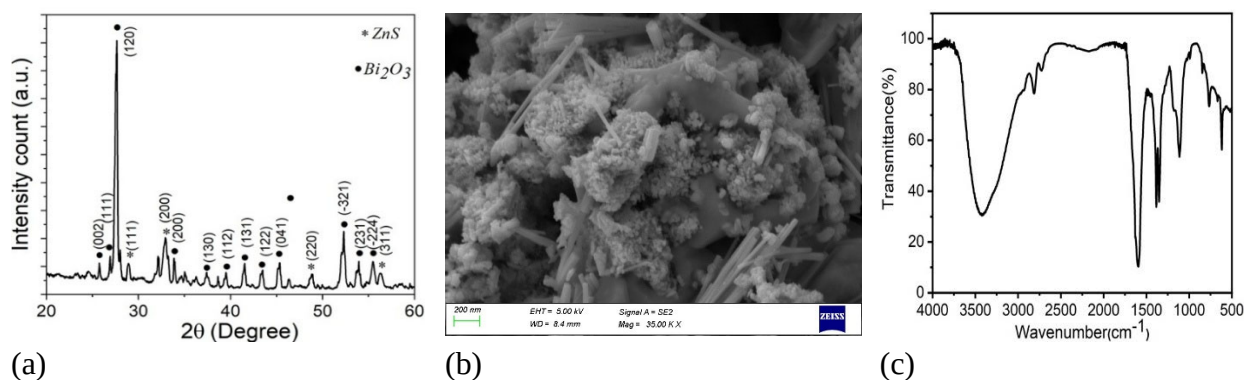


FIGURE 1. (a) XRD pattern, (b) FESEM image, and (c) FTIR spectrum of ZnS-Bi₂O₃ nanocomposite.

To study photocatalytic efficiency, MB degradation was carried out in the presence of the ZnS–Bi₂O₃ nanocomposite under UV–visible light. UV–Vis spectral analysis (Fig. 2a) revealed characteristic peaks at 290 nm and 663 nm [5], which steadily decreased over time, demonstrating effective photocatalytic activity [4, 5]. A steady decline in absorbance signifies the degradation of the chromophoric groups in MB, highlighting its structural breakdown. This also demonstrates that sustained light exposure promotes the mineralization of the dye with the aid of the photocatalyst. To evaluate the effectiveness of the composite material, control experiments were performed using pristine ZnS and pristine Bi₂O₃ under identical conditions. After 180 minutes of irradiation, pristine ZnS and Bi₂O₃ showed degradation efficiencies of approximately 79% and 81% respectively. But, ZnS–Bi₂O₃ nanocomposite demonstrated significantly enhanced photocatalytic activity, achieving approximately 84.01% degradation of MB within the same time frame. A synergistic interplay between ZnS and Bi₂O₃ is responsible for the enhanced efficiency, as it enables superior light absorption, minimizes electron-hole recombination, and promotes the formation of reactive species [1, 3, 4]. In such a heterostructure, photogenerated electrons and holes are spatially separated across the interface of the two semiconductors, thereby suppressing their recombination. ZnS having a 3.6 eV wide band gap, is active mainly under UV light and possesses strong oxidation ability [3]. However, its practical application is limited by its poor response to visible light and high recombination rate. Bi₂O₃, on the other hand, has a smaller band gap (~2.8 eV) and can absorb visible light but suffers from relatively low stability and redox potential [4]. The combination of the two materials in a nanocomposite allows for broader spectral absorption and more efficient utilization of incident light.

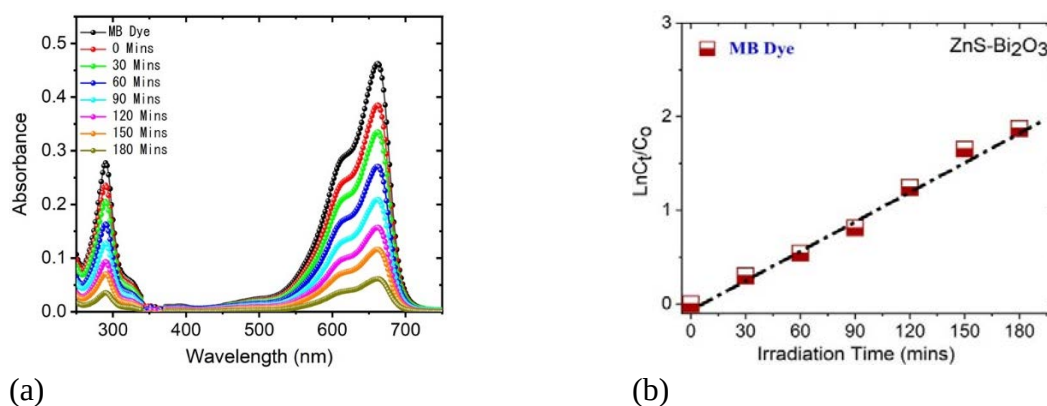


FIGURE 2. (a) Optical absorbance spectra of MB dye, (b) chemical kinetics plot for photodegradation.

To quantitatively analyze the degradation process, pseudo-first-order reaction kinetics were applied as given below:

$$\ln(C_0/C) = kt$$

In this context, C_0 represents the initial dye concentration, while C denotes its concentration at a given time t , and k corresponds to the rate constant. The linear dependence of $\ln(C_0/C)$ on time verifies that the reaction obeys pseudo-first-order kinetics. The calculated rate constant for MB degradation were found to be 0.0212 min^{-1} for the composite. The above result confirms that the ZnS–Bi₂O₃ nanocomposite exhibits superior photocatalytic properties compared to the individual components, making it a highly efficient material for environmental remediation, particularly in wastewater treatment involving organic dye pollutants [6-8].

CONCLUSION

The present study demonstrated the successful synthesis of ZnS-Bi₂O₃ nanocomposite via an ultrasound-assisted wet chemical method for potential environmental remediation applications. The nanocomposite was found to exhibit a crystalline structure, as evidenced by XRD measurements, indicating the coexistence of both ZnS and Bi₂O₃ phases without any impurity peaks, suggesting successful formation of the heterostructure. FTIR spectroscopy further supported the structural integrity by identifying characteristic vibrational bands corresponding to Zn–S and Bi–O bonds, confirming the presence of both constituents. Evaluation of the photocatalytic behaviour of the nanocomposite was carried out via MB dye degradation under UV–visible light. The composite exhibited superior degradation efficiency owing to enhanced charge separation and extended light absorption resulting from the combined effect of ZnS and Bi₂O₃. The study showed a significant decrease in dye concentration over time, showing the dye degradation process. Analysis of the reaction kinetics indicated that the degradation process obeys pseudo-first-order behaviour. The presence of a ZnS-Bi₂O₃ heterostructure enables enhanced interfacial charge transfer, leading to better photocatalytic performance. These findings confirm that ZnS-Bi₂O₃ is an efficient photocatalyst for environmental remediation.

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Effect Of Reducing Regents On the Properties Of Hydrothermally Synthesized ZnTe Nanomaterials

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Abstract. Zinc telluride (ZnTe) nanomaterials have been widely used in optoelectronics, sensors and various device applications due to its direct bandgap and high electron mobility. Here in we have investigated the influence of reducing agents, hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) and sodium borohydride (NaBH_4), on ZnTe nanomaterials by the hydrothermal technique. The nanomaterials were thoroughly characterized using UV-Visible spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The results reveal that the choice of reducing agent significantly affects the crystallite size, morphology, optical bandgap, and surface chemistry of ZnTe nanomaterials. Hydrazine hydrate promotes the formation of smaller, spherical nanoparticles with a bandgap of ~ 2.25 eV, while sodium borohydride yields larger, rod-like structures with a slightly reduced bandgap of ~ 2.15 eV. XRD confirms a cubic zincblende structure for both, with varying degrees of crystallinity. SEM and EDS reveals morphological differences and elemental purity. These findings underscore the role of reducing agents in tailoring ZnTe nanomaterials for specific applications, offering insights into optimizing synthesis protocols for enhanced optoelectronic properties.

INTRODUCTION

Zinc telluride (ZnTe), a II-VI semiconductor, is a promising material for applications in solar cells, light-emitting diodes, and photodetectors due to its direct bandgap (~ 2.26 eV) and high optical absorption coefficient. The properties of ZnTe nanomaterials are highly dependent on their size, morphology, and surface chemistry, which can be tuned through synthesis methods and processing conditions [1]. Hydrothermal synthesis is a versatile, eco-friendly, and scalable method for producing nanomaterials with controlled properties. The use of reducing agents during synthesis can significantly influence the nucleation and growth mechanisms, thereby affecting the structural and optical properties of the resulting nanomaterials. Hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) and sodium borohydride (NaBH_4) are commonly used as a reducing agent in nanomaterial synthesis due to their ability to control particle size and morphology. Hydrazine hydrate is known for its strong reducing capabilities and ability to stabilize nanoparticle surfaces, while sodium borohydride provides a rapid reduction process, often leading to different growth kinetics [2]. The comparative effects of these reducing agents on ZnTe nanomaterials synthesized via the hydrothermal method remain underexplored. This study aims to show the impact of hydrazine hydrate and sodium borohydride on the various properties of the hydrothermally synthesized ZnTe nanomaterials.

EXPERIMENTAL METHOD

ZnTe nanoparticles were synthesized via a hydrothermal method with precursor, 0.02 M ZnSO_4 and 0.02 mM TeO_2 powder dissolved in 80 mL deionized water under continuous magnetic stirring for 30 min at room temperature. For the hydrazine hydrate-assisted synthesis (ZnTe-HH), 1.0 M $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added dropwise to the solution, maintaining a pH of 9–10. For the sodium borohydride-assisted synthesis (ZnTe-NB), 0.5 M NaBH_4 was added instead. The resulting mixtures were transferred to a 120 mL tight Teflon-lined stainless-steel autoclave, sealed, and heated at 140°C for 24 hrs. After cooling to room temperature, the precipitates were collected, washed with ethanol and deionized water for several times, and dried at 60°C for 6 hrs.

UV-Visible Spectroscopy

UV-Visible absorption spectra of ZnTe-HH and ZnTe-NB were recorded to investigate the optical energy band gap. ZnTe-HH exhibited a sharp absorption peak at ~ 550 nm, corresponding to a bandgap of ~ 2.26 eV, indicative of quantum confinement in smaller nanoparticles. In contrast, ZnTe-NB showed a red-shifted absorption peak at ~ 565 nm, yielding a bandgap of ~ 2.20 eV, suggesting larger particle sizes [3]. The Tauc plot analysis confirmed direct bandgap transitions, with the differences attributed to the stronger reducing capability of NaBH_4 , which promotes faster nucleation and larger crystallite growth compared to $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

X-Ray Diffraction (XRD)

XRD patterns of both ZnTe-HH and ZnTe-NB confirmed a cubic zincblende structure, matching JCPDS card no. 15-0746, with prominent peaks at $2\theta = 25.3^\circ$, 41.8° , and 49.5° corresponding to (111), (220), and (311) planes, respectively. The average crystallite sizes, calculated using the Debye-Scherrer equation, were ~ 15 nm for ZnTe-HH and ~ 25 nm for ZnTe-NB, indicating that hydrazine hydrate facilitates smaller crystallite formation due to its slower reduction kinetics [4]. The sharper peaks in ZnTe-NB suggest higher crystallinity, likely due to the rapid reduction by NaBH_4 . Raman spectra exhibited longitudinal optical (LO) and transverse optical phonon modes at 205 cm^{-1} and 180 cm^{-1} respectively confirming the zincblende structure [5].

SCANNING ELECTRON MICROSCOPY (SEM)

SEM images revealed distinct morphological differences. ZnTe-HH exhibited spherical nanoparticles with an average diameter of ~ 20 nm, forming agglomerates due to high surface energy. In contrast, ZnTe-NB displayed rod-like structures with lengths of ~ 50 – 60 nm and diameters of ~ 15 nm, consistent with the larger crystallite sizes observed in XRD. The rod-like morphology in ZnTe-NB is attributed to the anisotropic growth induced by NaBH_4 , which alters the growth kinetics during hydrothermal synthesis [6]. EDS analysis was performed to determine the elemental composition and purity of ZnTe-HH and ZnTe-NB. For ZnTe-HH, the atomic ratio of Zn:Te was $\sim 1:0.93$, indicating near-stoichiometric composition with minor oxygen content attributed to surface hydroxyl groups from hydrazine hydrate. ZnTe-NB showed a Zn:Te ratio of $\sim 1.2:0.90$, with slightly higher oxygen content due to partial surface oxidation [7]. The atomic percentage concentration of Zn and Te obtained for both sample is tabulated in “Table 1”. SEM images, Tauc Plot, Raman spectra, and XRD spectra of the ZnTe-HH and ZnTe-NB nanomaterial are given in “FIGURE1”(A), (B) and (C).

CONCLUSION

This study demonstrate the hydrazine hydrate and sodium borohydride distinctly influence the structural, morphological, and optical properties of hydrothermally synthesized ZnTe nanomaterials. ZnTe-HH forms smaller, spherical nanoparticles with a bandgap of ~ 2.26 eV, while ZnTe-NB yields larger, rod-like structures with a bandgap of ~ 2.20 eV. XRD, SEM, Raman, and EDS analyses confirm the zincblende structure, morphological variations, and surface chemistry differences. These results provide a foundation for optimizing ZnTe nanomaterials for specific optoelectronic applications by selecting appropriate reducing agents.

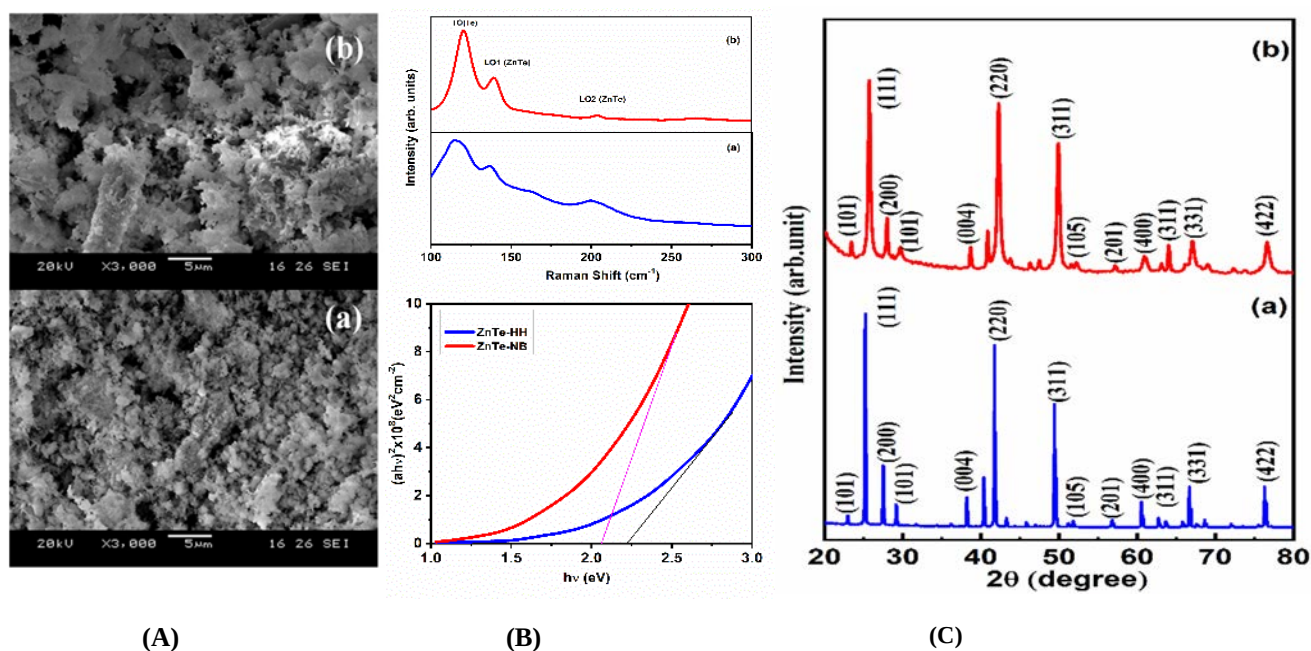


FIGURE 1. SEM images (A), Raman spectra and Tauc Plot $(\alpha h\nu)^2$ versus $(h\nu)$ (B) and XRD spectra (C) for the ZnTe-HH a) and ZnTe-NB b) samples.

Table 1. Atomic percentage composition of Zn and Te element of ZnTe-HH and ZnTe-NB samples.

Element atomic composition (%)	Zn	Te
ZnTe-HH	48.31	51.69
ZnTe-NB	55.36	44.64

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Tuning the Electronic and Magnetic Properties of Graphullerene via Pd, Y, and Mg Doping: A DFT Study

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Abstract: We exploit the electronic and magnetic properties of pristine and doped graphullerene (GF) with Mg, Y and Pd. Here we observe highest magnetic moment $2.0\mu_B$ in GF@Mg due to the structure distortion. On the other hand, energy band gap of GF@Y increased as compare to the Mg doped in case of spin-up and opposite trend was seen for spin-down. Further Pd doping keeps the material non-magnetic. Moreover, in case of Y or Mg doping first nearest neighbor are contributing most in magnetic moment as compare second and third nearest neighbor. These magnetic and electronic characteristics are very applicable to next-generation technologies. Due to GF@Mg large magnetic moment, it holds promise for high density magnetic storage and spintronics, where the magnetic state can be used to incode information.

INTRODUCTION

Graphullerene (GF) is an emerging carbon allotrope that integrates characteristics of both graphene and fullerene. It is formed by joining individual C_{60} molecules through covalent bonds, producing an extended framework that mirrors the honeycomb pattern of graphene [1]. This interconnected design preserves the distinctive molecular traits of fullerene while incorporating the continuous lattice connectivity of graphene, resulting in adjustable electronic, optical and mechanical properties suitable for diverse applications such as nanoelectronics, energy storage systems, and catalysis [2]. In our study we used density Functional theory (DFT) to insight the effects of doping on the electronic and magnetic characteristic of graphene doped with Mg, Pd and Y (graphullerene@ X (X=Mg, Pd, Y)) paying the way of their application in spintronics, nanoelectronic devices and energy-related technologies.

COMPUTATIONAL DETAILS

Density functional theory (DFT) calculations were carried out using the SIESTA code [3]. The exchange-correlation energy was described using the Perdew-Burke-Ernzerhof (PBE) functional [4] within the generalized gradient approximation (GGA). Relativistic pseudopotentials were employed and a double-zeta polarized (DZP) basis set with a confinement energy of 20 meV was used for all calculations. A mesh cutoff energy of 300 Ry was employed. The studied systems were investigated using $10 \times 10 \times 1$ Monkhorst K-point mesh.

Structural Properties

Here, we focus on the unit cell of 2D GF and compare the properties of 2D GF unit cells when we attempt to dope them. Three different doping materials Pd, Mg, and Y separately are used here namely GF@Pd, GF@Mg and GF@Y, and the findings are quite intriguing. As displayed below in **FIGURE 1 and 2**. Binding energy analysis (**TABLE 1**) shows that pristine GF is the most stable (-7.412 eV), followed by Y-doped (-7.297 eV) and Mg-doped (-7.184 eV) systems, with Pd-doped (-7.276 eV) also exhibiting competitive stability. Although doping slightly reduces stability due to structural distortions, all doped forms retain energetically favorable configurations, confirming that substitutional doping is feasible while preserving structural integrity.

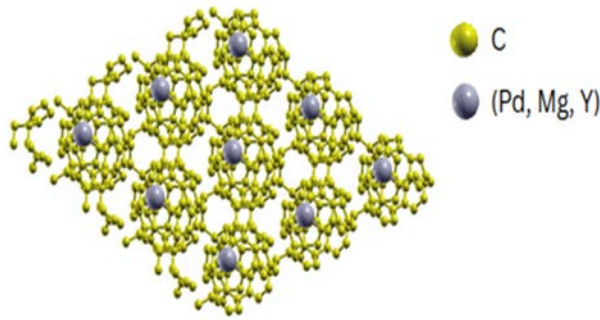


FIGURE 1. Front view of doped GF

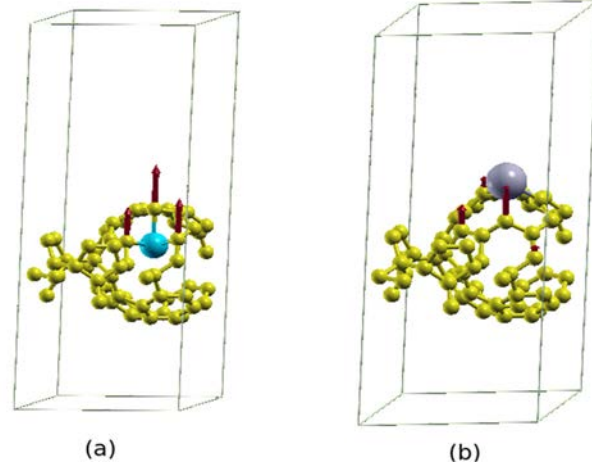


FIGURE 2. (a) Front view of GF@Mg and (b) GF@Y unit cell along with spin vectors.

Electronic and Magnetic Properties

There is significant change in the energy band gap upon doping. As shown in the TABLE 1, the pristine **Grafullerene** has an indirect energy band gap of 0.869 eV and in comparable with available result [3]. However, in general doping with Pd, Y and Mg reduced the energy band gap. For Pd energy band gap reduces to 0.358 eV and the system remains non-magnetic. On the other-hand doping with Y and Mg make the system magnetic in nature as clear from asymmetric DOS and spin resolved band structure (FIGURE 2). This creates distinct values of energy band gap for spin-up and spin-down states. The Yttrium-doped system shows a gap of **0.693 eV (spin-up)** and **0.283 eV (spin-down)**, while the Magnesium-doped system has values of **0.519 eV (spin-up)** and **0.522 eV (spin-down)**.

TABLE 1. Binding energy (E_b), Energy band gap (E_g), spin moment μ (μ_B), magnetic moment of dopant μ_D (μ_B), magnetic moment of first nearest neighbor μ_{1NN} (μ_B), magnetic moment for 2nd or 3rd nearest neighbour $\mu_{2,3NN}$ (μ_B) for the studied systems.

System	E_b (eV)	E_g (eV)	μ (μ_B)	μ_D (μ_B)	μ_{1NN} (μ_B)	$\mu_{2,3NN}$ (μ_B)
GF	-7.412 (7.440) ^[5]	0.869 (I) (0.92 (I)) ^[5]	0.000	---	---	---
GF@Pd	-7.2762	0.358 (D)	0.00	---	---	---
GF@Y	-7.297	0.693(↑) 0.283(↓)	0.958	0.088	0.605	0.264
GF@Mg	-7.184	0.519(↑) 0.522(↓)	2.000	-0.088	1.834	0.254

The table shows that pure **GF** and the **GF@Pd** system are non-magnetic, with zero magnetic moments. In contrast, doping with Yttrium and Magnesium creates a magnetic moment. The **GF@Y** system has a total spin moment of 0.958(μ_B), with the largest contribution coming from the first nearest neighbors i.e three nearest C atoms (0.605(μ_B)) as clear from spin vector arrow (FIGURE 2 (b)) and smaller contributions from the dopant (0.088(μ_B)) and second/third nearest neighbors (0.264(μ_B)). The **GF@Mg** system has an even larger spin moment of 2.00(μ_B), where the first nearest neighbors (three nearest C atoms as clear from spin vector arrow (FIGURE 2 (a)) contribute most (1.834(μ_B)). Interestingly, the Magnesium dopant has a negative moment of -0.088(μ_B), indicating an opposing alignment to the overall spin. This demonstrates that the magnetic moment is a collective property distributed among the dopant and its surrounding atoms.

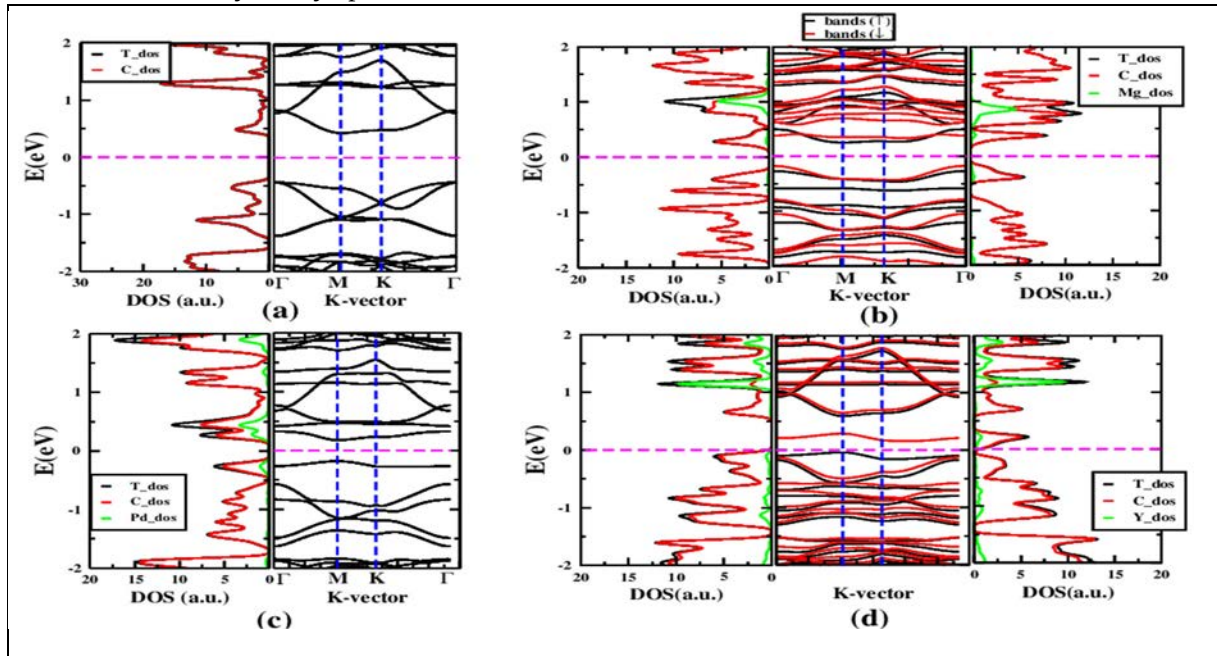


FIGURE 3. Band structure and PDOS for (a) GF, (b) GF@Mg, (c) GF@Pd and (d) GF@Y for both spin up and down.

CONCLUSION

Density functional theory calculations reveal that the pristine GF is a non-magnetic semiconductor with a moderate band gap. Substitutional doping with Y and Mg induces magnetism, with Mg producing the largest moment ($2.0 \mu_B$) accompanied by pronounced structural distortion, while Pd doping preserves non-magnetic behavior but modifies the band gap. Binding energy analysis confirms pristine GF as the most stable form, followed by Y- and Mg-doped systems, with Pd-doped structures exhibiting competitive stability. These results demonstrate that selective doping can effectively tailor the electronic and magnetic properties of GF, enabling engineered functionalities for applications in spintronics, nanoelectronics and energy-related technologies

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Dielectric Studies of Cobalt Substituted Lithium Ferrite

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Abstract. Lithium ferrites with inverse spinel structure have potential applications in microwave devices and magnetic recording due to their high Curie temperature and magnetization. This study investigates the effect of cobalt substitution on the dielectric and magnetic properties of $\text{Li}_{0.5}\text{Co}_x\text{Fe}_{2.5-x}\text{O}_4$ ferrites. The results show that dielectric loss decreases with increasing frequency, while permeability exhibits dispersion at lower frequencies. Magnetic loss decreases with increasing frequency, and dielectric constant is high at low frequencies. The study suggests that these ferrites have potential applications in magnetic devices, particularly in frequency ranges where permeability is constant. The addition of cobalt ions influences the magnetic loss behavior, making it suitable for specific applications.

INTRODUCTION

Lithium ferrites come to the family of spinel ferrites as it has inverse spinel structure where the both monovalent lithium cation occupy the octahedral site and trivalent iron cation occupy both the octahedral and as well as tetrahedral site. These are promising materials for microwave devices, magnetic recording and a potential cathode material in rechargeable lithium ion batteries. These potential technological applications being discussed are result of properties like high curie temperature, square hysteresis loop and high magnetization. Effect of Cobalt substitution on structural, optical, electrical, magnetic properties of lithium ferrite ($\text{Li}_{0.5}\text{Co}_x\text{Fe}_{2.5-x}\text{O}_4$, $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$) has been discussed in the previous paper. The structural studies reveal the ordered α – phase, morphological and topographical studies confirmed the formation of cubic spinel chemistry. The optical studies revealed the formation four frequency bands ν_1, ν_2, ν_3 and ν_4 in which each frequency band signifies the stretching of metal cation and oxygen anion in the spinel lattice. Spectroscopic studies confirmed the formation of spinel phase. Electrical studies showed the change in conduction process from metallic to semiconductor behavior attributed to the hopping mechanism [1,2]. Dielectric properties of material include dielectric constant, dielectric loss and loss tangent can be optimized by synthesis route and sintering temperature. Ferrites are magnetic material and also shows significance dielectric properties. In the present studies the dielectric behavior of the cobalt substituted lithium ferrite has been discussed.

EXPERIMENTAL DETAILS

The properties of the nanostructured ferrites can be altered by doping of appropriate cations in the spinel lattice of oxygen anions. Cobalt substituted Lithium ferrite has been prepared by citrate precursor method in which citric acid used as chelating agent. The details of the method have been discussed in the previous paper [1,2]. Citrate precursor is a non-conventional method for the preparation of nanomaterials. Non-conventional methods are chemical methods in which reactants are in the form of sulphates, chlorides and nitrates. These reactants undergo a chemical reaction in the presence of reacting medium such as acids, bases to form a nanomaterial. The citrate precursor method results in the homogeneous mixing of ions at the molecular level.

RESULT AND DISCUSSION

The behavior of the charge carriers such as electronic, ionic or spin can be studied by dielectric properties of a material. The relative permittivity (ϵ_r) shows dispersion in the frequency range under observation as shown in Figure 1(a). According to Rabkin and Novika the dielectric polarization decreases with the increase in frequency because of the electronic exchange between Fe^{2+} and Fe^{3+} [3]. The local displacement of electrons within the lattice

in the direction of applied field cause polarization results in steady increase of permittivity with increase in frequency. The dielectric loss shows a normal behavior with frequency for which it decreases with increase in frequency for all the concentration as shown in Figure 1(b) [8]. At low frequency region, the dielectric loss decreases rapidly but for high frequency region the dielectric loss become independent of frequency. The cause of such behavior is that the low frequency region affected by the high resistivity grain boundaries and hence more energy required for electron exchange with the interaction of Fe^{3+} ions at the octahedral sites which results in high dielectric loss at low frequency region. The dispersion of permeability for all the compositions at lower frequency is attributed to the domain wall displacement while as shift towards the high frequency region permeability became constant as shown in Figure 1(a) (c). The value of magnetic loss is higher for lower value of frequency in MHz and decreased as the frequency increases as approaches to GHz and become constant Figure 1(d)[8]. It was found that the value of dielectric constant for $\text{Li}_{0.5}\text{Co}_x\text{Fe}_{2.5-x}\text{O}_4$ (for $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 0.6) being high at low frequency, then goes on decreasing sharply as the frequency goes on increasing but as the frequency shifted to higher side the decrease become slower and reached a constant value. The analysis clearly visualize that dielectric constant is high at low frequency, and goes on decreasing sharply as the frequency goes on increasing but as the frequency shifted to higher side the decrease become slower and reached a constant value. The higher value of dielectric constant at lower frequency was explained by Koops theory that in polycrystalline ferrites there are high resistive grain boundaries to separate the grains in the morphological range [4]. The hopping of the charge carriers at the grain boundaries give rise to the interfacial polarizations which is the cause of higher value of dielectric constant at low frequency region [5].

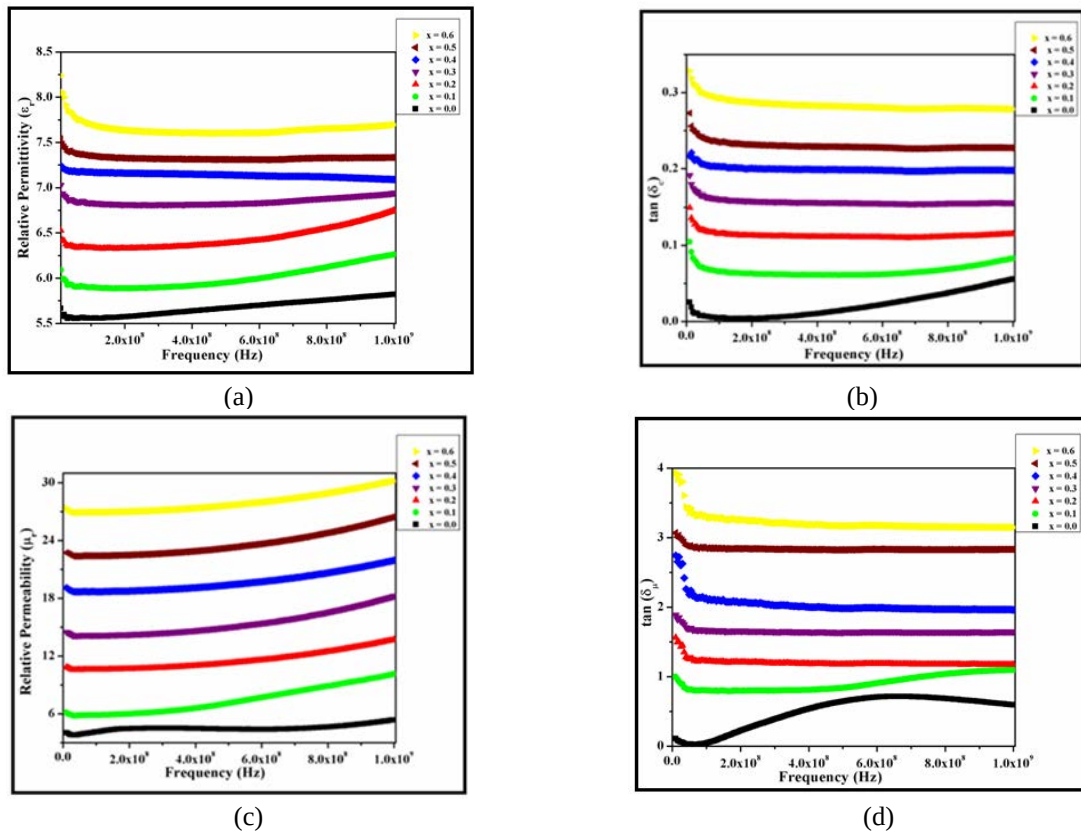


FIGURE 1 (a) Permittivity of $\text{Li}_{0.5}\text{Co}_x\text{Fe}_{2.5-x}\text{O}_4$ ($0.0 \leq x \leq 0.6$, step = 0.1) (b) Dielectric loss of $\text{Li}_{0.5}\text{Co}_x\text{Fe}_{2.5-x}\text{O}_4$ ($0.0 \leq x \leq 0.6$, step = 0.1) (c) Permeability of $\text{Li}_{0.5}\text{Co}_x\text{Fe}_{2.5-x}\text{O}_4$ ($0.0 \leq x \leq 0.6$, step = 0.1) (d) Magnetic loss of $\text{Li}_{0.5}\text{Co}_x\text{Fe}_{2.5-x}\text{O}_4$ ($0.0 \leq x \leq 0.6$, step = 0.1)

It is reported that the high frequency and ultra-high frequency region is the frequency region greater than 10^6 [6]. The domain wall displacement is the cause of dispersion of permeability at lower frequency which in this frequency region descends greatly. This type of behavior in certain region of frequency where the permeability is constant having useful in magnetic applications [7]. The magnetic loss shows anomalous behavior for pristine lithium ferrite. But as the

concentration of cobalt ions goes on increasing in the lattice of lithium ferrite the magnetic loss is higher for low frequency and there is decrement in the loss value as frequency increased and at last hence become constant.

CONCLUSION

Key findings of the study reveals that ($\text{Li}_{0.5}\text{Co}_x\text{Fe}_{2.5-x}\text{O}_4$, $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$) ferrites exhibit frequency-dependent dielectric and magnetic properties. Dielectric loss decreases with increasing frequency due to grain boundary effects. Permeability shows dispersion at lower frequencies due to domain wall displacement. Magnetic loss decreases with increasing frequency. Dielectric constant is high at low frequencies and decreases sharply with increasing frequency. The low dielectric constant of the material under investigation have application in high frequency. The study suggests that these ferrites have potential applications in magnetic devices, particularly in frequency ranges where permeability is constant. The addition of cobalt ions influences the magnetic loss behavior, making it suitable for specific applications.

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A Computational Study of bg-C₃N₄: From Monolayer to Nanoflake

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Abstract: We investigate the electronic and magnetic properties of triangular and disk shaped nanoflakes derived from buckled graphitic carbon nitride (bg-C₃N₄) using first principle calculations. While the monolayer is nonmagnetic, nanoflakes exhibit geometry-dependent magnetism and band gap modulation. We find out that triangular flakes become magnetic and have smaller band gap, while disk shaped flakes show strong spin asymmetry. The magnetism mainly contributed from edge atoms, and its distribution depends on the flake's geometry. These results show that by simply changing the shape of bg-C₃N₄ nanostructure, we can tune its properties for future spintronics and optoelectronic technologies.

INTRODUCTION

In an era of rapid technological advancement, researchers are primarily focused on enhancing the performance and efficiency of microelectronic devices, driven by the demand for smaller and more portable technology [1]. Two-dimensional (2D) materials like graphene, transition metal dichalcogenides and graphitic carbon nitride are valued for their high surface area, tunable band gaps and layer-dependent properties. When scaled down to zero-dimensional (0D) nanoflakes, these materials can gain entirely new functionalities due to edge effects, quantum confinement and broken symmetry; enabling magnetic and catalytic behaviour, which is sometimes absent in their monolayers. In this study, first-principles calculations show that reducing buckled graphitic carbon nitride (bg-C₃N₄) from a non-magnetic 2D sheet to a triangular 0D nanoflake induces magnetism and narrows the band gap, revealing potential for multifunctional applications beyond photocatalysis.

COMPUTATIONAL DETAILS

First-principles calculations based on density functional theory (DFT) were carried out using the **SIESTA** (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code [2]. The exchange–correlation interactions were described using the **Perdew–Burke–Ernzerhof (PBE)** functional within the generalized gradient approximation (GGA) [3]. Geometry optimizations of buckled graphitic carbon nitride (bg-C₃N₄) nanoflake structures were performed in a non-periodic framework with a $1 \times 1 \times 1$ k-point grid. Relativistic pseudopotentials were employed along with a **double-zeta polarized (DZP)** basis set and a confinement energy shift of 20 meV for all calculations. We used a 300 Ry mesh cutoff for reliable and high accuracy.

RESULTS AND DISCUSSION

This study demonstrates the construction of two distinct nanoflakes: a triangular nanoflake (TNF) and a disk nanoflake (DNF) namely C₃₆N₄₆ and C₁₈N₁₈ respectively as shown in Figures 1(a1) and 1(b1). For baseline comparison, we first examine the electronic and magnetic properties of pristine two-dimensional buckled graphitic carbon nitride (bg-C₃N₄) monolayer. Consistent with previous reports, the optimized bg-C₃N₄ monolayer maintains its typical buckled structure, exhibits a non-magnetic ground state and showed a binding energy of –5.51 eV per atom with a lattice constant of 6.390 Å [4]. Figure 2(a) and 2(b) illustrate the fully relaxed geometries of distinctive nanoflake along with the spin vectors. During geometry optimization, both triangular and disk nanoflakes show slight distortion

in the system symmetry compare to their initial configurations, introducing the edge-induced structural relaxation effects.

The binding energy (E_b) was calculated for both systems to assess the structural stability. The triangular flake exhibited a value of -5.477 eV/atom, while the disk-shaped flake showed a slightly lower value of -5.3307 eV/atom, indicating that the disk nanoflake is comparatively less stable. This difference may be attributed to variations in edge atom coordination and strain distribution in the two geometries.

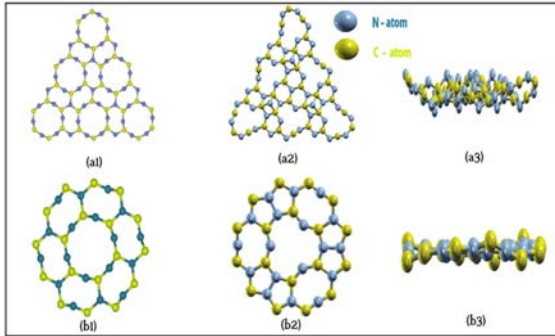


FIGURE 1. Initial(a1/b1) and relaxed(a2,a3/b2,b3) atomic structures of (a) $C_{36}N_{46}$ TNF and (b) $C_{18}N_{18}$ DNF.

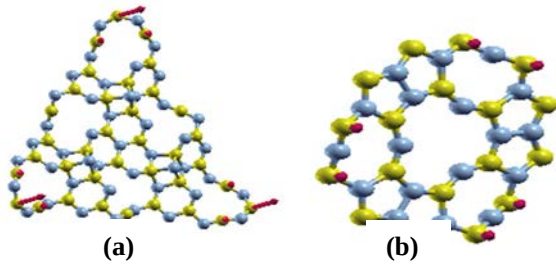


FIGURE 2. Spin vectors of (a) $C_{36}N_{46}$ TNF and (b) $C_{18}N_{18}$ DNF.

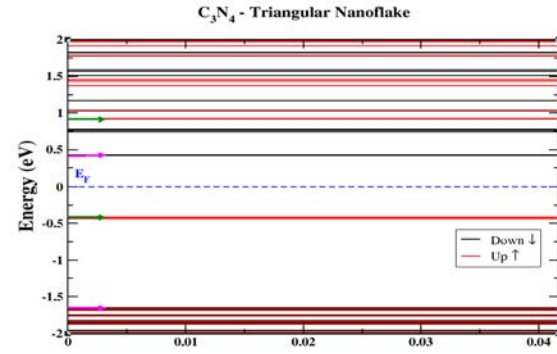


FIGURE 3. Energy level diagrams for $C_{36}N_{47}$ TNF.

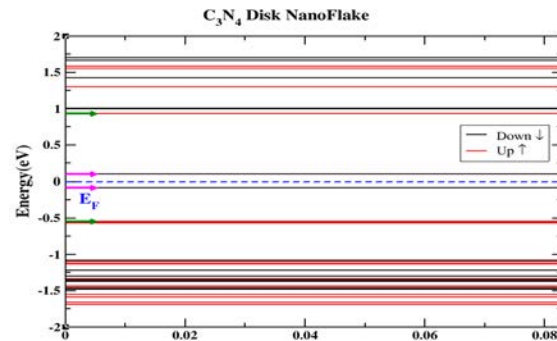


FIGURE 4. Energy level diagrams for $C_{18}N_{18}$ DNF.

The energy level diagrams reveal clear differences in the electronic behaviour of the two nanoflakes. The triangular flake has band gaps of **1.330 eV** (spin-up) and **2.021 eV** (spin-down) (listed in TABLE 1), showing strong spin polarization. In comparison, the disk flake shows a band gap of **1.480 eV** (spin-up) but a much smaller **0.177 eV** (spin-down) (listed in TABLE 1), indicating a greater spin-dependent asymmetry than the triangular flake.

Overall, the relatively large spin-down band gap in the triangular flake and the large spin-up band gap in the disk flake suggest that these nanostructures could be promising candidates for **spin-polarized optoelectronic applications**.

TABLE 1: The estimated binding Energy (E_b), HOMO-LUMO energy gap (E_{H-L}) and magnetic moment contribution of corner C and N atoms ($\mu_{C/N}$) and the total magnetic moment (μ_B) of the studied systems

Structure	E_b (eV)	$a(\text{\AA})$	E_{H-L} (eV)	μ_C (μ_B)	μ_N (μ_B)	μ (μ_B)
bg-C3N4 (ML)	5.51, (5.51) ^[4]	6.390 (6.390) ^[4]	---	---	---	---
$C_{36}N_{46}$ (TNF)	-5.477	---	1.330($\uparrow$), 2.071($\downarrow$)	5.128	0.872	6.00
$C_{18}N_{18}$ (DNF)	-5.3307	---	1.480($\uparrow$), 0.177($\downarrow$)	1.497	0.530	2.00

An investigation of magnetic moment reveals that the triangular nanoflake exhibits a total magnetic moment of $6.00\mu_B$, with maximum contribution arising from the corner atoms, indicating localized magnetic states at the edges. Whereas the disk nanoflake shows a lower magnetic moment of $2.00\mu_B$, with its magnetism also primarily arising from the edge atoms due to edge effect. This indicate that the size and shape of the flake affect the contribution of edge atoms to its electronic properties, larger the flake more the edges, and most of the unpaired electrons are hosted by these edges, which affect the electronic and magnetic behaviour of the system [5].

CONCLUSION

Overall, the results indicate that that the finite size reduction of bg-C₃N₄ monolayer into triangular and disk nanoflakes, introduce magnetism from the edge localized unpaired electrons, despite the monolayer's non-magnetic semiconducting nature. The triangular nanoflake shows a magnetic moment of $6.00\mu_B$ with band gaps of 1.330 eV ($\uparrow$) and 2.071 eV ($\downarrow$), while the disk nanoflake has $2.00\mu_B$ with 1.480 eV ($\uparrow$) and 0.177 eV ($\downarrow$). In triangular nanoflake the magnetism primarily arises from corner atoms, on the other hand in disk nanoflake it mainly arises from the octagonal-ring edge atoms. Even though the disk flake is less stable then the triangular nanoflake, both the structures exhibit energetic stability. Taken together, these finding demonstrate that the geometry dependent nanoflakes can efficiently modify magnetic and electronic properties of a system, thereby making them a potential candidate for future spintronic and optoelectronic applications.

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Fundamental Principles, Structural Design, And Advanced Applications Of Single-Electron Transistors

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Abstract. The basic ideas behind Single-Electron Transistors (SETs) are thoroughly examined in this article, with particular attention paid to the devices' design, workings, and the quantum mechanical processes that control their behaviour. The extensive range of applications of SETs in many fields, such as gas sensing technologies, logic circuitry, memory storage systems, and artificial neural networks, is methodically explored in this paper. The research also critically compares these implementations with foregoing reporting in the literature, highlighting both execution approach advancements and differences. By delving into the advantages and implicit difficulties of these technologies, the paper aims to clarify the potential and limitations of SETs in modern and developing technological environments, placing recent advancements within a more comprehensive contextual analysis.

INTRODUCTION

The relentless drive for downsizing has transformed miniaturization from a design choice into a technological necessity. As demand grows for faster, energy-efficient, and integrated systems, compact electronics have become essential. This trend enhances the capabilities of devices like smartphones, wearables, and medical tools within increasingly smaller form factors. The basic building blocks of contemporary electronics, transistors, have always followed the scaling trajectory outlined by Moore's Law [1], which forecasts an exponential rise in transistor density on integrated circuits. As traditional MOSFETs near physical and quantum limits, their performance and efficiency gains are diminishing. This challenge underscores the urgent need for innovative nanoscale transistor designs. Single-electron transistors (SETs) have emerged as a leading candidate to redefine the future of Nano electronics.

The ultra-small size, low power consumption, and great sensitivity of single-electron transistors (SETs) make them an attractive substitute for traditional transistor technologies. SETs, compatible with CMOS and driven by quantum control of individual electrons, offer ultra-low power consumption, high charge sensitivity, and dense integration, making them ideal for memory, logic, and gas-sensing applications. Their compact size supports hybrid systems combining traditional and advanced electronics. In neuromorphic computing, SETs and graphene-based devices enable efficient, brain-inspired architectures through precise charge control and high mobility. SETs operate by controlling electron flow one at a time, using the Coulomb blockade effect to prevent additional electrons from tunneling unless a threshold voltage is applied [2]. This article reviews SET principles, fabrication techniques, challenges, and applications in gas sensing, memory, logic gates.

FUNDAMENTALS AND DESIGN OF SINGLE ELECTRON TRANSISTORS

A generic SET consists of three basic elements. Electrons are then injected and removed from the device at the source and drain electrodes. Its role is to suppress the tunneling of electrons through the barrier which connects the source and drain to the island. The Coulomb Island (or quantum dot) is a very small conducting region that may hold a certain number of electrons. It forms the third element. They are major in the sense they determine the energy of the Coulomb blockade and in that their size is adjusted to allow the exact placement of the electrons in the device [3]. The components of an SET are; the source, drain and gate, with a clear quantum dot (Coulomb island) sandwiched between source and drain. The gate manages the island's electrostatic potential and hence electron flow very efficiently. SETs function by enabling the passage of one electron at a time, which tunnels through the island under the Coulomb

blockade condition. This ability to provide exact electron control is why SETs are well-suited for low-power and ultra-sensitive charge sensing applications.

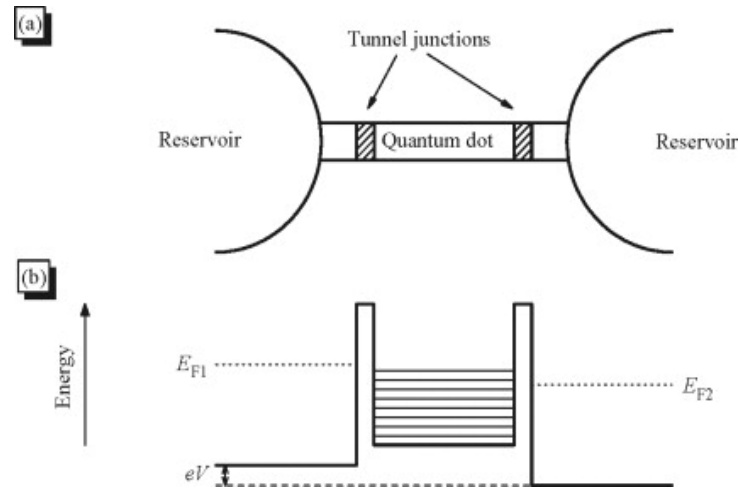


Figure 1. The illustration of a quantum system to examine Coulomb blockade effects and energy distribution upon application of an external voltage through the dot. The dot's values vary depending on how many electrons it contains (N).

Manufacturing methods and difficulties with Single-Electron Transistors

The manufacturing procedures and difficulties of single-electron transistors (SETs) are examined in this section. To achieve the precision needed for SETs at the nanoscale, key techniques including focused ion beam (FIB) milling, electron beam lithography (EBL), and scanning tunneling microscopy (STM) are crucial [4]. These techniques make it possible to create precise parts like electrodes and the Coulomb island.

However, there are a number of obstacles that SETs must overcome, such as the inability to operate reliably at room temperature, their susceptibility to external influences (such as temperature swings and electromagnetic interference), and problems with scaling for mass manufacturing. Compatibility issues make integrating SETs with current CMOS technology even more difficult. In order to overcome these obstacles, methods including material engineering, innovative manufacturing processes, and hybrid circuit designs that combine SETs with traditional semiconductor technologies are being investigated in an effort to enhance integration, performance, and yield.

While STM enables atomic-level component placement accuracy, fabrication techniques such as EBL use electron beams to shape nanoscale features. Ion beams are used in FIB milling to fine-tune component dimensions. Self-assembled nanoparticles are occasionally employed for the Coulomb island, which is positioned between electrodes by chemical reactions.

Modeling a single-electron transistor theoretically

A Single-Electron Transistor (SET) is a highly sensitive device that operates using the Coulomb blockade effect. While it shares basic components with a FET gate, source, and drain their working principles differ significantly. Unlike FETs, SETs lack a continuous conductive channel and use a quantum dot or “island” between tunnel junctions. Applying voltage to the gate alters the island’s potential, enabling control of electron flow one at a time. In a Single-Electron Transistor (SET), applying a positive potential allows electrons to tunnel through the island, shifting it from a blocked to a conducting state a phenomenon governed by the Coulomb blockade. This occurs because adding another electron requires excess Coulomb energy, leading to strong repulsion within the quantum dot that defies Ohm’s law. SETs exhibit exceptional charge sensitivity, capable of detecting the motion of a single electron. This makes them ideal for ultrasensitive electrometers and detecting nanoscale charge variations.

They are widely applicable in biochemical diagnostics for protein binding, DNA hybridization, and single-molecule detection. Additionally, SETs serve in chemical sensing, environmental monitoring, and scanning probe microscopy for precise nanoscale measurements.

Uses of Single-Electron Transistors in memory tools and sensing

The exceptional sensitivity of (SETs) to electrical charge proves them highly promising as sensing devices. Even a sole electron's fluctuation can be tracked by SETs, which allows them to be utilized in super-sensitive electrometers that can gauge minuscule alterations in charge.

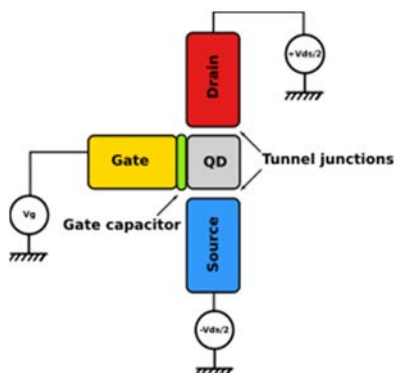


Figure 2. Diagrammatic representation of single-electron transistor

Like if any gas's interactivity with such ultra-sensibility may alter the localized electrostatic set-up in the vicinity of the SET's Coulomb quantum dot [5]. A discernible alteration in the electrical properties of these devices results from this interactivity, which influences the current generated by electron tunneling through the source and drain electrodes. SETs are capable of detecting the presence and low concentration of particular gases by tracking these changes. This qualifies them for spotting the molecular-scale interactions in biochemical and medical diagnostics, together with the DNA hybridization, protein binding, and sole-molecule exposure. SETs may also be employed as memory tools to build non-volatile memory structures that are incredibly small and power-efficient. This offers promising possibilities for the creation of sophisticated memory systems. Because of this ability, the idea of single-electron memory cells was developed, which store and retrieve data at the single-electron level via the Coulomb blockade effect.

Some major issues with the deployment of Single Electron Transistors

Single-Electron Transistors (SETs) face major obstacles to practical use, including their requirement for cryogenic temperatures (below 4 K) to enable the Coulomb blockade effect, making them unsuitable for mainstream electronics. Their nanoscale tunnel junctions demand extreme fabrication precision, where minor defects can impair performance. SETs are also vulnerable to background charge noise and electromagnetic interference, reducing stability and requiring complex shielding. Their ultra-low current limits speed and integration with conventional circuits, while short retention times hinder use in non-volatile memory. Additionally, material challenges like aluminum's oxidation and the need for further R&D on silicon or graphene delay commercialization.

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Measurement of Diethorn Constants of Ar+CH₄ filled X-ray Proportional Counter

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Abstract. X-ray proportional counters for energy Spectroscopy are used for various applications such as X-ray fluorescence spectroscopy, thin film thickness gauging and Mossbauer studies. Gas filled proportional counters with high Z gases Ar or Kr show good detection efficiency for photons in soft X-ray region <50 keV, as well as Kr shows absorption edge at 14 keV. Linear range of gas gain is essential for accurate calibration of energy and thus any variation in X-ray energy due to absorption, emission, Mossbauer effect will be recorded accurately. Avalanche formation in proportional counters determine internal gas amplification factor i.e. gas gain. The linear region of Diethorn plot reflects proportional region accurately. Diethorn gas constants are measured for Ar+CH₄ (9:1) gas using the pulse mode operation. These values of Gas constants for the given purity level of the gas are derived with good accuracy. These values are very useful to determine the operation parameters of any detectors with complex anode-cathode geometry and filled with the given gas purity.

INTRODUCTION

X-rays and low energy gamma rays are energetic photons widely used in physics for elemental analysis and material characterization. In the low-energy range (less than 50 keV), the photoelectric effect dominates over Compton scattering and pair production. These have the ability to ionize the material through photoelectric effect they pass through, making them detectable. Photoelectron emitted carries energy of photon, minus the binding energy and incident photon energy is detected using the detector.

Accurate energy detection is possible through gas filled, semiconductor or scintillation-based detectors. Gas filled proportional counters offer a simple design, good signal-to-noise ratio due to internal amplification and cost effective. A gas-filled proportional counter consists of a central thin anode wire mounted within a cylindrical cathode. Primary charge cloud drifts towards the anode under the influence of an applied electric field. As the electrons approach near the anode wire, the field becomes sufficiently strong ($\sim 10^6$ V/cm) to accelerate the electrons enough to cause further ionizations, resulting in an electron multiplication. This amplification process is quantified by the gas gain M [1]

GAS GAIN AND DIETHORN GAS CONSTANTS

Photons interact with the gas through Photoelectric Effect, photoelectron, which is emitted, ionizes the gas medium, producing a primary cloud of electrons. The number of primary electrons N_0 generated are proportional to the energy deposited by the photon (X). The work function w of the gas, is energy needed to create one ion pair, thus it gives $N_0 = X/w$. These electrons are then amplified by the factor of gas gain M . The secondary charge is collected through feedback capacitor C_f of preamplifier which results in the voltage pulse V_a at the anode, which is proportional to X . It subsequently gives the expression for gas gain $M = wC_fV_a/Xe$. The Diethorn equation (Eq 1) [2] has a linear form between $\ln(M)$ and anode bias V_0 , which is utilized to determine the gas constants, ΔV , the potential needed for an electron to gain energy to create a new ion pair and K , the critical electric field at which secondary ionization starts. Anode and cathode radii are noted by a and b respectively, p is gas pressure. The original Diethorn expression [2] is modified in the form of $y = mx+c$:

$$\left[\frac{\ln(b/a)}{V} \cdot \ln(M) \right] = \frac{\ln(2)}{\Delta V} \cdot \left[\ln \left(\frac{V}{P \cdot a \cdot \ln(b/a)} \right) \right] - \frac{\ln(2)}{\Delta V} \cdot \ln(K) \quad (1)$$

Diethorn Constants were calculated using values of m and c of the plots to get, $\Delta V = \frac{\ln(2)}{m}$ and $K = \exp \left(\frac{-c \cdot \Delta V}{\ln(2)} \right)$

EXPERIMENTAL METHOD

The proportional counter shown in Fig 1a is evacuated and filled with Ar +CH₄ (9:1) gas at 1.01 bar pressure. It is tested using a pulse processing set up (Fig 1b), consisting of a high-voltage DC power supply, charge-sensitive preamplifier, shaping amplifier and 1K multichannel analyzer (MCA) for accurate measurement of output pulse height. A precision pulser is connected to the test input of the preamplifier. It serves as a reference pulse to normalize the electronic gain of the entire circuit. ⁵⁷Co γ ray source, with energies 6.3 keV and 14.4 keV in soft x-ray region, is used for the gas gain measurements. The output of the preamplifier is fed to a shaping amplifier and signal is monitored on an oscilloscope and digitized using MCA for data acquisition. The gas gain measured from radiation-induced signal is noted [3] with reference to primary charge and for various anode bias V_0 . Fig 2A shows the energy spectrum of ⁵⁷Co for a gas gain of $\sim 10^4$ and Fig 2b shows the measured gas gain variation with anode bias of the detector, for both the photon energies. It indicates that $\ln(M)$ varies linearly with anode bias V_0 .

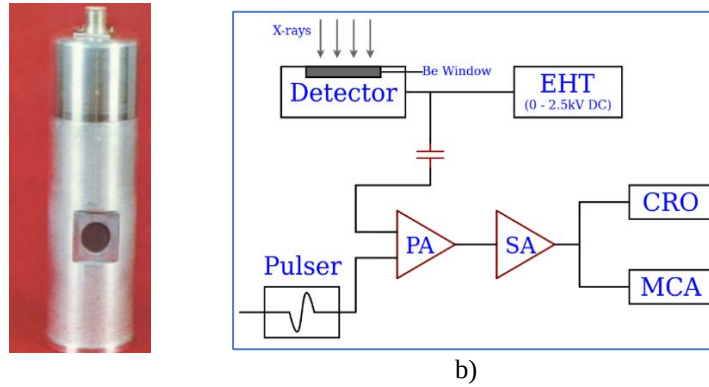


FIGURE 1. a) Picture of a X-ray proportional counter. b) Schematic of the Pulse processing electronics for a X-ray detector

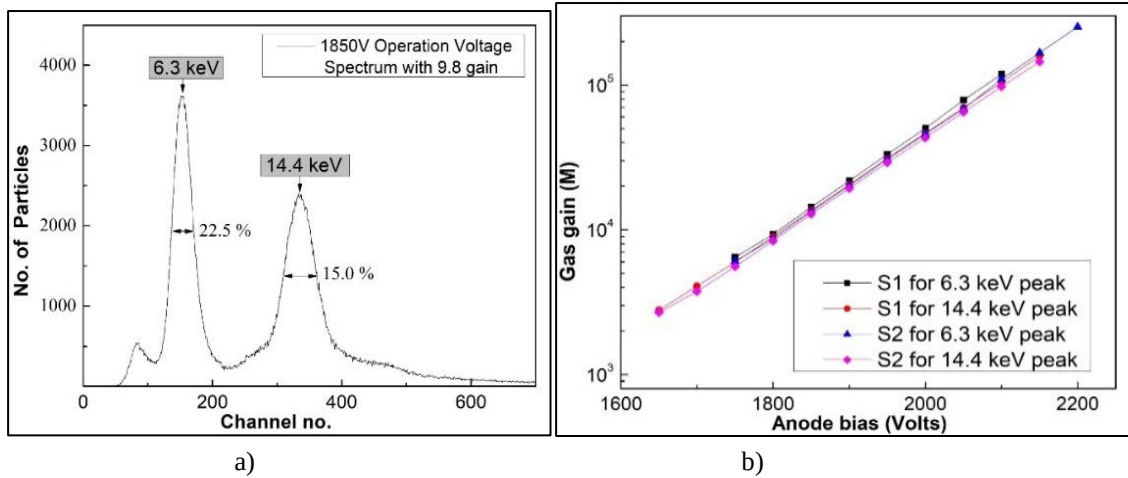


FIGURE 2. a) Energy spectrum of ⁵⁷Co source showing energy peaks of 6.3 keV and 14.4 keV at $V_0=1850$ V. b) Variation of measured gas gain values with anode bias V_0 for the detector filled with Ar +CH₄ at 1 bar.

RESULTS AND DISCUSSION

Gas gain measurements were carried out for two datasets labeled as Set-1 and Set-2 corresponding to the 6.3 keV and 14.4 keV peaks, respectively as shown in Table 1. All four sets showed strong linearity in the Diethorn plot indicating proportional region. The Pearson's correlation coefficient r was greater than 0.999 for each case, confirming a good linear fit. Each set was fitted with a straight line. The standard errors in slope and intercept were used to calculate the values of errors in ΔV and K using standard error propagation formulas with σ_m and σ_c .

TABLE 1. Measured values of Diethorn Gas Constants for Ar+ CH₄ from the plots shown in Fig 3a and 3b

Energy (keV)		Deithorn Gas Constant	
		ΔV (V)	K (V.cm.bar)
Set-1	6.3	28.57 $\pm$ 0.33	3.70E+04 ($\pm$ 1.31E+03)
	14.4	30.97 $\pm$ 0.29	3.26E+04 ($\pm$ 1.00E+03)
Set-2	6.3	29.49 $\pm$ 0.39	3.55E+04 ($\pm$ 1.47E+03)
	14.4	30.60 $\pm$ 0.51	3.37E+04 ($\pm$ 1.82E+03)

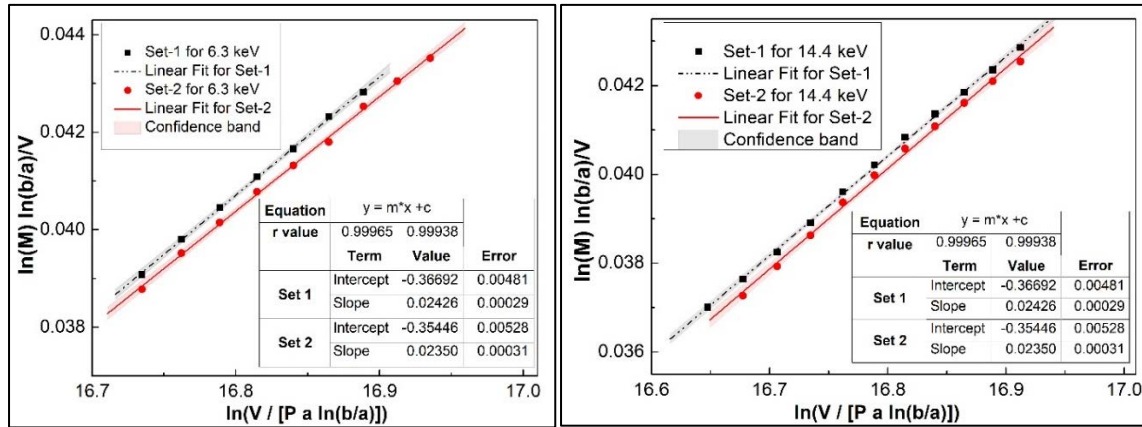
**FIGURE 3.** a) Diethorn plots for 6.3 keV peaks b) Diethorn plots for 14.4 keV peaks of ⁵⁷Co photon source

Table 1 gives the measured values of Diethorn Gas Constants of the Ar+CH₄ gas, with the acceptable error (<3%) and values from all four sets are averaged to find the $\Delta V = 29.91$ V and $K = 3.47E+04$ V.cm.bar.

CONCLUSION

X-ray proportional counter is successfully assembled, filled with gas and measured values of Diethorn Gas Constants are derived with good accuracy. These gas constant values are specific for the given gas combination and purity. These are useful for the design of a detector, to estimate its operation parameters, that will be filled with this gas and has complex anode-cathode geometry. These detectors are useful for application at Mossbauer Spectroscopy.

ACKNOWLEDGEMENT

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Design of Multiwire Based Sense and Readout Electrodes for 2-Dimensional Position Sensitive Neutron Detector

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Abstract. 2-D position sensitive detector for neutron based on multiwire structure and delay line readout method is indigenously designed and is being fabricated. Position Sensitive Detector (PSD) gives the neutron intensity over the entire sensitive area unlike that of 1D PSD. Small Angle neutron scattering (SANS) Spectrometer at GT Lab consists of fan-like multiPSD system that gives neutron intensity distribution with near 2D sensitive area but with few blank spaces. Continuous data is essential for the thorough analysis of the sample. Multiwire grids are the heart of the 2D PSD and are responsible for determining the properties such as linearity and uniformity of the data. Uniform drift field and high electric field for avalanche formation depends on the microscopic perfection of these grids. Each grid consists of an array of equi-spaced wires and all these three grids are arranged in the gas volume. Design of grids, engraving the desired pattern and gold coating on the PCB of size 720 mm x 720 mm was a challenge. Gerber files for field grid, X and Y cathode grids and drift grids were generated. Readout grids have mounting pads for the L and C components for delay line, at the end of each wire. Details of the design and function of these grids is presented.

INTRODUCTION

Small Angle neutron scattering (SANS) Spectrometer at GT Lab consists of a fan-like multi-Position Sensitive Detector (PSD) system that gives neutron intensity distribution with near 2D sensitive area but with few blank regions. Continuous intensity profile is essential for the thorough analysis of the sample. 2-D PSD [1-3] based on multiwire structure and delay line readout method is indigenously designed and is being fabricated. 2D PSD gives the neutron intensity over the entire sensitive area unlike that of a single 1D PSD or multiPSD arrangement. 2D PSD consists of a gas enclosure with X and Y orthogonal grids sandwiching the field grid as anode. Drift electrode channelizes the direction of electron drift velocity and lateral diffusion of electrons, affecting the centroid size, is controlled to the minimum.

DESIGN ASPECTS OF MULTIWIRED GRIDS

Multiwire grids are the heart of the 2D PSD and are responsible for determining the properties such as linearity and uniformity of the data. Grid assembly is most crucial part of the PSD, as any nonuniformity of wire tension, inter wire spacing and intergrid spacing may result in image distortion or voltage breakdown. Winding of wires, soldering and mounting delay line SMDs, and mounting of grids and drift electrodes determines the success of the PSD. Uniform drift field and high electric field for avalanche formation depends on the microscopic perfection of these grids. Each grid consists of an array of equi-spaced wires and all these three grids are arranged in the gas volume. Design of grids, engraving the desired pattern and gold coating on the PCB of size 720 mm x 720 mm was a challenge. Readout grids have mounting pads for the L and C components for delay line, at the end of each wire.

Gerber files for field grid, X and Y cathode grids and drift grids were generated. Designs of the gerber files for readout electrodes are prepared using electronic design automation software such as KiCad [4] and OrCAD [5]. All the gerber designs for these electrodes with 1 μm accuracy are prepared indigenously for tailor-made size and operating parameters of the detectors. Metal pattern is coated with gold for long life of grids for continuity over the time.

2-D PSD with sensitive area 640 mm x 640 mm consists of three multiwire frames and 2 drift grids. Alignment of these grids is shown in the Fig 1a and b. Each of them consists of an array of perfectly parallel wires. Anode grid consists of a multiwire frame of 25 μm $\varnothing$ gold plated tungsten wires placed at 5 mm pitch, X and Y cathode frames are mounted orthogonal to each other and are made up of 60 μm $\varnothing$ gold-plated tungsten wires with 5 mm pitch. Drift

bias (-ve) is applied through gold plated PCB-based electrode, mounted on both the sides of wire frame. 2-D position is obtained using pulses from these three multiwire grids. Anode holds high voltage and creates an avalanche around anode, pulse formed induces equal and opposite polarity pulses on X and Y orthogonal cathode grids. Delay line consists of discrete surface mount devices (SMD); inductances (L) and capacitors (C), mounted on multiwire grid and delay taps are directly connected to cathode wires. Time delay between each consecutive taps is ($\tau_d = \sqrt{L \times C}$) ~ 4.2 nsec and total impedance of the line is ($Z_o = \sqrt{L/C}$) $\sim 51.1 \Omega$. Design parameters of the chamber are as follows):

- Overall dimensions of PSD: 850 mm x 850 mm x 200 mm, and sensitive area: 640 mm x 640 mm
- Orthogonal multiwire grids: Anode, X cathode and Y cathode, anode PCB mounted with 25 μm Au-W wires at 5 mm pitch and $\pm 50 \mu\text{m}$ position accuracy and 1 μm read accuracy, 130 wires mounted on the PCB,
- Inter-grid spacing 7 mm, drift electrodes coated with gold and applied with negative bias,
- Capacitance of a grid 4.16 pF
- Position resolution: 5 mm, equal to wire spacing of multiwire array
- Neutron detection efficiency: 75% at 5.6 $\text{\AA}$ (for 3 bar) and 40 mm path length
- Time resolution between each wire 4.2 ns/tap, 132 taps ~ 550 ns

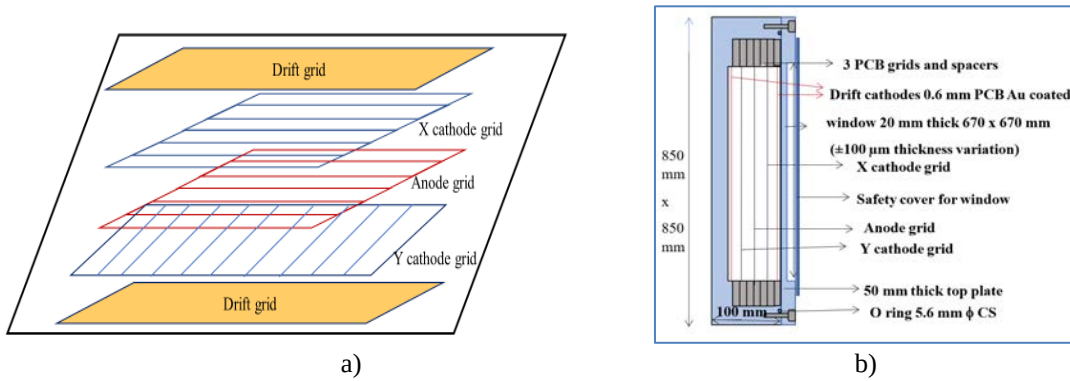


FIGURE 1. Schematic of a) anode cathode grids and drift electrodes, b) Schematic view of chamber and grid arrangement

SIGNAL PROPOGATION AND DELAY LINE READOUT

The anode provides the high electric field required for avalanche formation to give internal charge amplification. With high voltage applied to the anode grid, equipotential lines that are concentric to the wires are developed in the vicinity of each anode wire. The electrostatic field near each anode wire in the multiwire proportional counter [1] is given by

$$E = \frac{V}{\frac{d}{2} \left(\left[\frac{\pi l}{s} - \ln \left(\frac{\pi d}{s} \right) \right] \right)} \quad (1)$$

where d is anode wire diameter, s is the wire spacing, l is anode-cathode gap and V is anode voltage. Alignment of field lines and direction of drift field from anode to cathode and extent of high field region around anode resulting in gas amplification is shown in the Fig 2b. Electric field $\sim 10^4$ V/mm is critical field for avalanche formation. Pulses from readout grids are processed using current sensitive preamplifier. Delay line is terminated with the impedance equal to $Z_o = \sqrt{L/C}$. Signal arriving at the preamplifier characterises the information of pulse arrival timing proportional to position. The perturbation of electric field at the electrodes due to avalanche results from rapid displacement of ions in the high field region in close vicinity of the anode. Contribution from the slower component caused due to ion movement away from anode is not considered as the amplitude carries no importance in readout process.

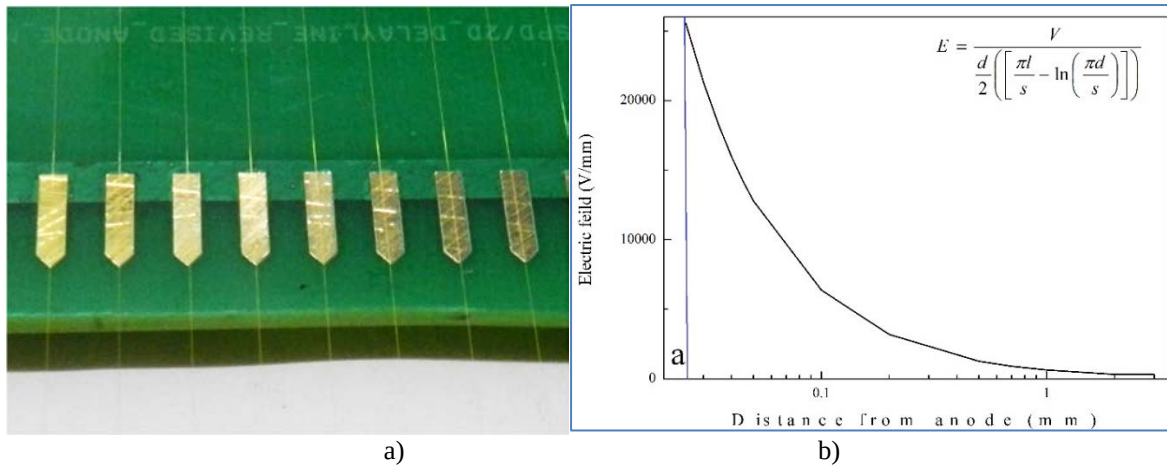


FIGURE 2. a) Anode grid with solder pads for wire alignment b) Electric field profile near anode surface of multiwire geometry

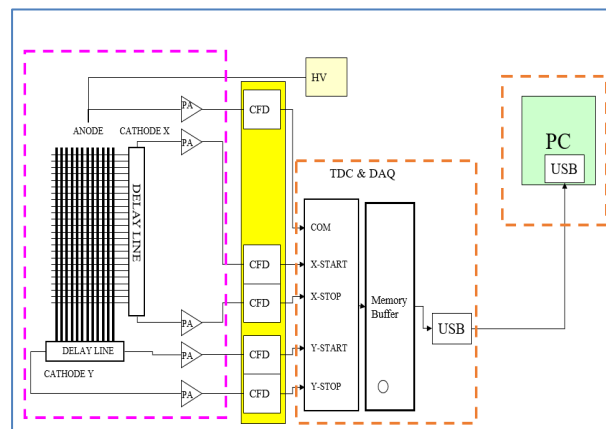


FIGURE 3. Pulse processing circuit for delay line based 2D Position readout

Delay line components integrate the signal whereas the preamplifier inverts and differentiates it. These pulses carry timing information but vary in rise time and amplitude, even when the pulses are arising from the same avalanche. These pulses are fed to Constant Fraction Timing Discriminator. It generates a standard NIM signal with a position in time that is independent of the amplitude and rise time of the input pulses. The data acquisition system operates with the signals of well-defined shapes and time coordinates. Position data is obtained by measuring the time difference between the two pulses assigned as START and STOP and converting into digital value, supported by the anode signal as a trigger pulse for coincidence. Total process time of each pulse can be minimised to 500 ns, which enables to handle the count rate of few hundred-kilo Hertz. Multiwire grids and Gerber files for 2D PSD are designed with accuracy.

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Synthesis, Characterization and Application of $\text{GdMnFe}_2\text{O}_4$ as an Advanced Humidity Sensor

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Abstract. Gadolinium-doped manganese ferrite ($\text{GdMnFe}_2\text{O}_4$) demonstrates significant potential for humidity sensing due to its enhanced electrical and adsorption properties. Introducing Gd through doping boosts water vapor adsorption, resulting in a noticeable variation in resistance in response to changing humidity levels. In comparison to non-doped ferrite, $\text{GdMnFe}_2\text{O}_4$ showcases improved conductivity and quicker response (7 seconds) and recovery (6 seconds) times, making it well-suited for applications in environmental monitoring and industrial sensing.

INTRODUCTION

Gadolinium-doped manganese ferrite ($\text{GdMnFe}_2\text{O}_4$) is turning a lot of heads right now, especially in the world of humidity sensors [1]. In this study, we look at what happens when you add gadolinium into the regular manganese ferrite structure and why that tweak makes such a difference for humidity sensing [2,3]. We really focus on how $\text{GdMnFe}_2\text{O}_4$ stacks up against plain manganese ferrite, especially when it comes to sensitivity and how quickly it reacts. Accurate and fast humidity detection matters a lot, whether you're monitoring the environment or running industrial equipment, so finding materials that deliver on both fronts is key [4].

To test how well $\text{GdMnFe}_2\text{O}_4$ senses humidity, we measured its resistance. $\text{GdMnFe}_2\text{O}_4$ showed a much bigger drop in resistance, which means its conductivity increased more than regular manganese ferrite [5]. Adding gadolinium ions into the crystal structure helped the material grab onto more water vapor, so its resistance reacted a lot more when humidity changed [4,6]. This sharp sensitivity makes $\text{GdMnFe}_2\text{O}_4$ a solid pick for humidity sensors, especially where we need quick and accurate readings. Beyond that, these results shed new light on how gadolinium doping works with manganese ferrite. We also push humidity sensor technology forward, which could really help with things like environmental monitoring and fine-tuning industrial processes.

MATERIALS AND METHODS

We synthesized $\text{Gd}_x\text{MnFe}_2\text{O}_4$ nanocomposites with different amounts of gadolinium with x values- 0.025, 0.050, 0.075, and 0.1 using the sol-gel method. Firstly we started by dissolving 17.8 grams of iron nitrate and 5.6 grams of manganese nitrate in 35 grams and 12 grams of distilled water, one after the other. We mixed everything together and stirred it at room temperature. Then we added 15 milliliters of ammonia solution as a catalyst. Next, we slowly poured in a solution of citric acid (that's 23.2 grams of citric acid in 15 milliliters of water) to act as a chelating agent. After that, we let the mixture sit undisturbed for five hours so the gel could form.

Once the gel was ready, we heated it up to 250°C to trigger combustion. Afterward, we calcined the resulting material at 400°C. Finally, we ground the powders and stored them away.

RESULTS AND DISCUSSION

Figure 1(a) shows the X-ray diffraction (XRD) pattern for $Gd_xMnFe_2O_4$ ferrites with different amounts of Gd. The pattern has clear reflections that match the cubic spinel structure, and the (400) peak stands out as the strongest. We also spotted other peaks, like (111), (222), (311), (422), and (511). All these match the standard reference (JCPDS 74-2401), with peak angles at 16° , 30° , 32° , 46.34° , 57.42° , and 62.18° [6].

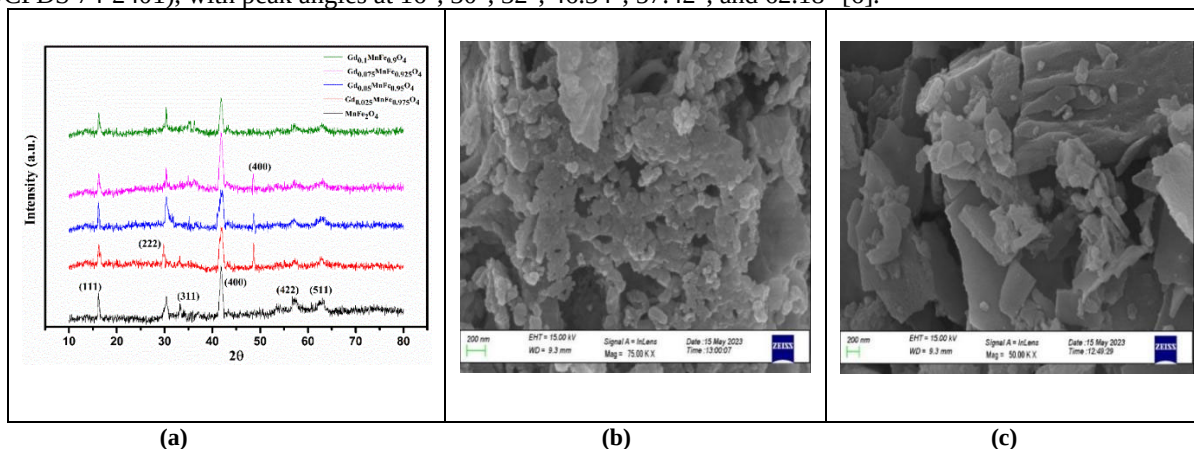


FIGURE 1. (a) XRD pattern of $MnFe_2O_4$ and $Gd_xMnFe_2O_4$ nanocomposites with distinct peaks indicating composition and crystallographic details. (b, c) FESEM images of $MnFe_2O_4$ and $Gd_{0.1}MnFe_2O_4$ nanocomposites.

To see how Gd gets into the material, we used FESEM-EDX to check the surface of both $MnFe_2O_4$ and Gd-doped $MnFe_2O_4$. In Fig. 1(b), we can spot those agglomerated, flake-like shapes- which matches what other people have reported before [7]. The Gd-doped sample in Fig. 1(c) looks pretty similar, still showing clear crystalline features. Then, if we look at the EDX mapping in Fig. 2, we'll notice distinct peaks that confirm Gd's actually in there.

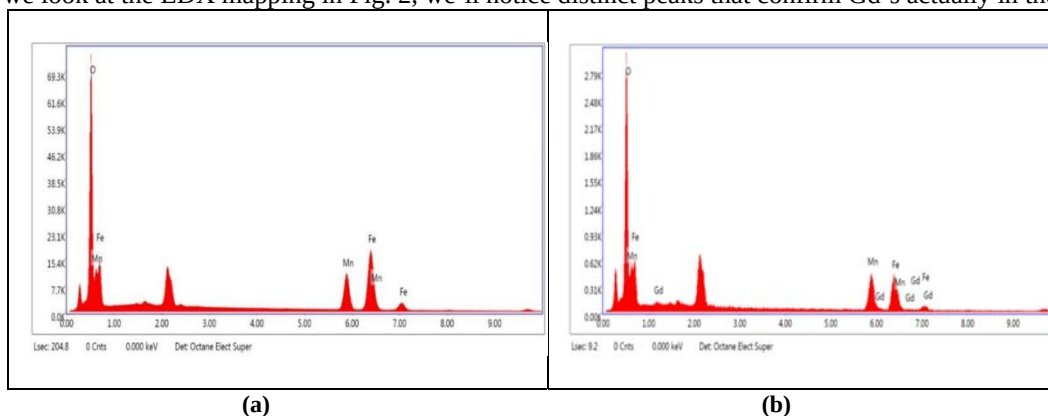


FIGURE 2. EDX spectra of (a) $MnFe_2O_4$ and (b) $Gd_{0.1}MnFe_2O_4$ nanocomposites signifying the presence of key elements in the synthesized nanocomposites.

HUMIDITY SENSING PROPERTIES

Figure 3(a) makes it clear that manganese ferrite starts out with high resistance when there's not much moisture around, but that resistance drops as moisture goes up. When just 0.1% gadolinium was added, the resistance falls off even faster because the gadolinium creates more places for moisture to stick [8,9]. That's what drives the change. When we look at the nanocomposite's performance, it reacts quickly: response time clocks in at 7 seconds, and it recovers in just 6 seconds, as we can see in Fig. 3(b).

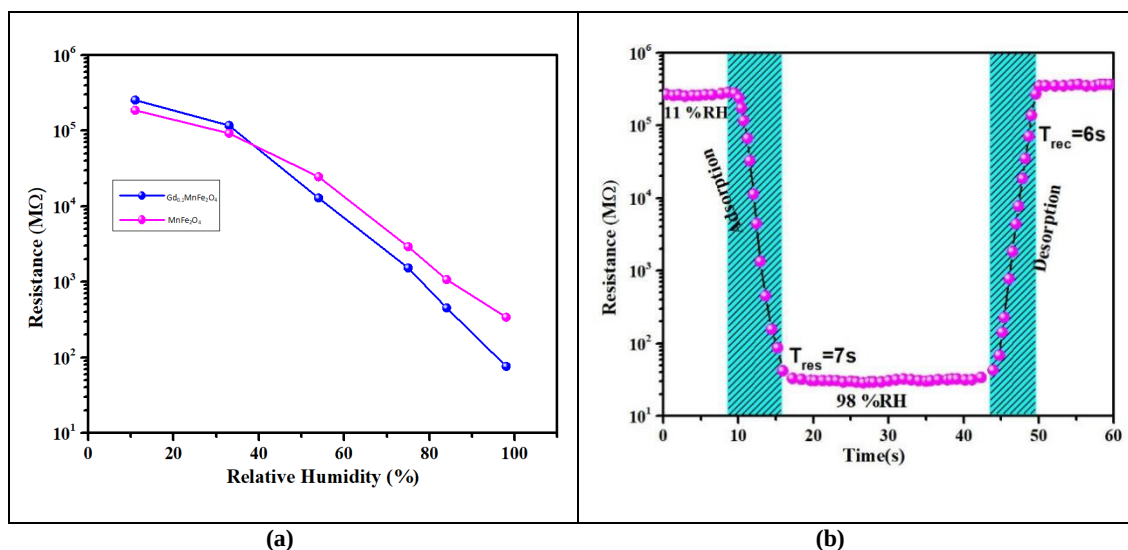


FIGURE 3. Humidity sensing behaviour of MnFe_2O_4 and $\text{Gd}_{0.1}\text{MnFe}_2\text{O}_4$ nanocomposites.

CONCLUSION

We made $\text{Gd}_x\text{MnFe}_2\text{O}_4$ nanoferrites using the sol-gel method. XRD results confirmed they have a cubic spinel structure, and the lattice got larger when we added Gd^{3+} . Looking at the material with FESEM, we can see flake-like shapes and some clumping. EDX analysis shows the composition is pure, just what we want. That's thanks to plenty of active adsorption sites and nice, linear sensing behavior. Also, the whole process is eco-friendly and straightforward, making this material promising for practical use.

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Development of electron gun with deflectors for enhancement of IR signal post electron beam irradiation on condensed phase matter

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Abstract. In this paper, we describe the development and testing of a low energy electron gun with the X-Y deflectors along with its scanning software. The algorithm implements the tracking mode type of scanning. The electron gun is tested and mounted with an experimental set-up developed for studying low energy electron induced chemistry in the condensed phase. It is observed that intensities of IR signal post irradiation are enhanced by nearly 5 times in comparison with intensities using electron gun without deflectors.

INTRODUCTION

Study of low energy electron induced chemistry is vital for understanding its role/process in various phenomena occurring in interstellar medium, in planetary atmospheres, in radiation biology [1, 2], plasma etching in semiconductor industry [3]. Electron-atom/molecule collision studies are being carried out in gas phase for nearly a century. But similar studies in condensed phase are not as abundant due to different challenges and moreover they have recently started gaining enhanced importance due to their relevance in astrochemistry [4]. The electron-atom/molecule collision process in condensed phase has higher number densities and additional multi-body interactions when compared with that of gas phase processes. Also they differ in absolute cross sections and branching ratios. In gas phase studies most commonly implemented methodology is the crossed electron beam – atom/molecule beam geometry [5] in which the interaction volume is imaged on to the detector. This demands low energy spread and small diameter for electron beam and a high number density of target molecules in the collision zone. On the contrary, in condensed phase experiments, the target atom/molecules are spread over a wide area on a cold substrate (~10K) and the number densities are less (few monolayers). Thus, if an electron gun without deflectors is used then the beam will collide with the target in a single spot, whereas if an electron beam with deflectors is used, then the electron beam can be irradiated over a larger surface area. In this paper we describe the design and working of a low energy electron gun with deflectors operating in tracking mode obtained using specially developed software. The comparison of IR signals intensities are studied for methyl acetate [6].

EXPERIMENTAL

1.0 The experimental setup

The experimental setup [7] is schematically shown in Fig. 1 (a). It consists of a low energy electron gun (Fig. 1 (b)) that produces a steady electron beam, a closed cycle liquid helium refrigerator based cold head for adsorption of sample, a gas inlet system, provision of controlled heating for a systematic thermal desorption, FTIR to measure the chemical state of the sample and Residual Gas Analyzer for partial pressure quantification of ambient molecules and computer controlled data acquisition software. The entire experimental system is maintained in UHV at around 1×10^{-10} mbar.

1.1 Experimental methodology and design of electron gun

A gold coated/plated substrate is connected to the cold head of the closed cycle helium refrigerator, which cools down the substrate to ~12K. A Sapphire disk (40 mm dia, 2 mm thick) is used to electrically insulate and thermally connect the substrate to the cold head of the helium refrigerator. A gas-inlet system with calibrated leak valve is used for depositing the sample on the cold substrate. Sample molecules are adsorbed on the cold substrate in a monolayer by

monolayer fashion. Their number density of the deposited molecules is estimated from the peak intensity of FTIR signal, using Langmuir method [7, 8]. To study the electron – molecule reactions, the FTIR signal of the target in “as-deposited” condition is measured. The target is then irradiated by nearly mono-energetic electrons from a ‘Pierce-type’ electron gun in the range 5 to 500 eV with currents ranging from few nA at lower energies to few μ A. The electron beam diameter is < 3 mm on the surface of the substrate. This electron gun consists of two pairs of deflectors as shown in Fig. 1(b).

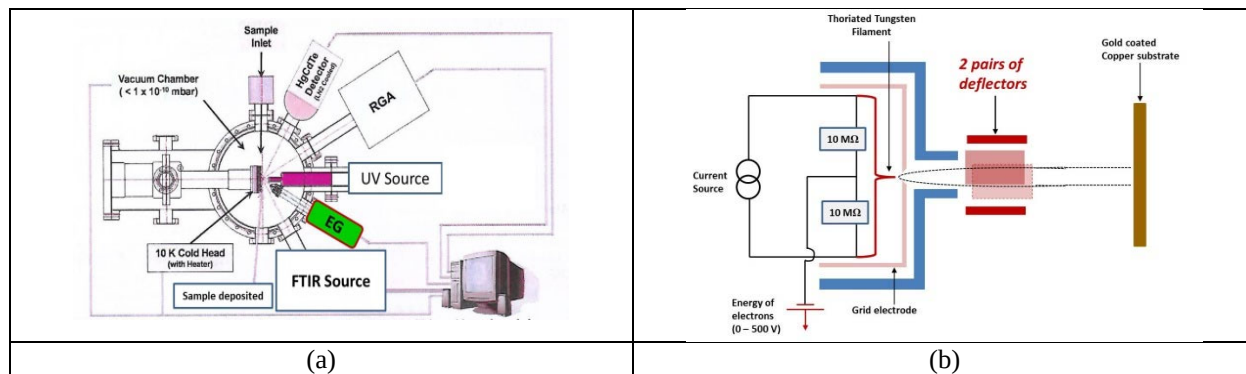


FIGURE 1. Schematic of the experimental setup for low energy electron collision on condensed phase matter

SIMION 8.0 [9] was used to study the amount of deflection of electron beam for various energies and electron beam diameters for deflection voltages in the range of ± 10 V in “tracking mode” as shown in Fig. 2.

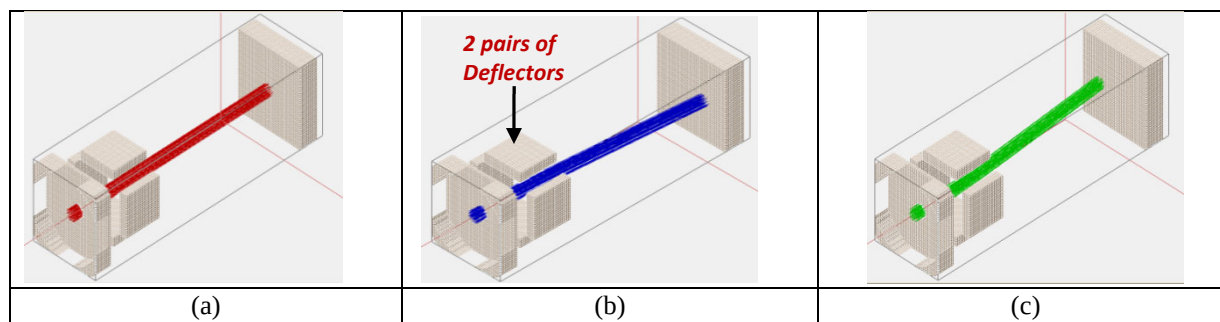


FIGURE 2. SIMION 8.0 simulation studies on the role of deflectors, (a) with 0 V on deflectors, (b) and (c) with maximum of ± 10 V on deflectors for electron beam energy of 100 eV and beam diameter 3 mm.

RESULTS, DISCUSSION AND CONCLUSION

The FTIR signal intensity is mathematically a function of number of ionic or molecular species deposited sample. The electron gun without deflectors will irradiate substrate area around 7 mm^2 , whereas if deflectors are employed then it will irradiate the area around 100 mm^2 as shown in Fig. 3 (a) and Fig. 3 (b). This deflection is achieved through software developed in VB.NET using an algorithm such that the deflectors are in “tracking mode” type. This ensures that electron beam energy remains same during the scanning of deflectors. The software provides scan interval voltages between of 0.1 V (Fig. 3 (b)) and 1 V (Fig. 3 (a)). In our current experiments, FTIR is used in Reflection Absorption (RAIR) mode over the wavenumber range 800 to 4000 cm^{-1} with a resolution of 0.5 cm^{-1} to identify the chemical composition of the samples on the cold substrate. A Liquid nitrogen cooled Mercury Cadmium Telluride detector connected to special data read-out electronics is utilized to detect & measure the IR signals. As a test case, Methyl Acetate was deposited on the cold substrate and FTIR studies were conducted using electron beam with and without deflectors. All experiments were carried out in identical conditions of temperature (12 K) and pressure around 5×10^{-10} mbar in “once-through” mode. In “once-through” mode, the sample (in this case Methyl Acetate) is desorbed and pumped out from the cold surface by warming the surface up to room temperature after every electron beam irradiation study.

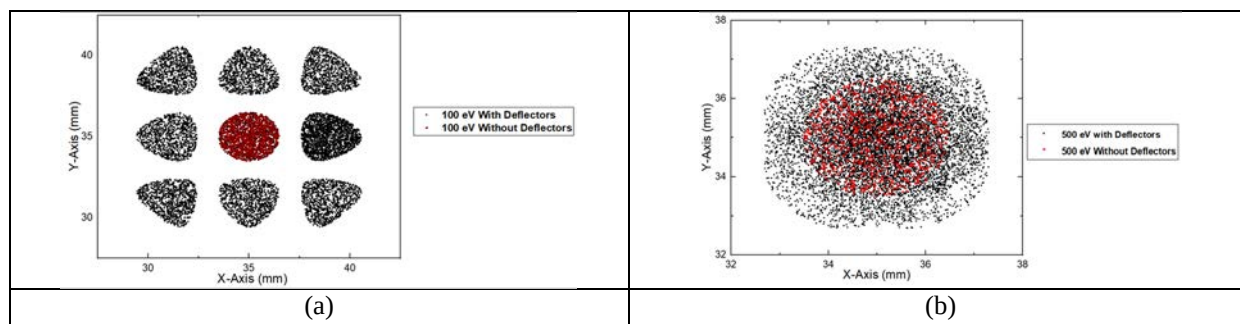


FIGURE 3. Total irradiated area by a 3 mm diameter electron beam: (a) with 100 eV and (b) with 500 eV

This ensures, that fresh unreacted sample is always available in “as-is” condition for new electron beam irradiation studies. The electron currents from both the type of guns were maintained for same values. The results of these FTIR experiments are shown in Fig. (4a) and (4b).

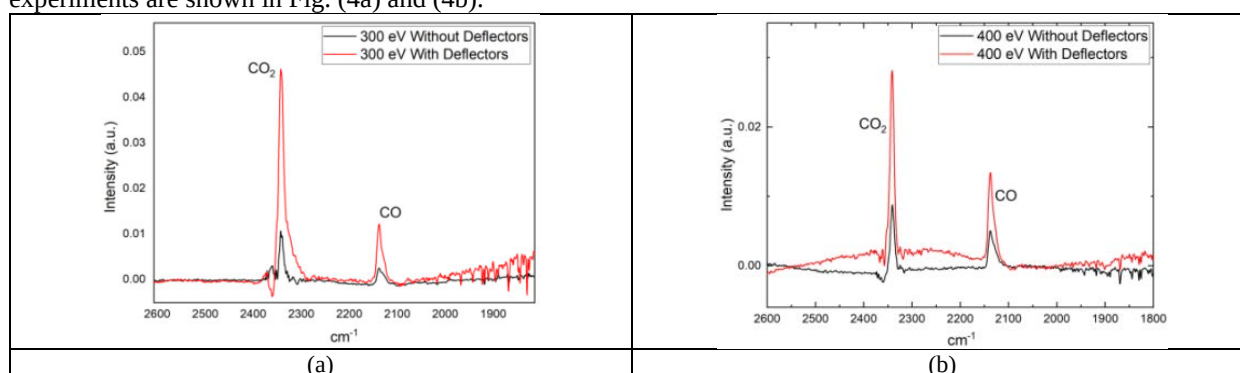


FIGURE 4. FTIR spectrum of Methyl Acetate for electron irradiation of 300 eV and 400 eV with and without deflectors

It is seen that the IR signals obtained for electron gun with scanning deflectors are clearly higher than for electron gun without deflectors at energies 300 eV and 400 eV. The IR signals are enhanced by a factor of nearly 4X times, thus making weaker signals clearly observable. Furthermore, the results also indicate that the electron beam nearly completely overlaps over the area of the IR beam impinging on the sample. These shows, the reaction products post-irradiation are present over the entire area of irradiation by the electron beam and no an-isotropy is present in the sample.

ACKNOWLEDGMENTS

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***In situ* spectroscopy investigations under severe plastic deformation at high pressures**

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Abstract. An integrated confocal micro-Raman and ruby fluorescence imaging setup has been established for rotational diamond anvil cell based *in situ* investigations on materials subjected to severe plastic deformation at high pressures. With a spatial and depth resolution of $\sim 2 \mu\text{m}$ and $40 \mu\text{m}$, respectively, the setup can be used for Raman piezometry and stress components mapping across entire sample at sample-anvil contact surface. The ruby fluorescence imaging with 10x optical magnification can be used for displacement field measurements in sample utilizing digital image correlation (DIC) method. A few benchmark experiments have been carried out to validate capabilities of the system.

INTRODUCTION

Unlike pressure-induced phase transitions (PT) where PT is driven by pressure and occur at pre-existing defects, plastic strain-induced phase transitions are driven by a combination of pressure and plastic deformation and occur at defects created during deformation [1,2]. Plastic straining at high-pressures may affect the PT pressures and sequence; stabilize metastable phases at ambient conditions; change nature of PT and pathways in configurational space; synthesize new novel phases which may not be accessible with hydrostatic compression, etc. *In situ* investigations under such conditions are important, not only for gaining more insight into the underlying mechanism, but also for working out optimal load-shear pathways for controlled plastic strain induced PT kinetics. With development of rotational diamond anvil cell (RDAC) [3] and availability of high-brilliance synchrotron sources, such *in situ* studies are gaining much interest these days with potential applications to condensed matter physics, geophysics and mechanochemistry [2,4]. Besides synchrotron X-ray diffraction, these *in situ* investigations also need to be complemented with laboratory based Raman and ruby fluorescence spectroscopy for accurate quantitative analysis. Recently developed digital image correlation based displacement field mapping methodology [5] is another important *in situ* measurement providing information about plastic deformation of sample and friction conditions at sample-anvil contact surface. These inputs are needed as boundary conditions for the macroscale finite element simulations of these processes. As a step forward, towards establishing RDAC based *in situ* investigations of plastic strain induced phase transitions at BARC, we have developed a customized confocal micro-Raman setup, integrated with magnified ruby fluorescence imaging optics. This setup can be used for obtaining heterogeneous elastic-plastic stress-strain field in sample. Subsequent sections describe the salient features of the setup validated with a few benchmark measurements.

OPTICAL LAYOUT

A confocal micro-Raman system is configured around Shamrock 500i spectrometer with Andor Newton 940 CCD detector. A 100 mW CW 532 nm DPSS-SLM laser is used as an excitation source. To enhance the capability of setup for recording low-wavenumber excitations down to 10 cm^{-1} , we have used OptiGrate volume Bragg grating filters to eliminate Rayleigh line. The system is also equipped with a 405 nm diode laser for ruby fluorescence excitation. The optical alignment of this laser is such that it illuminates entire culet. For recording ruby fluorescence image of the ruby particles loaded along with sample in RDAC, a CMOS camera based 10x magnification viewing arrangement is aligned in the setup with a combination of long-pass and short-pass filters to select a spectral range of 650 nm to 750 nm. With a white LED illuminator, the same arrangement is also used for viewing and sample alignment. The viewing arrangement and 405 nm laser have been placed at both sides of sample stage for displacement field measurements at

both side of sample surface. For precise sample alignment and scanning Raman/ruby fluorescence measurements we are using precision motorized XYZ stages. Fig. 1 shows the optical arrangement of the setup.

Depth resolution of the system depends on the pinhole of confocal optical arrangement. We have used a pinhole of diameter $\sim 50 \mu\text{m}$ which provides a spatial and depth resolution of $\sim 2 \mu\text{m}$ and $40 \mu\text{m}$, respectively. This also eliminates signal from unwanted regions. In some experiments where Raman scattering is weak or samples are under extreme conditions and signal loss is critical, we use a pinhole of diameter $300 \mu\text{m}$ pinhole, providing optimal balance between confocal discrimination and signal throughput.

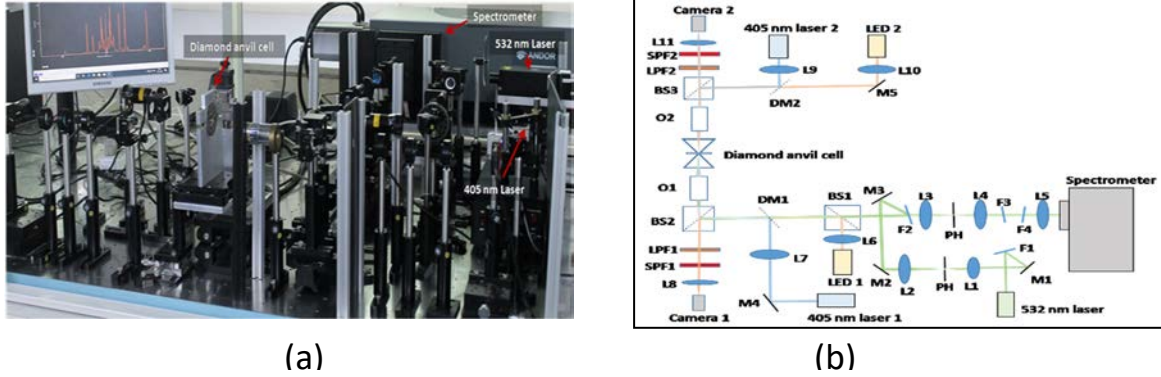


FIGURE 1: Confocal micro-Raman system (a). Optical layout of confocal micro-Raman system (b). F1-F4 are the OptiGrade volume Bragg grating Raman filter set; L1-L11 are achromat lenses; M1-M5 are optical mirrors; DM1 and DM2 are dichroic mirrors; BS1-BS3 are beam splitters; LPF1 and LPF2 are 650 nm long pass filters; SPF1 and SPF2 are 750 nm short pass filters; O1 and O2 are objective lenses; and LED is the white light LED source.

EXPERIMENTAL DETAILS AND RESULTS

For comparing pressure estimations using diamond Raman piezometry [6] and ruby fluorescence [7] methods, fine ruby particles of size $\sim 5 \mu\text{m}$ along with silicone oil as pressure transmitting medium was loaded in a sample chamber in DAC. The sample chamber was prepared by drilling hole of diameter $\sim 200 \mu\text{m}$ in a pre-indented steel gasket. The DAC was loaded to achieve pressures up to $\sim 20 \text{ GPa}$ in steps of $\sim 2 \text{ GPa}$. At each step ruby fluorescence and diamond Raman peak data was recorded. As diamond is under quite heterogeneous stress condition, from nearly no strain to maximum strain at sample anvil contact surface, normal stress in sample is estimated using the inflection point of the edge of diamond Raman peak. As can be seen in Fig. 2 (a), both diamond Raman edge and ruby fluorescence method provide very close, within 0.1 GPa pressure estimates in DAC.

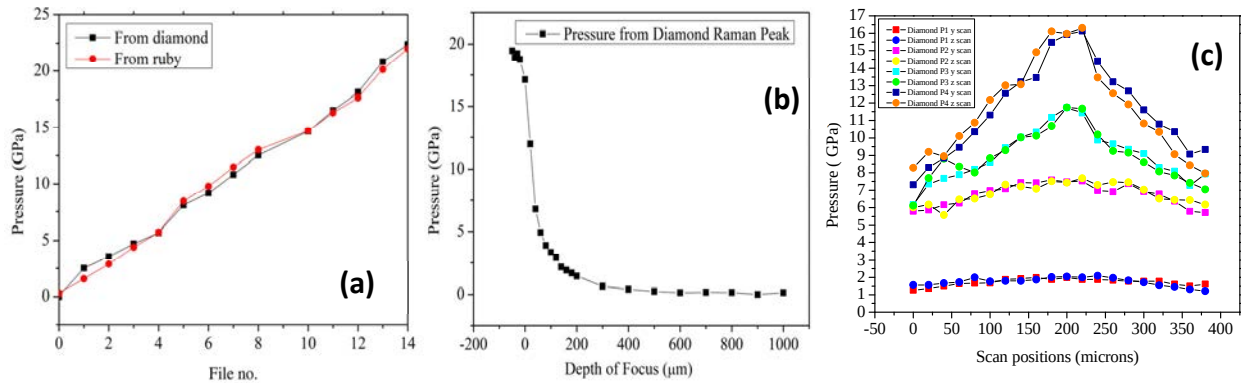


FIGURE 2. Comparison of ruby and diamond pressure calibration (a) Stress heterogeneities with depth of diamond (b) and surface of diamond culet (c)

To check depth-resolution and spatial-resolution of the system, pressure heterogeneities have been measured using diamond Raman edge method. The anvil was scanned along depth in the diamond as well as across anvil culet surface and diamond Raman data was recorded. For depth resolved study, diamond Raman data was recorded at $\sim 20 \text{ GPa}$ pressure at sample, whereas for radial profile study of pressure across culet, scanning diamond Raman data was

recorded at different load conditions along two orthogonal directions. Fig. 2 (b) shows the depth profile of pressure. Here 0 depth corresponds sample-anvil contact surface. Fig. 2 (c) shows pressure profiles across DAC culet at different load conditions. Nearly similar profiles along orthogonal diameters of culet confirm axial symmetry of stress environment in DAC.

To demonstrate ruby fluorescence imaging and spatially resolved data collection capabilities of the setup, a 2D ruby fluorescence scanning data was recorded around a ruby particle of size $\sim 20\ \mu\text{m}$. The data was recorded over a grid of $70\ \mu\text{m} \times 70\ \mu\text{m}$ in steps of $2\ \mu\text{m}$. Fig. 3 shows the fluorescence image of the ruby particle and the intensity map of ruby fluorescence peak. Both the methods give nearly similar size of the ruby particle confirming high spatial resolution of the setup. The spatial resolution of the ruby fluorescence imaging is diffraction limited and is $\sim 1\ \mu\text{m}$ which is suitable for displacement field measurements.

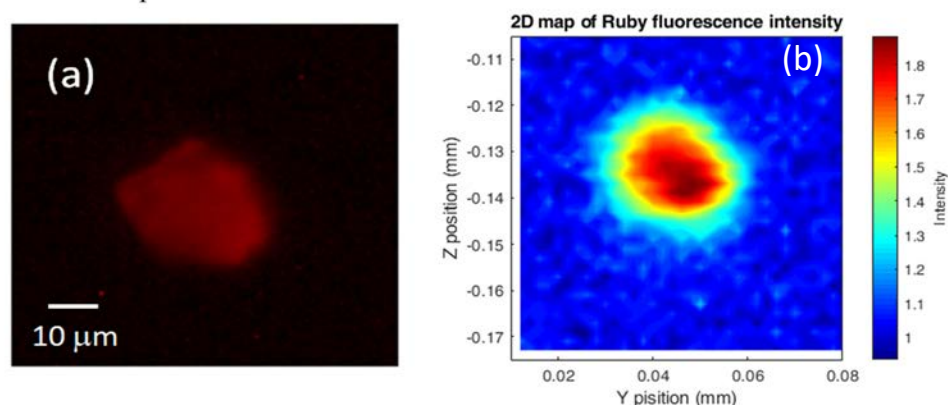


FIGURE 3. Ruby fluorescence image using 405 nm laser (a) and 2D map of ruby fluorescence intensity (b)

CONCLUSION

A depth-resolved and spatial-resolved experimental setup has been developed for Raman spectroscopy and displacement field measurements in DAC and RDAC at BARC. Spectral resolution of $\sim 2\ \text{cm}^{-1}$, spatial resolution of $\sim 2\ \mu\text{m}$ and depth resolution of $\sim 40\ \mu\text{m}$ have been achieved with a $50\ \mu\text{m}$ pinhole in the confocal optical arrangement. Using this facility, low wave number Raman mode scan be recorded down to $10\ \text{cm}^{-1}$.

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Non-Volatile and Digital Memristive Switching in Solution Synthesized Nanostructured VO₂ Thin Film-Based Metal-Insulator-Metal (MIM) Devices

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Abstract. In this study, we demonstrate the resistive switching of solution-based VO₂ thin film device under the influence of bias voltage. Fabrication and characterization of Ag/VO₂/SiO₂/Si metal-insulator-metal (MIM) devices is described here where VO₂ is synthesized using sol-gel technique. Further, x-ray diffraction studies indicate crystalline structure of VO₂ thin film with (011) and (022) monoclinic planes. XPS spectra of the VO₂ thin film shows presence of V⁴⁺ and V³⁺ states at room temperature. A two order of binary threshold switching is found when the voltage sweeps from 0 V → 15 V → -15 V → 0 V. A finite current in the *I-V* characteristics observed for the devices at zero voltage bias proves its non-volatile properties. The XPS data indicates that the threshold switching is probably originates from a mixed contribution of oxygen vacancy and Joule heating effect.

INTRODUCTION

Resistive switching devices have garnered immense attention as promising candidates for next-generation non-volatile memories, neuromorphic computing, and logic applications due to their simple architecture, high scalability, and low power consumption [1, 2]. Among various materials explored for resistive switching, transition metal oxides have emerged as prominent contenders owing to their diverse electronic states and defect-driven switching mechanisms. The nonlinear *I-V* response of correlated materials is of great interest for advanced electronic devices, a fact underscored by the discovery of memristors [2]. In particular, VO₂ is highly attractive due to its reversible semiconductor-metal transition (SMT) at ~ 68 °C associated with a sharp change in electrical conductivity and a rich interplay between electronic correlations and structural transformations [3, 4]. This unique characteristic of VO₂ provides an opportunity to exploit its correlated electronic states for memristive applications, enabling both analog and digital resistive switching modes. Memristive behavior in VO₂ thin films has typically been demonstrated using sophisticated techniques such as pulsed laser deposition, sputtering, molecular beam epitaxy etc. Although these approaches produce high-quality films, they are often complex, costly and less compatible with large-area, flexible substrates [4]. Solution-based synthesis routes offer an attractive alternative due to their low cost, scalability and tunable nanostructure formation, which can significantly influence defect states and ion migration, key factors in resistive switching phenomena. The epitaxial integration of high-quality VO₂ thin films with silicon substrates represents a critical advancement towards the realization of VO₂-based ultrafast electronic switching devices.

EXPERIMENTAL SECTION

The precursor solution for deposition of VO₂ thin film was prepared by utilizing a sol-gel approach as portrayed [5]. The minor change was made by utilizing polyvinyl pyrrolidone (PVP; K30) as antecedents for the film-shaping advertiser replacing polyvinyl alcohol. The *p*-type silicon wafer cut into small pieces and duly thermally oxidized to get a 10 nm-thick SiO₂ layer, were used as substrate to grow VO₂ thin film. At the beginning, Si substrate was ultrasonically cleaned with soap solution, acetone and isopropanol for 30 min in each step. After completion of one cleaning step, the substrates were rinsed in deionized water for two min. Finally, the cleaned and dried substrates were exposed to O₂ plasma to eliminate lingering hydrocarbon from the surface of the substrates and make it hydrophilic. Precursor solutions were then deposited using spin coater at 3500 rotation/min for 40 sec and then dried on hot plate at 90 °C for 5 min to remove excessive solvent and moisture content. A 200 nm thin Ag film was then deposited on

VO₂ thin film using electron beam deposition system and then patterned to 400×400 μm² Ag-electrodes to get MIM structure.

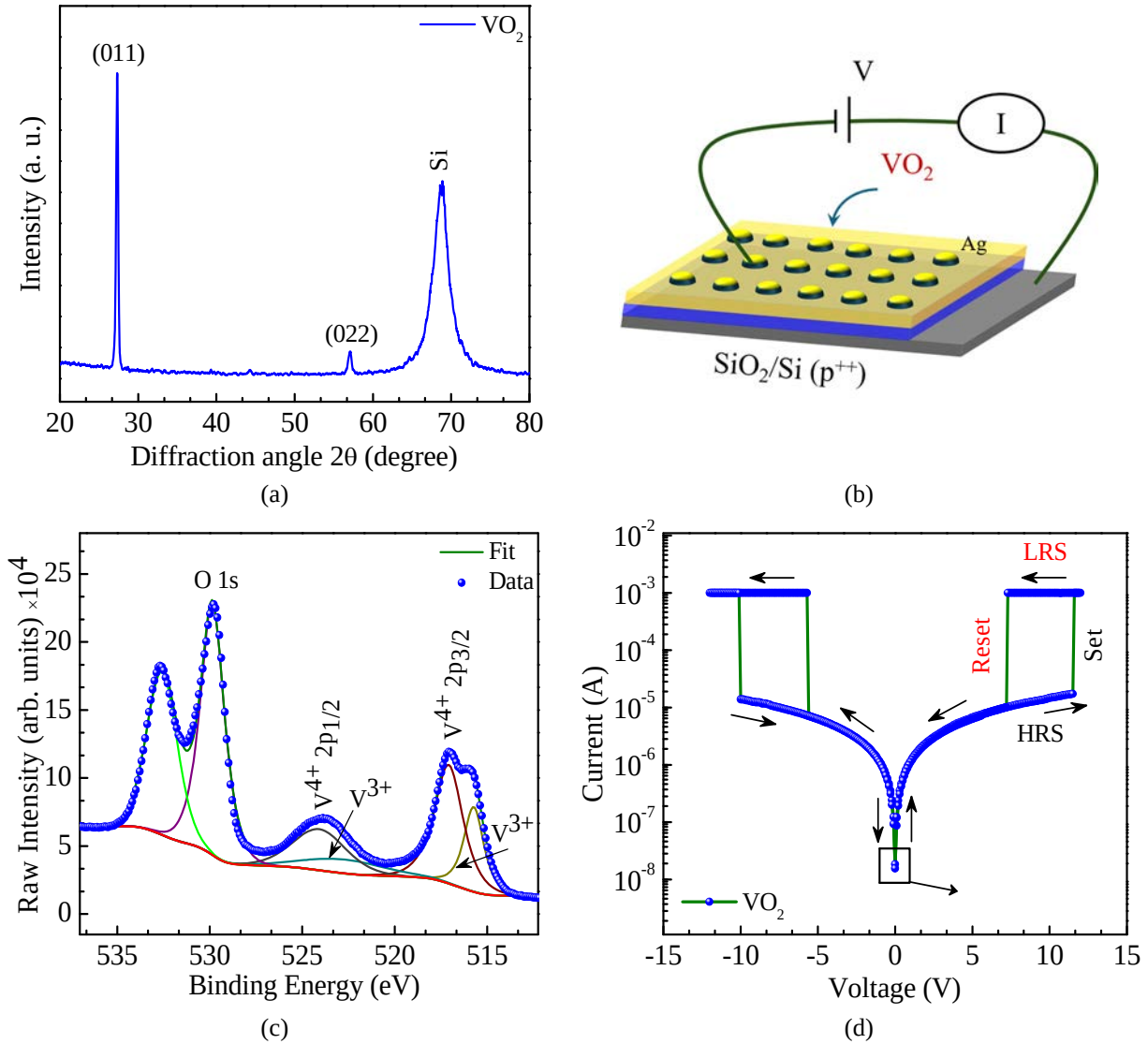


FIGURE 1. (a) XRD pattern of VO₂ thin film annealed at 823 K, (b) MIM device structure, (c) XPS spectrum of VO₂ thin film, (d) Non-volatile and digital memristive switching characteristics of VO₂ thin film at room temperature.

RESULT AND DISCUSSION

The x-ray diffraction (XRD) profile of the VO₂ thin film deposited on a Si substrate is presented in Fig. 1(a). The diffraction pattern reveals distinct crystalline peaks demonstrating a well-defined polycrystalline structure of the thin film with high phase purity. The most intense diffraction feature is observed at $2\theta = 27.32^\circ$ which corresponds to (011) reflection of monoclinic phase of VO₂ thin film (JCPDS No. 01-082-0661). This prominent peak confirms the successful formation of the thermodynamically stable VO₂ phase. Another noticeable peak is detected around $2\theta = 57.1^\circ$ attributing to the higher-order (022) reflections of VO₂ thin film. Additionally, the sharp and intense peak at $2\theta = 68.8^\circ$ originates from the underneath Si substrate. Fig. 1(b) shows a schematic view of MIM device. Fig. 1(c) depicts deconvoluted high-resolution XPS spectra of the VO₂ thin film where the valence states of vanadium and oxygen are identified along with the phase composition of the thin film. The V 2p spectrum exhibits a characteristic doublet

corresponding to $V 2p_{3/2}$ and $V 2p_{1/2}$ components, observed at binding energies of 517.08 and 524.18 eV, respectively, consistent with the V^{4+} oxidation state with the spin-orbit coupling data [6]. The O 1s spectrum shows two distinct peaks at 529.78 eV, associated with lattice oxygen in V-O bonds, and another at 532.68 eV attributed to a mixture of oxygen vacancy and surface-adsorbed molecular species such as H_2O . Additionally, a satellite features indicative of V_2O_3 are present in the V 2p region suggesting a trace amount of V^{3+} species. Overall, the XPS analysis confirms VO_2 as the dominant phase, with a minor contribution from V_2O_3 [7].

VO_2 thin film is studied due to its unique Joule-heating mechanism-based switching that provides reliable operation of memristor [8]. The I - V sweep of the MIM device as indicated in Fig. 1(d) show abrupt, threshold resistive switching behaviour between a high-resistance state (HRS) and a low-resistance state (LRS) in both the cycles where dc voltage sweeps of $0\text{ V} \rightarrow 15\text{ V} \rightarrow -15\text{ V} \rightarrow 0\text{ V}$ is applied across the electrodes at room temperature. When the voltage is swept to positive values (right branch), the device “sets” ($HRS \rightarrow LRS$) at a threshold voltage, V_{set} at 11.5 V. The threshold switching shows a symmetric I - V curve with a nonlinear switching behavior and without initial electroforming operation [9]. When the polarity is reversed the device again changes its resistance state from $HRS \rightarrow LRS$ at a threshold voltage of -5.6 V and reaches HRS again upon increase in voltage. Therefore, the switching is bipolar and symmetric in nature. The zoomed figure, shown at the inset of Fig. 1(d) shows the current does not return to its zero value at zero voltage bias indicating the non-volatile nature of the device. Further, I - V characteristics follow a hysteresis path and making a loop without remembering its path during ascending and descending voltage sweep. The XPS data indicates that the threshold switching is probably originates from a mixed contribution of oxygen vacancy and Joule heating effect.

CONCLUSION

We successfully demonstrate the non-volatile and threshold resistive switching behaviour of VO_2 -based MIM devices with $\sim 10^2$ ON/OFF ratio. It is observed that sufficiently large electric field/Joule heating drives VO_2 locally from its semiconducting to more conductive LRS state digitally (Set) and reduction of the electric field disrupts the conductive path bringing the device back to HRS (Reset). The non-zero value of current is retained at zero voltage bias indicating the non-volatile memory behaviour of the device. XPS studies confirm the contribution of oxygen vacancy and Joule heating effect on the threshold switching of the devices.

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Study of host to activator energy transfer in ZrO_2 : Sm^{3+} phosphor through photoluminescence analysis

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Abstract. This work explores the development and characterization of ZrO_2 incorporated with Sm^{3+} ions at different doping levels, synthesized using a solution combustion technique. The phase properties of the produced phosphor materials were investigated using the XRD technique, which shows that monoclinic phase of ZrO_2 predominates with a tiny peak of the tetragonal phase in doped samples. PL spectra of ZrO_2 recorded at 285 nm excitation shows strong emission in the range of 400 – 650 nm, while some additional emission bands due to transitions $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ of Sm^{3+} ions, in doped samples. Beyond 0.3 mol% doping, a concentration quenching effect of Sm^{3+} ions was seen. PL data of the samples further utilized to study the energy transfer from ZrO_2 to Sm^{3+} ions.

INTRODUCTION

Phosphor materials, crafted from inorganic compounds intentionally infused with impurity ions like those of rare earth elements and transition metals, find widespread use across a range of fields, from solid-state lighting and plasma display panels to non-contact optical temperature sensing, medical imaging, and beyond[1]. Zirconium oxide is widely regarded as a promising material for optical applications due to its high hardness, optical transparency, and high refractive index. Its exceptional chemical and photochemical stability, along with superior mechanical, electrical, thermal, and optical properties, makes it a highly suitable candidate for use in photonic technologies. Additionally, ZrO_2 has a wide band gap (5 eV) and low phonon energy of about 470 cm^{-1} , which decrease the probability of non-radiative transitions[2]. ZrO_2 is also a self-activating fluorescent material and exhibits a blue-white emission. With maxima between 475 nm – 500 nm when excited below its band gap energy (5 eV), which provides compelling evidence that the emission from ZrO_2 is genuinely caused by defect energy levels within the ZrO_2 band gap[3]. Moreover, ZrO_2 can also transfer energy to most of rare earth ions, as the excitation spectra of some of rare earth ions strongly correlates with the emission spectra of ZrO_2 . In this work, we have synthesized ZrO_2 doped with various concentrations of Sm^{3+} ions using the solution combustion synthesis method, followed by an in-depth study of its phase structure. Photoluminescence study of synthesized samples has been done to provide experimental evidence of non-radiative energy transfer between monoclinic ZrO_2 and Sm^{3+} ions.

MATERIALS AND SYNTHESIS

To synthesize ZrO_2 : xmol% Sm^{3+} (where x = 0.1, 0.3, 0.5, 0.7, and 0.9), a solution combustion method assisted by urea was employed. Initially, stoichiometric quantities of $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and NH_2CONH_2 were dissolved in 20 mL of deionized water, stirred at 80°C to form a slurry and then placed in a preheated muffle furnace at 600°C for 15 minutes. The obtained fluffy powder was then crushed and transferred to an alumina crucible and annealed at 1200°C for 2 hours, and finally the annealed powder was crushed again to ensure uniformity, making it suitable for further research.

XRD ANALYSIS

ZrO_2 and $\text{Zr}_{(1-x)}\text{Sm}_x\text{O}_2$ (x= 0.1 to 0.9 mol%) phosphors were phase characterized by using the X-ray diffraction pattern as shown in FIGURE 1(i). As can be seen in the figure, the diffraction pattern of undoped ZrO_2 correlate to

the standard monoclinic phase of ZrO_2 (Ref. Code: 00-007-0343). While, the diffraction pattern of $\text{ZrO}_2 : x\%\text{Sm}^{3+}$ consist of small diffraction peak of the tetragonal phase of ZrO_2 (Ref. Code: 01-079-1764) along with the major monoclinic phase. The phase transition of ZrO_2 from pure monoclinic phase to mixed monoclinic and tetragonal phase is because of the generation of oxygen vacancies caused by the substitution of Zr^{4+} by Sm^{3+} ions for charge compensation. The oxygen vacancy concentration and consequently, tetragonal phase peak intensity both increases with higher Sm^{3+} doping levels[4]. Additionally, the generation of oxygen vacancies could lead to ionic rearrangement and modification of phase structure from monoclinic to tetragonal or mixed monoclinic and tetragonal phase[4]. Literature suggests that intermediate doping of trivalent rare earth ions in ZrO_2 leads to a mix of monoclinic and tetragonal phase. To confirm the crystal structure and assess the doping effect, Rietveld refinement was performed on pristine and Sm^{3+} -doped ZrO_2 using Full Prof software, as shown in the refinement profiles in FIGURE 1(ii).

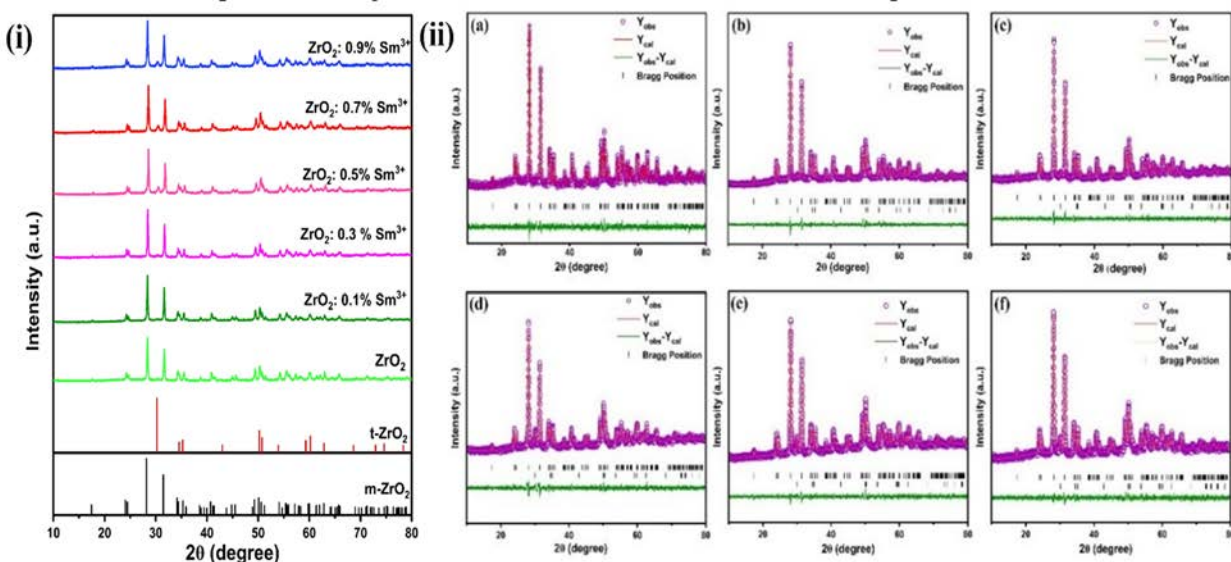


FIG 1. (i) XRD spectra of pristine- ZrO_2 and $\text{ZrO}_2: x\% \text{Sm}^{3+}$ ($x = 0.1, 0.3, 0.5, 0.7$, and 0.9), (ii) Rietveld refinement profile of (a) pristine- ZrO_2 , (b) $\text{ZrO}_2: 0.1\% \text{Sm}^{3+}$, (c) $\text{ZrO}_2: 0.3\% \text{Sm}^{3+}$, (d) $\text{ZrO}_2: 0.5\% \text{Sm}^{3+}$, (e) $\text{ZrO}_2: 0.7\% \text{Sm}^{3+}$, (f) $\text{ZrO}_2: 0.9\% \text{Sm}^{3+}$.

FTIR STUDY

FTIR spectra obtained for all the samples is depicted in FIGURE 2(i), which revealed a characteristic peak at 1105 cm^{-1} , attributed to C-O stretching vibration. The presence of this absorption peak may be due to the presence of traces of urea (NH_2CONH_2). Other characteristics absorption peaks observed at 3420 cm^{-1} , 514 cm^{-1} , 445 cm^{-1} , and 421 cm^{-1} are attributed to Zr-O vibrations in undoped and doped samples [5].

PHOTOLUMINESCENCE STUDY

The luminescence properties of $\text{ZrO}_2: x \text{ mol}\% \text{Sm}^{3+}$ were thoroughly studied, with the findings presented in FIGURE 2ii. The photoluminescence excitation of ZrO_2 lies in broad excitation range $238 \text{ nm} - 350 \text{ nm}$, peaking at 285 nm with a shoulder peak at 256 nm . FIGURE 2ii(a), presents the emission spectrum of pristine ZrO_2 and $\text{ZrO}_2: x\%\text{Sm}^{3+}$ ions (where, $x = 0.1, 0.3, 0.5, 0.7$, and 0.9), at 285 nm excitation. The m- ZrO_2 host exhibits blue-white emission with a broad band centered at 489 nm , consistent with reported studies. This blue luminescence is attributed to oxygen vacancy related defects. While, upon 285 nm excitation, Sm^{3+} doped m- ZrO_2 shows three sharp emission bands at 571 nm , 618 nm and 660 nm originating from $4f-4f$ transitions of Sm^{3+} ions viz: $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ and $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ were observed[5], along with the characteristic emission band of m- ZrO_2 , which strongly indicate an energy transfer from m- ZrO_2 to Sm^{3+} ions. The dependence of photoluminescence (PL) behaviors of $\text{ZrO}_2: x\% \text{Sm}^{3+}$ phosphor, excited at 285 nm , on Sm^{3+} doping concentration is also illustrated by FIGURE 2ii(a). As shown in FIGURE 2ii(b), ZrO_2 emission intensity decreases with increasing Sm^{3+} doping amount, while Sm^{3+} emission rises up to $0.3 \text{ mol}\%$ and then declines due to concentration beyond this level, illustrated in FIGURE 2ii(c). This inconsistent behavior of the change in PL intensity of ZrO_2 and Sm^{3+} ions with increasing doping concentration further validate

the energy transfer from ZrO_2 to Sm^{3+} ions in ZrO_2 : x% Sm^{3+} phosphor. Consequently, the following formula was used to assess the efficiency of the energy transfer between ZrO_2 and Sm^{3+} ions in order to quantitatively explain it.

$$\eta = 1 - \frac{I_s}{I_{s0}} \quad 1$$

Where, η represents the energy transfer efficiency and I_s and I_{s0} are the integrated emission intensities of ZrO_2 with and without Sm^{3+} ions, respectively. Such, that the energy transfer efficiency of ZrO_2 to Sm^{3+} ions, depending upon their concentrations is well illustrated in FIGURE 2ii(d).

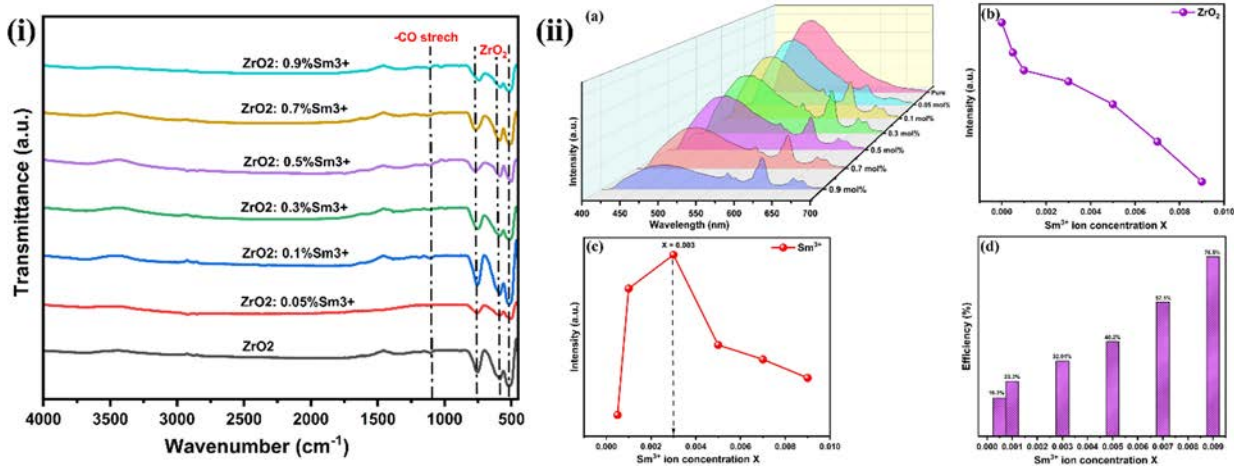


FIGURE 2. (i) FTIR spectra of pristine- ZrO_2 and ZrO_2 : x% Sm^{3+} ($x = 0.1, 0.3, 0.5, 0.7$, and 0.9), (ii) PL spectra of ZrO_2 : x% Sm^{3+} ions (a), plot of integrated emission intensity of ZrO_2 (b) and Sm^{3+} (c) versus the Sm^{3+} ions concentration, (d) bar graph representing the energy transfer efficiency from ZrO_2 to Sm^{3+} , based on Sm^{3+} ions content.

CONCLUSION

Pristine and Sm^{3+} doped ZrO_2 samples were synthesized via solution combustion method. XRD and Rietveld refinement confirmed a monoclinic phase in pristine ZrO_2 , while doped samples showed a predominant monoclinic phase with minor tetragonal phase. Photoluminescence analysis indicates energy transfer from ZrO_2 to Sm^{3+} ions.

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Lead-Free Cs₂AgBiBr₆-Based Self-Biased Photodetector via One-Step Vapor Deposition

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Abstract. We report the fabrication and characterization of a self-powered photodetector based on lead-free Cs₂AgBiBr₆ thin films synthesized via a one-step thermal vapor deposition method. The resulting films exhibit excellent phase purity, uniform grain morphology, and strong optical absorption. A vertical ITO/Cs₂AgBiBr₆/Ag device was constructed and evaluated under white-light illumination (0.5 mW/cm²). The device demonstrates a low dark current, clear rectifying behavior, and a significant photocurrent enhancement at zero bias, confirming effective internal electric field-driven carrier separation. The detector showed a rise and decay time of 125/350 ms with an on/off ratio of ~70. The calculated responsivity and detectivity were found to be $\sim 3.3 \times 10^{-3}$ A/W and $\sim 3.2 \times 10^{10}$ Jones, respectively, under zero bias. These results establish vapor-deposited Cs₂AgBiBr₆ as a promising, stable, and environmentally benign material for low-power optoelectronic applications.

INTRODUCTION

Organic halide perovskites are gaining attention for optoelectronic applications due to their tunable properties and low-temperature processability [1]. However, lead-based variants like MAPbI₃ and CsPbBr₃ pose challenges related to toxicity and instability [2]. Inorganic, lead-free double perovskites such as Cs₂AgBiBr₆ offer a promising alternative, combining environmental safety with excellent thermal and structural stability. With a cubic *Fm3m* structure and an indirect bandgap of ~2.2–2.3 eV, Cs₂AgBiBr₆ is suitable for visible-blind UV detection [3]. Its robust crystallinity, low ion migration, and suppressed dark current make it ideal for photodetectors [4]. However, the existing reports on In-alloyed Cs₂AgBiBr₆ rely on solution processing or grinding, which limit large-scale reproducibility and often result in non-uniform and defect-prone films.

In this work, we report a self-powered photodetector based on lead-free Cs₂AgBiBr₆ thin films synthesized through a one-step thermal vapor deposition process. The resulting films exhibited high phase purity, uniform morphology and stable optical properties. A vertical ITO/Cs₂AgBiBr₆/Ag device architecture was investigated, demonstrating low dark current, rectifying behavior, and a strong self-biased photoresponse under white-light illumination.

MATERIAL AND METHODS

The Cs₂AgBiBr₆ thin film (TF) was synthesized via one-step thermal vapor deposition technique. High purity CsBr, AgBr, and BiBr₃ nano powders, all procured from Sigma-Aldrich, were carefully weighed in 2:1:1.5 molar ratio and thermally co-evaporated from a Tungsten boat under a maintained pressure of $\sim 2 \times 10^{-5}$ mbar. Films were deposited onto pre-cleaned ITO-coated glass substrates at room temperature, with one side masked to preserve the ITO contact area. The as-deposited films were annealed at 150 °C inside a muffle furnace for 10 hrs to obtain the desired phase and remove residual precursors. For device fabrication, circular Ag top electrodes (area ~ 0.03 cm²) were deposited through a shadow mask onto the active film, forming an ITO/Cs₂AgBiBr₆/Ag vertical device structure.

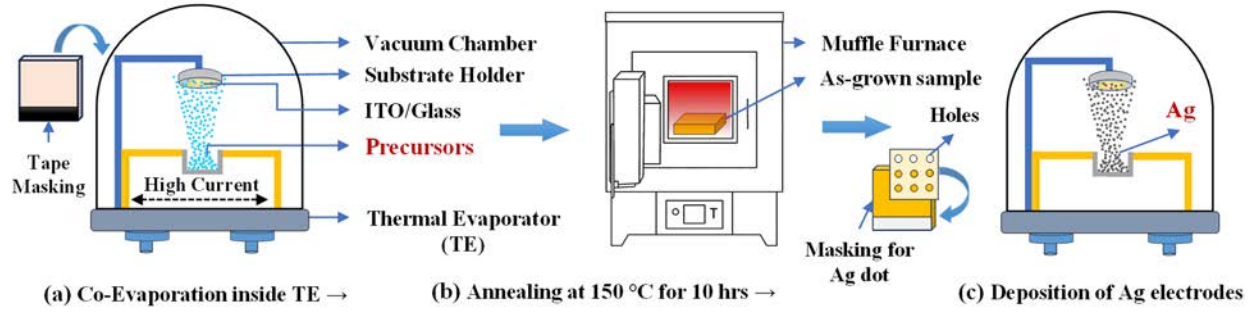


FIGURE 1. Process flow of the $\text{Cs}_2\text{AgBiBr}_6$ TF synthesis procedure.

RESULT AND DISCUSSION

Structure and Morphology

The crystalline structure of the vapor-deposited $\text{Cs}_2\text{AgBiBr}_6$ TFs was examined by Rigaku SmartLab X-ray diffractometer (XRD). As shown in **Fig. 2(a)**, the film exhibits prominent reflections at 2θ values of approximately 15.7° , 22.3° , 27.45° , 31.75° , 39.15° and 45.50° , which can be indexed to the (200), (220), (222), (400), (422) and (440) planes of a cubic $Fm\bar{3}m$ phase, consistent with the standard JCPDS card (No. 01-084-8699) for $\text{Cs}_2\text{AgBiBr}_6$ [4]. The asterisk (*) indicates the position of reflections from the side phases AgBr (PDF:00-001-0950) and $\text{Cs}_3\text{Bi}_2\text{Br}_9$ (PDF:00-044-0714), respectively. The sharp and well-defined diffraction peaks further suggest good crystallinity and long-range ordering, which are critical for efficient charge transport in optoelectronic devices.

The surface morphology of the film, observed via Carl ZEISS Sigma field emission scanning electron microscopy (FESEM), is presented in **Fig. 2(b)**. The cross-sectional image revealed a compact film of thickness $\sim 1.2 \mu\text{m}$. The inset micrograph reveals a dense and continuous film composed of uniformly distributed polycrystalline grains with average lateral sizes of approximately 300–350 nm, as shown in the histogram in **Fig. 2(c)**. The compact grain structure with minimal voids or pinholes reflects the effectiveness of the one-step vapor deposition method in achieving uniform film coverage. Such a morphology is favorable for minimizing grain boundary recombination and enhancing the photoresponse stability of the device.

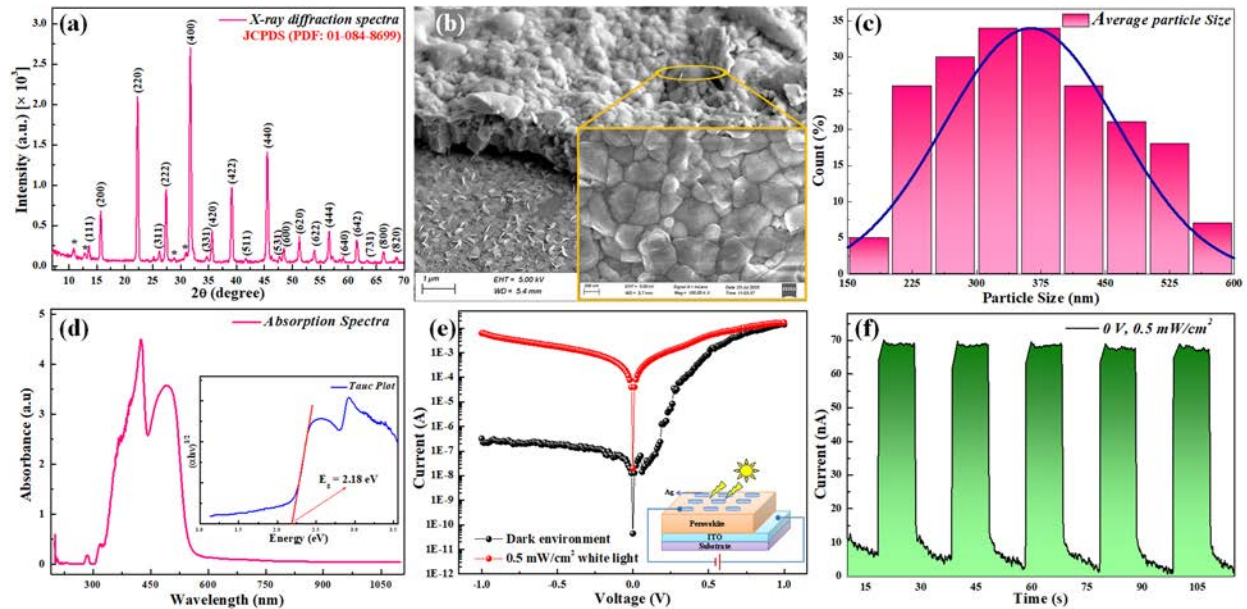


FIGURE 2. (a) XRD pattern of the $\text{Cs}_2\text{AgBiBr}_6$ film. (b) Cross-sectional FESEM image of the synthesized $\text{Cs}_2\text{AgBiBr}_6$ film [top view of the film surface is shown in the inset] (c) Histogram of average particle size distribution evaluated from FESEM top view image. (d) Absorption spectra of the $\text{Cs}_2\text{AgBiBr}_6$ film. [Tauc plot for bandgap estimation in the inset] (e) I-V characteristics of the device under dark and white light illumination. [Device architecture in the inset] (f) Temporal response of the device at 0 V.

Optical Characterization

The optical properties of the vapor-deposited Cs₂AgBiBr₆ TFs were investigated using PerkinElmer Lambda 365+ UV–Visible spectrophotometer in the 200 nm – 1100 nm range. The absorbance spectrum, shown in **Fig. 2(c)**, exhibited a sharp absorption edge near 555 nm, corresponding to an indirect optical bandgap of ~2.18 eV, calculated using Tauc's relation for indirect transitions. This value aligns well with previously reported results for Cs₂AgBiBr₆, confirming the material's suitability for visible-light detection and its intrinsic lead-free semiconducting behavior [4].

Device Response

To evaluate the device response of the ITO/Cs₂AgBiBr₆/Ag device, the positive terminal of a Keithley 2450 source meter was connected to the ITO and the negative terminal to the Ag electrode, as illustrated in the **inset of Fig. 2(d)**. The current–voltage (I–V) characteristics, measured under dark and white-light illumination (0.5 mW/cm²), displayed typical rectifying behaviour, as shown in **Fig. 2(d)**. Under illumination, the photocurrent at –1 V increased by nearly four orders of magnitude compared to the dark current (~10^{–6} A vs. ~10^{–2} A), demonstrating a strong photoresponse and low recombination losses.

Temporal switching measurements at 0 V bias demonstrated sharp rise and decay edges with excellent repeatability, which is indicative of efficient photocarrier dynamics. [**Fig 2(e)**]. The photocurrent arises from the separation and collection of photogenerated carriers by the built-in electric field directed from ITO to Cs₂AgBiBr₆ TF, facilitating self-powered operation. The response time of the device was evaluated to be 125 ms/350 ms, with an on/off ratio of ~70, which is comparable to other reported values in the literature [4–5]. Additionally, the responsivity (*R*) and detectivity (*D*) of the device were calculated using the following equation:

$$R = \frac{I_{ph}}{A \times P} \quad \& \quad D = \sqrt{\frac{A}{2 \times e \times I_{dark}}} R \quad (1)$$

where, *I_{ph}* is the photocurrent (~50 nA), *A* is the active device area (0.03 cm²); *P* is the optical power of the incident light (0.5 mW/cm²); *e* is the electronic charge (1.602 × 10^{–19} C); and *I_{dark}* is the device dark current (~2 nA). Equation 1 yields a moderate *R* of ~3.3 × 10^{–3} A/W and a high *D* of ~3.2 × 10¹⁰ Jones, highlighting the material's ability to deliver high-sensitivity detection under self-biased conditions.

Conclusion

In summary, a self-biased photodetector based on vapor-deposited lead-free Cs₂AgBiBr₆ thin films was successfully demonstrated. The synthesis method produced dense, polycrystalline films with high phase purity and favorable optical properties. The device exhibited stable operation under ambient conditions, low dark current, and a strong photoresponse even without external bias. Fast and repeatable switching behavior confirmed the film's low trap density and efficient built-in electric field-assisted carrier extraction. Despite a moderate responsivity, the device exhibits high detectivity and stable self-powered functionality, underscoring its suitability for eco-friendly and energy-efficient photodetection applications. These findings reinforce the promise of vapor-deposited Cs₂AgBiBr₆ as a scalable, lead-free candidate for next-generation optoelectronic technologies.

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Lead-Free $\text{Cs}_3\text{Bi}_2\text{I}_9$ -Based Resistive Switching Memory Device for Artificial Synapse Emulation

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Abstract. Lead-free halide perovskite-based resistive switching memory devices (RSMDs) are promising for next-generation memory and neuromorphic systems due to their straightforward fabrication and non-toxic nature. In this study, we report a lead-free RSMD based on $\text{Cs}_3\text{Bi}_2\text{I}_9$ thin films (TFs), fabricated via low-cost, solution-processed spin-coating method. The X-ray diffraction spectra revealed a phase-pure $\text{Cs}_3\text{Bi}_2\text{I}_9$ with high crystallinity and an indirect bandgap of ~ 2.22 eV was estimated from the optical absorption spectra. The Al/ $\text{Cs}_3\text{Bi}_2\text{I}_9$ /ITO device exhibits stable bipolar switching with good ON/OFF ratio (~ 10) and excellent endurance over 500 consecutive cycles. In addition to the memory functions, the device successfully emulates key synaptic behaviors under various electrical pulse stimulations. These results highlight the potential of $\text{Cs}_3\text{Bi}_2\text{I}_9$ material in mimicking biological synapses, establishing it as a promising candidate for next-generation non-volatile memory and artificial synaptic devices.

INTRODUCTION

Next-generation non-volatile memory devices got significant attention to overcome the bottlenecks of traditional von Neumann architecture. Various new types of memory devices emerging including phase-change memory (PCM), magnetic random access memory (MRAM), ferroelectric random access memory (FeRAM) and most recently, the resistive random access memory (ReRAM) [1]. Among these, ReRAMs got significant attention due to their simple structure, low operating voltage, high ON/OFF ratio, long term data retention power and potential for mimicking biological synapses. Inspired by the complex architecture and efficiency of human brain, artificial synapses are the building blocks for implementing brain like computing systems [2]. Recently, lead free all-inorganic halide perovskites have emerged as alternatives for conventional lead-based systems.

In this work, we systematically developed lead-free $\text{Cs}_3\text{Bi}_2\text{I}_9$ TF based RSMD and explore its artificial synaptic behaviours under electrical pulse stimulation. The device exhibits stable bipolar switching with excellent endurance over 500 cycles. Furthermore, it demonstrates key synaptic features such as spike width dependent plasticity (SWDP), spike number dependent plasticity (SNDP), paired pulsed facilitation (PPF) highlighting its potential as an artificial synaptic device for future neuromorphic and brain-inspired computing systems.

EXPERIMENTAL

Indium Tin Oxide (ITO) coated glass substrates were cleaned through sequential ultrasonication in acetone, ethanol, and deionized water, each for 15 minutes, followed by drying in ambient air. The precursor solution was prepared by dissolving a 3:1 molar ratio of Cesium Iodide (CsI, 99.99%, SRL) and Bismuth Iodide (BiI_3 , >98%, TCI) in a mixed solvent system of Dimethylformamide (DMF) and Dimethyl Sulfoxide (DMSO) (1:3 v/v). The solution was stirred at 65 °C for seven hours to ensure complete dissolution. The prepared solution was spin-coated onto ITO-coated glass substrates, and the films were subsequently annealed at 120 °C for 15 minutes to obtain uniform, polycrystalline $\text{Cs}_3\text{Bi}_2\text{I}_9$ TFs. Finally, Aluminium (Al) top electrodes were deposited using a shadow mask in a thermal evaporator vacuum chamber at $\sim 10^{-5}$ mbar.

RESULTS AND DISCUSSION

Material characterizations

To examine the crystallinity of $\text{Cs}_3\text{Bi}_2\text{I}_9$ TFs, the X-ray diffraction (XRD) measurement was performed as shown in Fig. 1(a). Dominant peaks were observed at 12.01° , 25.24° , 27.59° , 29.7° , and 32.4° corresponding to (100), (006), (203), (204) and (205) planes of hexagonal phase (space group $P6_3/mmc$) respectively which are consistent with previous reports [3, 4]. To evaluate the optical absorption, UV-Vis measurement was done for the films, Fig. 1(b). The absorption edge appears at ~ 559 nm and the optical band gap of ~ 2.22 eV is calculated from Tauc plot, in good agreement with previous report [4].

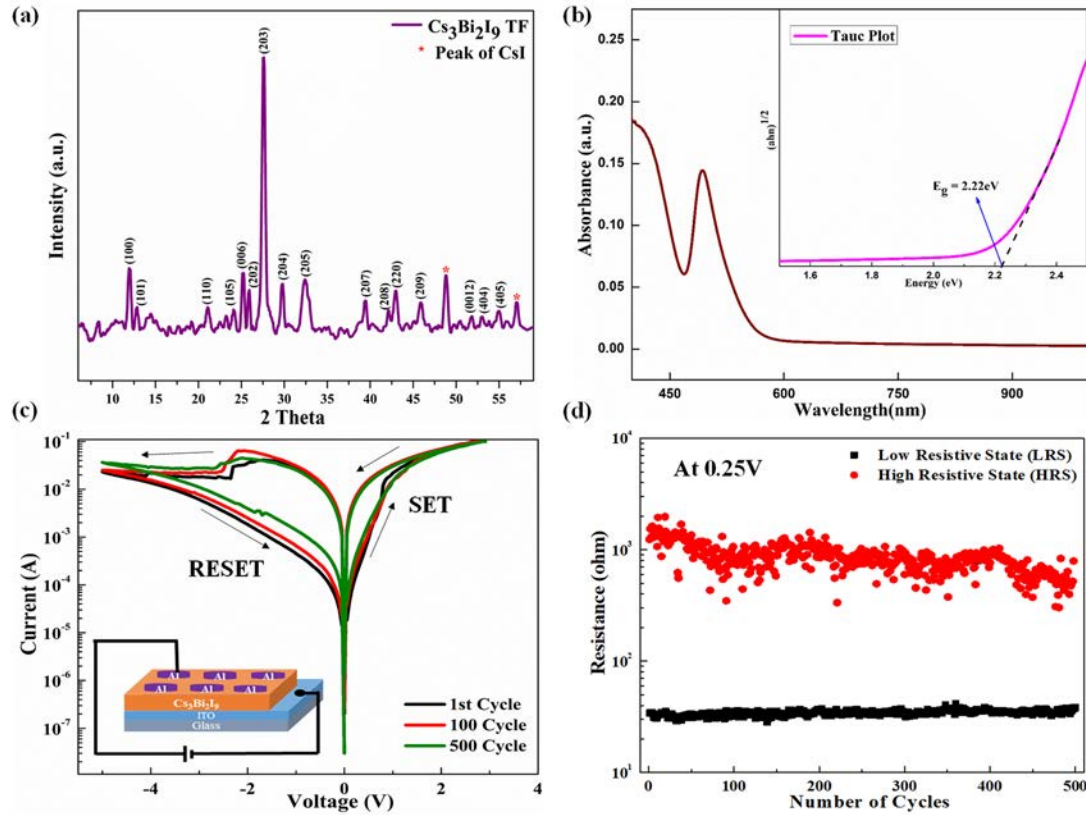


FIGURE 1. (a) XRD patterns of $\text{Cs}_3\text{Bi}_2\text{I}_9$ TF. (b) Absorption spectra of $\text{Cs}_3\text{Bi}_2\text{I}_9$ TFs (inset: Tauc plot). (c) Resistive switching (RS) characteristics of Al/ $\text{Cs}_3\text{Bi}_2\text{I}_9$ /ITO device. (d) Endurance analysis at 0.25 V.

Resistive switching characteristics:

The current (I) – voltage (V) characteristics and endurance measurements of Al/ $\text{Cs}_3\text{Bi}_2\text{I}_9$ /ITO device measured at room temperature is shown in Fig. 1(c, d). The device demonstrated stable bipolar resistive switching when subjected to scanning voltage of $0 \rightarrow 3 \rightarrow 0 \rightarrow -5 \rightarrow 0$. During the forward voltage sweep from 0 to 3V, device remained in the low current stage, corresponding to high resistive state (HRS) and the gradual increase of current make the transition to the low resistive stage (LRS), termed as SET process. The device maintained the LRS when voltage swept in the reverse direction (3 to 0V). Upon applying negative voltage sweep from 0 to -5V, the current drops, indicating a transition back to HRS- termed as RESET process. The device maintains an ON/OFF ratio greater than 10 and reliable endurance over 500 cycle while retaining 37.25% of its initial memory window, highlighting its potential for next generation non-volatile memory application.

Artificial synaptic emulation:

To investigate the synaptic behaviour of Al/Cs₃Bi₂I₉/ITO device, conductance modulation study was performed under different repetitive voltage pulses. Key synaptic functions such as SWDP, SNDP and PPF was observed under different pulse protocols. From the Fig. 2(a), Fig. 2(b), it was found that pulse widths and pulse numbers, both impacts greatly on the conductance values. As the pulse width was increased from 185ms to 370ms at a fixed amplitude (2V), conductance value increased by 2.94%. Moreover, as the number of pulses increases conductance value was also improved. When two consecutive pulses (1V, 370ms) are applied to the device, the conductance value for second pulse (A_2) is greater than the conductance value for first pulse (A_1), demonstrating the PPF behaviour analogous to the biological synapses, maintaining PPF ratio of 114.79%.

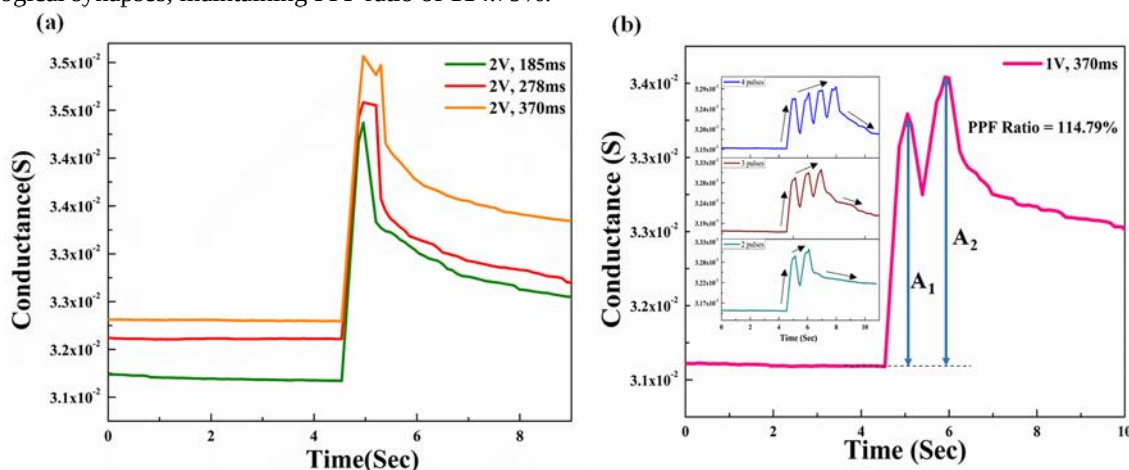


FIGURE 2. Synaptic characteristic of the Al/Cs₃Bi₂I₉/ITO device: (a) SWDP (b) Conductance responses (inset: SNDP)

CONCLUSION

In summary, we successfully fabricated high quality Cs₃Bi₂I₉ TF with one-step spin-coating method, as confirmed by the XRD. The Al/Cs₃Bi₂I₉/ITO device showcased stable bipolar resistive switching behaviour with ON/OFF ratio always greater than 10 and endurance over 500 cycles, confirming its suitability for next generation non-volatile memory devices. Moreover, the device successfully mimics key synaptic behaviours such as SWDP, SNDP, PPF under pulse stimulations which highlights its promise as a lead-free, low cost and brain-inspired memory device for future artificial synaptic devices.

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Characterization of neutron beam at DURGA facility, DHRUVA reactor by absolute measurement techniques

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Abstract. The paper presents the absolute methodology for determination of neutron fluence rate at the irradiation position of DURGA facility, DHRUVA reactor (40 MW_{th} power) using standard gold foil activation technique. An absolute standard, $4\pi\beta\gamma$ coincidence system along with a HPGe spectrometer was used for the determination of induced activity. Based on the cadmium difference method, the ‘Cadmium Ratio’ was found to be (9.62 ± 0.51) . The thermal and epithermal neutron fluence rate were found to be $(1.18 \pm 0.02) \times 10^6$ and $(1.33 \pm 0.07) \times 10^4$ n/cm²/s, respectively. The values will be extremely useful for the nationwide utilization of the facility for various nuclear and solid-state physics applications.

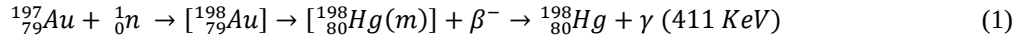
INTRODUCTION

The availability of a high-efficiency gamma-ray spectrometers using multiple detectors in a research reactor facility for prompt- as well as decay-spectroscopy studies in γ - γ coincidence mode, is mostly sparse. The FIPPS (Fission Product Prompt γ -ray Spectrometer) at ILL, Grenoble, France, has only been such a facility. Recently, a novel facility, **DURGA** (Dhruva Utilization in Research using Gamma Array), has been developed at Dhruva reactor (R3001 neutron beam-port), BARC, Mumbai, in order to extensively carrying out basic nuclear structure as well as application-oriented researches using thermal-neutron beam generated from fission spectrum of reactor [1]. The facility consists of eight Compton-suppressed segmented clover-HPGe detectors and ten LaBr₃(Ce) fast scintillators along with an in-house developed digital-signal-processing-based data acquisition system. Apart from Prompt Capture Gamma Spectroscopy (PCGS) and Prompt Fission Fragment Spectroscopy (PFFS), Decay-Gamma Coincidence Spectroscopy (DGCS), at times even in combination with the Pneumatic Carrier Facility (PCF) at Dhruva, has also been one of the major research activities in this facility [2, 3]. Currently, national experimental users’ campaign is going in this facility, in which most of the experiments are being carried out at 40 MW_{th} power. Hence, it is imperative to accurately measure the neutron-beam fluence rate at the geometric center (sample/target position). The present measurement provides an important characterization of the neutron-beam profile as well as a crucial input to understand the already acquired yields and estimate data-throughput in future experiments.

MATERIALS AND METHODS

Basic principle:

The measurement of neutron fluence rate (ϕ) is based on the principle of determination of reaction rate in a particular material whose cross section is absolutely known as a function of neutron energy. ¹⁹⁷Au is one of the most widely used materials for the measurement of thermal neutron fluence rate due to several key advantages over others viz. reasonable activation cross section ($\sigma = 98.6$ barn for 0.0253 eV) following (1/v) law, moderate half-life of ¹⁹⁸Au (2.696 days), simple decay scheme etc. [4]. A thin sheet of ¹⁹⁷Au foil is irradiated for specific time (t_{irr}) in the experimental location leading to the buildup of induced activity (A) of ¹⁹⁸Au emitting beta as well as gamma radiations (equation 1) which are measured by absolute standard and thermal neutron fluence rate is determined as per equation 2 where, N is the number of ¹⁹⁷Au atoms, ‘ λ ’ is decay constant, ‘ t_d ’ is decay time and ‘ R_{Cd} ’ is the “Cadmium ratio”.



$$\phi_{\text{thermal}} = \frac{A \left(1 - \frac{1}{R_{Cd}}\right)}{N \sigma (1 - e^{-\lambda t_{irr}}) e^{-\lambda t_d}} \quad (2)$$

As thermal neutrons are produced by moderation of fast neutrons only therefore, there always exists epithermal and fast components. ' R_{Cd} ' is defined as the ratio of saturation activity of bare foil (A) to that of Cadmium covered foil ($A_{Cd \text{ cov}}$). Its significance stems from the fact that ^{197}Au has high cross section (1150 barn) due to resonance peak at 4.9 eV which also gives rise to induced activity, therefore, thermal neutron fluence rate is determined after R_{Cd} corrections. Various equipments used in the present study are given as follows:

Standard Gold (^{197}Au) foil:

Two foils (purity 99.99%, diameter: 10 mm, make: Advent) were used; one is thin (G2) and other is thick (SS2) having thickness of 12.5 and 111 μm , respectively. A circular cadmium (1 mm thick and 12 mm outer diameter) box was used wherein SS2 foil was covered during irradiation.

$4\pi\beta\gamma$ coincidence system:

It is an absolute standard for the measurement of radioactivity which consists of a 4π gas-flow proportional counter ($4\pi\beta$ counter) for detection of beta particles and a NaI (Tl) scintillation detector for the detection of gamma rays. The system is shown in **FIGURE 1a**. The irradiated ^{197}Au foil is placed over a mylar film located exactly at the center of the openable chamber. The gamma detector is placed below the proportional counter. The outputs of both the detectors are connected to pre-amplifiers, amplifiers, single channel analyzers (SCA), variable delay unit and a coincidence unit. As a result, three different output signals for beta, gamma and coincidence are obtained through an indigenously developed software and the activity is measured using the following equation [5]:

$$\frac{N_\beta N_\gamma}{N_C} = A \left[1 + \left(\frac{1 - \varepsilon_\beta}{\varepsilon_\beta} \right) \left(\frac{\alpha \varepsilon_{ce} + \varepsilon_{\beta\gamma}}{1 + \alpha} + \frac{\varepsilon_c}{\varepsilon_\gamma} \right) \right] = A (1 + K) \quad (3)$$

Where, N_β , N_γ and N_C are the count rates for beta, gamma and coincidence channels which in principle gives the activity. However, due to various interfering interactions within the system, a correction factor 'K' is evaluated which is associated with the following terms: ε_β , ε_{ce} and $\varepsilon_{\beta\gamma}$ which are the detection efficiency of the $4\pi\beta$ counter for beta particles, conversion electrons and gamma ray emissions from ^{198}Au foil, respectively. ε_γ is the detection efficiency of the gamma detector, ε_c is the probability that a coincidence will be observed when the beta particle is undetected, and ' α ' is the conversion coefficient defined as the ratio of intensity of conversion electrons to that of gamma ray (411 keV) intensity.

High Purity Germanium (HPGe) Detector:

It is worth mentioning that, for thick foils, $4\pi\beta\gamma$ coincidence system poses several problems viz. source self-absorption leading to very low detection efficiency of $4\pi\beta$ detector and multiple interaction of gamma ray photons within the source material itself which generates significant contribution of additional photoelectrons and Compton electrons which contributes large correction factor as well as associated uncertainty [6]. Therefore, in the present scenario, a HPGe detector (coupled with a spectrum analysis software) which is traceable to $4\pi\beta\gamma$ coincidence system was used for the measurement of activity of the thick foil by measuring the gamma photons from the foil. The activity ($A_{Cd \text{ cov}}$) of the foil can be determined using the following equation:

$$A_{Cd \text{ cov}} = \frac{C \left(\frac{\mu x}{1 - e^{-\mu x}} \right)}{\varepsilon e^{-\lambda t_d} \left(\frac{1 - e^{-\lambda t_c}}{\lambda t_c} \right)} \quad (4)$$

Where, C is background corrected net count rate under photo peak, ' ε ' is the efficiency of the system, the term in parenthesis in numerator and denominators are correction factors due to "thickness" and "counting time", respectively wherein ' μ ' is the attenuation co-efficient for 411 keV photon, ' x ' is thickness of the foil and ' t_c ' is counting time.

EXPERIMENTS, RESULTS AND DISCUSSIONS

G2 and SS2 foils were kept within aluminium and cadmium discs, respectively which were pasted on a sample holder (made of teflon) which was then placed in such a way that the neutron beam falls on the foils. The top view of the irradiation facility is shown in **FIGURE 1b**. The experiment was conducted in two steps; first G2 foil was irradiated and after about a month later SS2 was irradiated, however, the reactor power in both the cases was kept nearly constant at 40 MW_{th}. It is important to mention here that after irradiation of 14.88 h of the G2 foil at 40 MW_{th}, the reactor was tripped for a period of ~1.5 h which was restored further to 40 MW_{th}, whereas power was constant

throughout at 40 MW_{th} in case of SS2 foil irradiation. Therefore, effective irradiation time was calculated for normalized 40 MW_{th} reactor power which were found to be 2.92 and 5.02 days for G2 and SS2 foils, respectively. After that, various operating parameters of the $4\pi\beta\gamma$ coincidence system were determined viz. operating voltage of beta detector, detection window of SCA for 411 keV gamma etc. Next, G2 foil was counted for several runs (each for 600s) over few days using the software which provided the removable activity (A, corrected for decay time) as per **equation 3** corresponding to both thermal (0.0253 eV) plus epithermal neutron energies. The measured activity of the foils is given in **TABLE 1**. The decay plot of the observed readings as shown in **FIGURE 1c** gave the half-life of ^{198}Au isotope which matched within 0.7% of the reported value of 2.696 days. SS2 foil was counted in the HPGe detector at a distance of 10 cm away from the detector surface for which efficiency was measured earlier by a standard ^{198}Au foil. The foil was counted for different runs (each for 900s) where a peak at 411 keV was observed as depicted in **FIGURE 1d**. The activity of the SS2 foil was calculated as per **equation 4** which is given in **Table 1**. Therefore, based on these, saturation activity i.e., activity per unit mass normalized to $(1 - e^{-\lambda t_{irr}})$ factor was calculated for both G2 and SS2 foils, the ratio of which gave rise to the value of Cadmium ratio (R_{Cd}) to be (9.62 ± 0.19) . It signifies that about 89.6% of the induced activity in the ^{197}Au foil was due to the presence of the thermal neutrons and remaining (10.4%) is due to epithermal neutrons specifically for the resonance components. Finally, the net thermal neutron fluence rate was calculated from **equation 2**. Moreover, the fluence rate of epithermal neutrons was also calculated using the resonance integral cross section ($\int_{0.55}^{\infty} \sigma_{act}(E) dE$) of 1150 barn [7]. The results are given in **Table 1**.

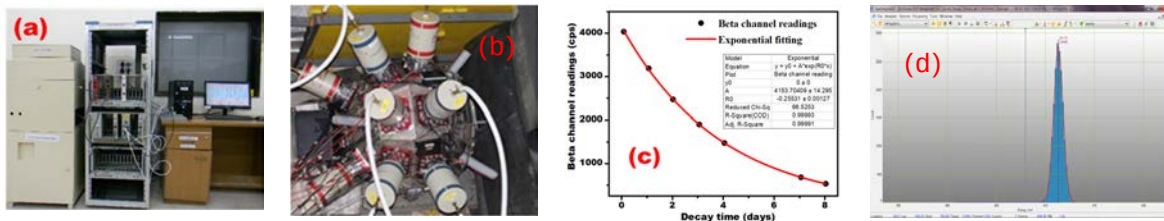


FIGURE 1. (a) $4\pi\beta\gamma$ coincidence system (b) Top view of DURGA Irradiation facility (c) Decay plot and (d) HPGe spectra of ^{198}Au

TABLE 1. Various measured parameters of neutron beam of the DURGA facility at reactor power of 40 MW_{th}

Parameters	Quantity of the parameter (For $k = 1$)
Measured activity of G2 foil	(6903.5 ± 72.1) Bq
Measured activity of SS2 foil	(5052.8 ± 245) Bq
Cadmium ratio (R_{Cd})	(9.62 ± 0.51)
Thermal neutron fluence rate	$(1.18 \pm 0.02) \times 10^6$ n/cm ² /s
Epithermal neutron fluence rate (> 0.55 eV)	$(1.33 \pm 0.07) \times 10^4$ n/cm ² /s

ACKNOWLEDGMENTS

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Interaction of RhodamineB and DMF studied by Spectroscopic Technique

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Abstract. The molecular structure fluorescence and photophysics of Rhodamine dyes are affected by chemical environment of the dyes. Therefore, it is significant to probe the chemical changes taking place between laser dyes and solvents. Fourier Transform Infrared spectrum of DMF is reported. Spectrum of RhodamineB(RhB) is also reported in DMF. Shift in band position and change in intensity is observed when RhB is added to DMF. These changes appear due to the interaction of DMF and RhB.

INTRODUCTION

Bonds distribution of a molecule can be studied with the help of vibrational spectroscopy generally. If the sample changes its state, then the interaction between the molecules may be investigated via variation in intensity, bandwidth and variation in the vibrational frequency. Generally, Raman or Infrared techniques are used to probe a molecule for its vibrations. Usually, infra-red spectroscopy itself provides sample of information to probe interaction taking place among molecules. On the other hand, if molecule absorbs strongly in infra-red region, then accuracy of information is incomplete. The solution of such situation is provided by FTIR spectroscopy. FTIR spectroscopy renders superior spectra.

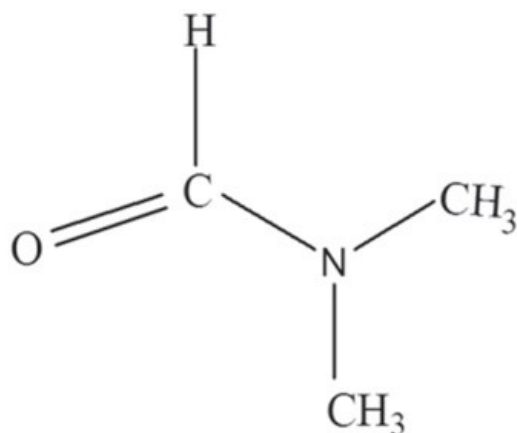
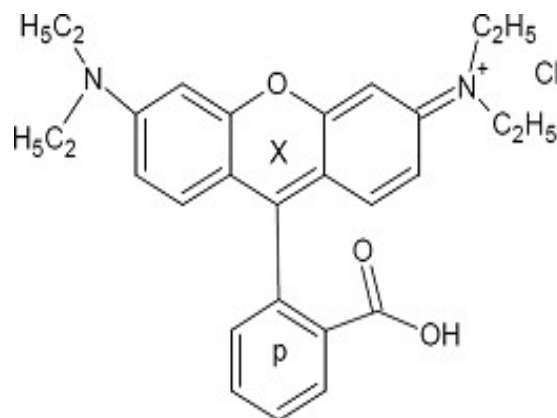
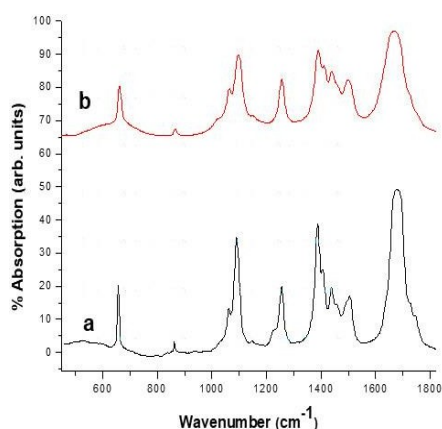
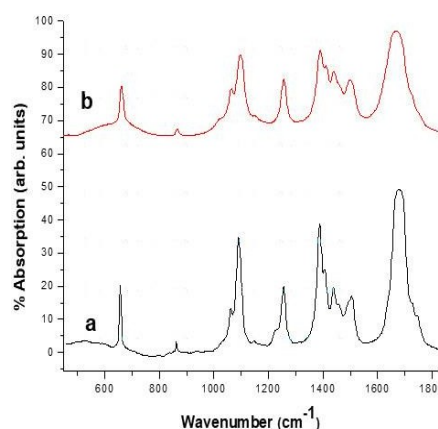
Researchers have key attention for the study of Laser dyes (Rhodamine dyes) from Xanthene family. These dyes essentially work as gain medium for dye lasers and in other various applications [1-10]. The performance of Rhodamine dyes gets affected through surrounding of dyes. Effect of different surroundings has been studied with various techniques [11-13]. This study shows the effect of DMF on RhB with the help of FTIR spectroscopy. The sensing properties of RhB and reliance of its fluorescence and lasing property on DMF may be understood by the present work.

EXPERIMENTAL

RhB obtained from Exciton, USA was taken without purifying it. Though Hitachi-330 UV-VIS-NIR spectrometer was used to verify its purity. DMF of spectroscopic grade was obtained from Qualigens Fine Chemicals, India. It was distilled and used as solvent. Infra-red spectra of RhB (crystalline powder) were recorded by using KBr pellet. Infra-red spectra of RhB in DMF (concentration $\sim 5 \times 10^{-3}$ M) was recorded using Perkin Elmer PE-Rx1 FTIR Spectrometer. FTIR spectrometer was configured with spectral resolution of 1 cm^{-1} throughout the experiment.

RESULTS AND DISCUSSION

The Figure 1 depicts structural representation of DMF. Figure 2 shows chemical configuration of RhB. The Infrared spectra of DMF in existence and non-existence of RhB are shown in figure 3 and 4 in $450 - 1850 \text{ cm}^{-1}$ and $1850 - 4000 \text{ cm}^{-1}$ range respectively. Table 1 shows the wave number positions and assignments of spotted FTIR peaks of DMF in absence and existence of RhB. The FTIR bands of DMF are assigned on the basis of earlier published work [13-15].

**FIGURE 1.** Molecular Structure of DMF**FIGURE 2.** Structure of Rhodamine B**FIGURE 3.** FTIR peaks; [a] DMF & [b] DMF +RhB in 450-1850 cm^{-1} **FIGURE 4.** FTIR peaks; [a] DMF & [b] DMF +RhB in 1750- 4000 cm^{-1}

It is clear from table 1 that few bands confirm shift in their wave number position on addition of RhB in DMF. Intensity of few bands also changes when RhB is added to DMF. Shift in wave number position is because of change in force constant whereas the intensity varies when there is a change in overlap of the wave function involved in the transition. The bands at 659, 1063, 1093, 1388 and 1408 cm^{-1} in pure DMF show increase in their wave number position. This confirms the interaction between DMF and RhB. Some bands do not show any shift on addition of RhB in DMF and appear at the same position as in DMF. For instance, The IR band at 1256 cm^{-1} does not change its position by adding the dye in DMF. This observation suggests the non-participation of nitrogen atom in the interaction between DMF and RhB.

TABLE 1: Location and assignment of FTIR peaks of DMF in the existence and non-existence of RhB

Band (cm^{-1})		Assignment
DMF pure	DMF+RhB	
659	661	O=C-N-C tor
865	865	N-CH ₃ sym st
1063	1064	Cm-H def.

1093	1097	N–Cm–H def.
1150	1150	Cm–H def.
1256	1256	N–CH ₃ st
1388	1389	C–N st
1408	1410	N–CH ₃ st.
1438	1439	N–CH ₃ def.
1492/1504	1499	C–N asym st
1678	1667	C=O st
2861	2867	C–H st(cis-methyl)
2931	2931	C–H st(cis-methyl)

CONCLUSIONS

Change in wavenumber position and intensity of FTIR bands on adding RhB to unadulterated DMF confirms the interaction of DMF and RhB dye. The interaction between DMF and RhB involves nitrogen and hydrogen atoms of dye and the O of aldehyde group in DMF. Therefore, the bands involving O atom of DMF show shift in their wavenumber position. The bands involving N-CH₃ stretching do not show any shift in their wave number position on addition of RhB to DMF.

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Micro-patterned Electroplated Indium on GaAs for X-ray Pixel Detector Integration

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Abstract: We report the development of a technique for electroplating Indium micro-dot arrays on GaAs substrates, aimed at realizing X-ray pixel detectors. Using an optimized electroplating process and photolithography-defined patterns, uniform Indium dots of 300 μm diameter and 16 μm height are deposited with a 600 μm pitch. These are successfully bonded to a custom-designed printed circuit board (PCB) to enable simultaneous electrical readout of 80 pixels in a 4×20 matrix. The Indium layer shows good adhesion, reasonable roughness, and a controlled geometry, that is crucial for bonding. This work lays the foundation for fabricating GaAs-based pixel detectors for hard X-ray imaging applications.

INTRODUCTION AND MOTIVATION

High-speed imaging in the hard X-ray regime ($E_x > 10 \text{ keV}$) is an emerging field with applications across several domains. Conventional Si-based charge-coupled devices (CCDs) are inadequate due to the conflicting requirements of detector thickness to achieve both high efficiency and fast response. This drives the need for high-Z materials, as the photoelectric absorption coefficient scales roughly with Z^4 , enabling better absorption in thinner detectors. [1] To leverage both the high-Z properties of materials and the processing capabilities of Si-based Application Specific Integrated Circuits (ASICs), hybrid detectors are used. In these, the semiconductor sensor and readout electronics are fabricated separately and connected via flip-chip bonding (Fig. 1a). [2] GaAs is a promising candidate for this application due to its superior absorption in the 10–25 keV range (Fig. 1b), higher saturation velocity (10^7 cm/s), and wider band gap (1.42 eV), which allows low-noise, room-temperature operation. [1,3] For bonding the GaAs detector to the readout circuit, a solder material with suitable properties must be deposited on each pixel with high precision.

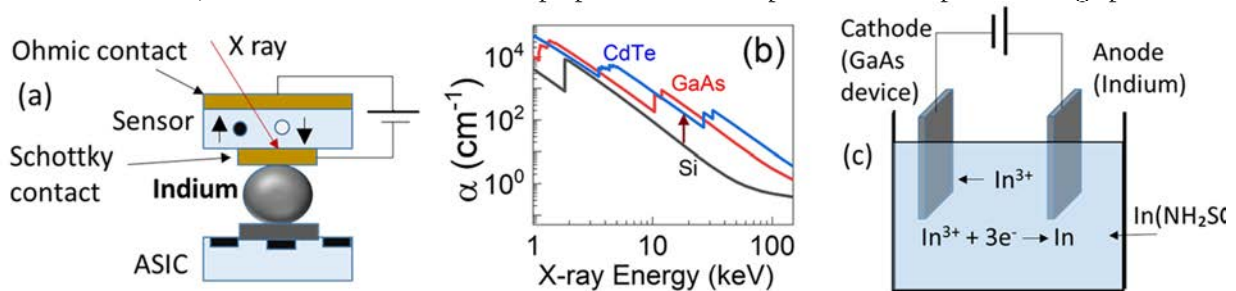


FIGURE 1. (a) Schematic of hybrid X-ray detector where sensor is bump bonded to ASIC, (b) Comparison of absorption coefficient of Si, GaAs and CdTe and (c) Schematic of electroplating procedure.

Indium has become the material of choice for demanding detector applications due to its favorable properties. Its softness helps to accommodate thermal expansion mismatches between GaAs and ASICs, preserving mechanical integrity. [4] With a low melting point of 156 °C, Indium minimizes thermal stress during assembly while maintaining electrical performance. Electroplating (Fig. 1c) is preferred for depositing Indium, on each pixel because it is efficient, near room temperature process and requires inexpensive equipment. GaAs single pixel detector operating in hard X-ray region (9-24 keV) has already been developed in RRCAT [5]. To implement the multi-pixel configuration, Indium

electroplating is required on each pixel. In this work, we present our recent results on electroplating an Indium dot matrix on a GaAs substrate and the procedure for bonding it to a custom-designed printed circuit board (PCB).

EXPERIMENTAL DETAILS

The process of Indium micro-pattern formation involves electroplating Indium onto GaAs substrates. For optimization, continuous Indium layers are first electroplated on both n-type and p-type GaAs substrates. Electroplating is performed using an Indium sulfamate electrolyte, with GaAs substrates ($2 \times 2 \text{ cm}^2$) serving as the cathode and an Indium bar ($6 \times 2 \text{ cm}^2$) as the anode in a 200 mL bath at room temperature (Fig. 1c). The deposition parameters are systematically varied, with current density ranging from 2 to 35 mA and plating time from 10 to 60 minutes. Optimized conditions are identified based on the surface morphology, deposition uniformity, and adhesion to the GaAs substrate. Once optimized, photolithography is used to define micro-dot patterns. Finally, a custom PCB mount is designed and fabricated to readout from such 80 Indium micro dots arranged in a 4×20 matrix. The Indium micro-dot patterned GaAs is further bonded to the PCB using PDR infrared rework stations, which utilize focused top and bottom side infrared heating.

RESULTS AND DISCUSSIONS

Fig. 2a shows the variation of Indium plating thickness with plating time at a constant current of 15 mA. The thickness increases rapidly during the initial stages, followed by a gradual saturation trend beyond 40 minutes. This behavior suggests that the deposition rate slows down with time, possibly due to depletion of Indium ions near the electrode surface or changes in surface morphology affecting further deposition. The maximum thickness that could be obtained is $22 \mu\text{m}$, which is measured at a distance of 1 mm from the plating bias electrode, which is attached to GaAs. However, with increase in this separation, Indium thickness is observed to decrease monotonically (Fig. 2b). Further, this non-uniformity is more in p-GaAs compared to n-GaAs under identical condition, indicating effects of substrate resistivity which promotes current crowding near the electrode. Furthermore, Fig. 2c and d show the thickness fluctuations (Δd) across a uniformly electroplated Indium layer with a mean thickness of $22 \mu\text{m}$ and SEM micrograph of the same sample. The profile reveals local fluctuations of approximately $\pm 5 \mu\text{m}$ over a scan length of $800 \mu\text{m}$, indicating moderate thickness fluctuations in the deposited film. These variations can arise from non-uniform current distribution, or limitations in mass transport during the plating. While the overall deposition is continuous, improving bath agitation and electrode geometry could help to enhance thickness uniformity. The hardness and adhesion of electroplated Indium is estimated by micro-indentation and tape test respectively and the results is found to be satisfactory. Once the electroplating parameters are optimized using continuous layers, photolithography is employed to define the micro-dot patterns on the GaAs substrate for selective Indium deposition.

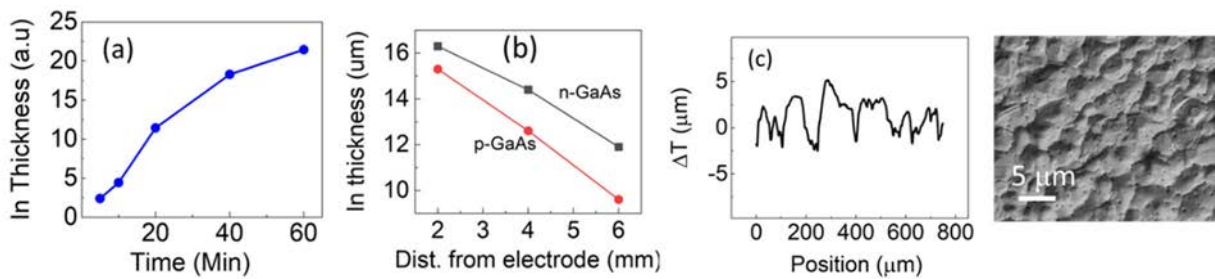


FIGURE 2. (a) Indium thickness versus time for a fixed current of 15 mA, (b) Indium thickness versus distance from the electrode, (c) thickness fluctuations (Δd) for 20 micron thick Indium layer, and (d) SEM micrograph of the sample.

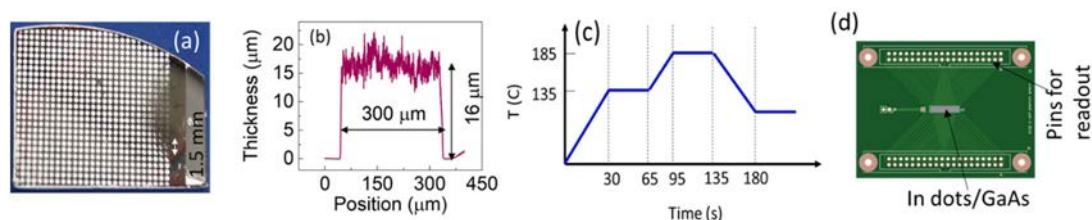


FIGURE 3. (a) Photograph of the micro-patterned Indium dots on GaAs, (b) Stylus profilometry of individual dot confirming its diameter (300 μm) and height (16 μm), (c) Reflow profile adopted to bond the Microdot arrays to PCB for readout, and (d) Picture of PCB mounted detectors, where each micro-patterned Indium dots are connected to one external pin.

A positive photoresist is spin-coated on the substrate and soft-baked to remove residual solvents. The resist-coated substrate is then exposed to UV light through a metal mask containing a periodic array of circular openings with a dot diameter of 300 μm and a pitch of 600 μm . After development, the exposed regions of the resist are removed, creating an array of circular windows in the resist layer. Indium is electroplated only in these openings, selectively forming well-defined micro-dots directly on the underlying GaAs. The remaining resist is finally stripped off, leaving behind a clean array of Indium micro-dots with uniform size and spacing. This patterning process enables precise control of geometry, which is critical for achieving reliable electrical contact and alignment in bonding with pixel readout electronics. Figure 3a presents the picture of uniform Indium micro-dot coated GaAs. Thickness and step profile measurements using a stylus profiler at several random positions confirmed an average height of $\sim 16 \mu\text{m}$ with a diameter of 300 μm (Fig. 3b). To enable simultaneous electrical readout, a matrix containing a total of 80 micro-dots (4 x 20) is cleaved from the full sample and bonded to the custom designed PCB using an infrared heating based reflow system, which comprises two critical stages; precision alignment and controlled reflow. Alignment is performed using a prism based optical module, which enables simultaneous visualization of both the top surface of the PCB and the bottom surface of the component on a common monitor. This facilitates high-accuracy alignment, with a resolution on the order of ten microns, aided by fine micrometric adjustment gauges. Once the solder balls are precisely aligned with the corresponding PCB pads, a customized thermal reflow profile is executed (Fig. 3c). The profile is ensured by the monitoring and feedback control using two independent sensors: a contact-based K-type thermocouple affixed to the PCB and a non-contact IR pyrometer directed at the component surface. A photograph of the PCB with the mounted sample, demonstrating good mechanical stability, is shown in Fig. 3d. Comprehensive electrical and mechanical characterization is currently in progress to assess interconnect reliability, contact resistance, and structural integrity under operational conditions.

In summary, we have developed a method to electroplate Indium microdot matrix on GaAs substrate. This substrate is further bonded to custom designed and fabricated PCB for easy readout of 4 x 20 pixels simultaneously. This procedure will now be implemented on GaAs detectors for the development of X-ray pixel detectors.

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Development and Characterization of Fast-Response Hard X-ray detector based on SI-GaAs

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Abstract: A semi-insulating GaAs (SI-GaAs) detector is designed and fabricated for high-speed hard X-ray detection with nanosecond temporal resolution. The 350 μm thick detector shows a low leakage current of 8.5 nA/mm² at 300 K, responsivity of 0.15 A/W at 870 nm, and a temporal resolution of ~ 7 ns. The detector is tested in current mode at applied bias upto 100 V under synchrotron X-ray between 9 to 24 keV. The detector exhibits an increase in the signal magnitude with X-ray energy, which seems to be in reasonable agreement with theoretical calculations. These results highlight GaAs's superior absorption efficiency, fast carrier transport, and low noise, making it a strong candidate for fast and high-energy photon detection for advanced X-ray applications.

INTRODUCTION AND MOTIVATION

High-speed detection of hard X-rays is essential for advanced applications such as time-resolved synchrotron studies, X-ray free-electron lasers, and high-count rate applications, where nanosecond timing is critical [1,2]. Achieving such a fast response necessitates a detector layers, with a maximum thickness of the order of a few hundred microns, which is limited by the electron saturation velocity (10^7 cm/s). However, in silicon detectors, this limits X-ray absorption, especially above 10 keV. A viable approach to overcome this trade-off is to use materials with higher atomic numbers, as photoelectric absorption scales with approximately Z^4 . In this work, we report the design, fabrication, and characterization of a semi-insulating GaAs (SI-GaAs) detector tailored for hard X-ray detection with nanosecond time resolution. GaAs provides superior absorption in the 10–25 keV range due to its high-Z elements (Ga and As), along with high electron mobility, fast saturation velocity, and low leakage current owing to its wide bandgap [3,4].

Figure 1a compares the absorption coefficients (α) of Si and GaAs, showing that GaAs exhibits an order of magnitude higher α , especially above 10 keV [5]. Using these values, the material thickness required for 90% X-ray absorption is calculated, which is then used to estimate the electron transit time by dividing the thickness by the saturation velocity. Figure 1b presents the resulting transit times in Si and GaAs for X-ray energy ranging from 10 to 30 keV. It represents the minimum achievable response time, excluding geometrical contributions. As seen, the response time for Si detectors increases significantly with energy, exceeding 20 ns at 24 keV. In contrast, GaAs maintains a transit time of just 3 ns at the same energy. This highlights that achieving nanosecond-scale detection while maintaining high absorption efficiency, which is not feasible with silicon is readily attainable using GaAs. Figure 1c further shows that GaAs thickness of about 250 μm is required for effective absorption above 25 keV.

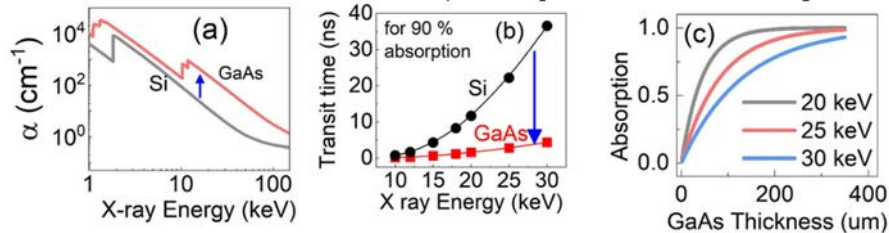


FIGURE 1. (a) Comparison of x-ray absorption coefficient for Si and GaAs, (b) Electron transit time in Silicon and GaAs as a function of X-ray energy for detector thicknesses corresponding to 90% absorption, and (c) X-ray absorption in GaAs as a function of detector thickness for various photon energies

DEVICE FABRICATION AND INITIAL CHARACTERIZATION

The fabricated detector consists of a 350 μm thick semi-insulating GaAs (SI-GaAs) layer, integrated with optimized Ohmic and Schottky contacts formed using Au-Ge/Ni/Au and Ti/Au metallization schemes, respectively. The device is mounted on a custom-designed printed circuit board, as illustrated in Fig. 2a. Prior to metallization, the GaAs substrate undergoes thorough surface cleaning and nitrogen drying to eliminate contaminants and ensure high-quality contact formation. The backside Ohmic contact is bonded to the mount using silver epoxy, whereas the front Schottky contact, defined over a 1.5 mm diameter circular area, is attached with a thin copper wire using indium solder. Room-temperature measurements under reverse bias conditions up to 100 V yield a leakage current of 14 nA, which further reduces to 0.8 nA, upon cooling the device to 270 K (Fig. 2b). To quickly assess material quality, charge collection efficiency, and carrier transport properties, the detector is characterized under visible and near-infrared illumination. As shown in Fig. 2c, a peak responsivity of 0.15 A/W is observed at 870 nm, along with a spectrally flat response in the 600–800 nm range, which are typical characteristics of a GaAs-based photodetectors. Time-domain response is evaluated using ultrafast laser excitation, employing Ti:Sapphire femtosecond laser Amplifier (peak wavelength: 800 nm, pulse duration ~ 35 fs, repetition rate ~ 1 kHz) while measuring the transient photocurrent using a fast oscilloscope. The instrument response function of measurement system is 1.75 ns. The signal exhibits a decay time of ~ 7 ns, estimated after single exponential fitting (Fig. 2d). The measured value is close to the calculated transit time of 3 ns and supports a fast response of the device.

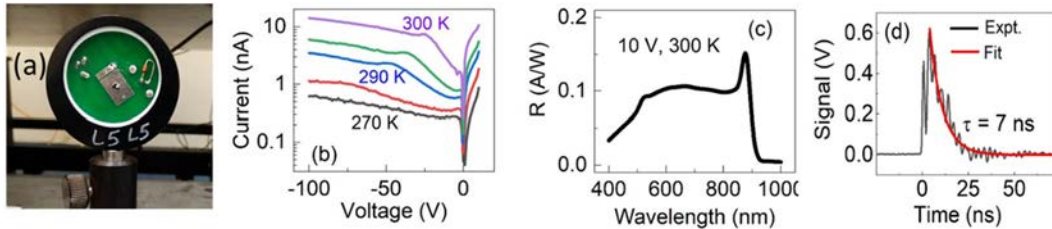


FIGURE 2. (a) Photograph of mounted detector, (b) Current-Voltage (I-V) response measured over 270-300 K temperature range, (c) Spectral response, and (d) Temporal response of the fabricated detector

SYNCHROTRON X-RAY MEASUREMENT AND ANALYSIS

To evaluate the detector's response to X-ray photons, measurements are performed using synchrotron radiation source at Beamline-4 (Imaging Beamline) of Indus-2, RRCAT, Indore. Figure 3a shows the photon flux (in photons/ $\text{mm}^2\cdot\text{s}$) available at this beamline as a function of photon energy. The detector is mounted on a translation stage and monochromatic X-rays between 9 to 24 keV in step of 3 keV, selected using a double crystal monochromator, are incident on it at normal incidence. The terminals of the detector are electrically connected to a Source Measure Unit (SMU), which applies a controlled bias voltage and measures the photocurrent. A broad area Silicon CCD camera is used in line with the detector for alignment purpose utilizing the transmitted X-ray through the PCB. At each energy setting, the CCD helps align the detector to the position of maximum X-ray flux, ensuring consistent and accurate measurements across the energy range. Figure 3b shows the result of the measurement along with the dark current. Under X-ray illumination, a clear photocurrent is generated, that enhances with the reverse bias and X-ray energy. At 100 V reverse bias, the current increases from 800 nA for 9 keV to 1 μA for 24 keV.

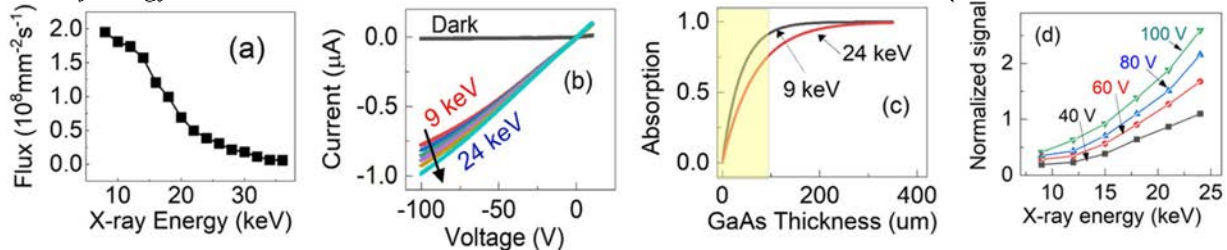


FIGURE 3. (a) Variation of X-ray flux with energy at BL-4, Indus 2 (b) Measured Current for X-ray of energy from 9 to 24 keV (c) Absorption of X ray of energy 9 and 24 keV as a function of GaAs thickness. Highlighted part is the estimated depletion width at 100 V (d) Comparison of calculated and measured signal magnitude.

One important observation is that for 9 keV, the magnitude of signal tends to saturate at high voltage, whereas for 24 keV it increases linearly with applied voltage, which is explained as follow. For a fixed energy, the strength of signal increases with applied bias because of increase in depletion width (w). In doped semiconductor, ' w ' varies with the square root of applied bias (V). Castaldini et al. [9] and McGregor et al. [10] have studied the depletion width (w) and electric field distribution in SI GaAs at high bias. They have observed that for Au/SI GaAs, ' w ' varies linearly with V with an empirical relation $w = w_0 + bV$, $w_0 = 24 \mu\text{m}$ and $b = 0.7 \mu\text{m/Volt}$. This means, at 100 V applied bias, the depletion width is approximately 94 μm . For 9 keV X-ray, the absorption length ($= 3/\alpha$) is 104 μm , whereas for 24 keV X-ray, it is 200 μm (Fig. 3c). Therefore, 9 keV X-rays are fully absorbed within the depletion width at 100 V and any further increase in the voltage causes only a minimal increase in the signal. On the other hand, 24 keV X-rays are only partially absorbed and it would require 200 V applied bias to completely absorb it. Therefore, signal corresponding to 24 keV X-rays does not show saturation even at bias 100 V. Measurement at further higher voltage will thus show saturation of even 24 keV signal.

To measure the spectral response of the detector at X-ray regime, we have normalized the current at 100 V for each X-ray energy with respect to the measured flux at that energy. In Fig. 3d, these results are shown for selected applied voltage, and the magnitude of signal is observed to increase with X-ray energy. It should be noted that the magnitude of current is proportional to the number of electron hole pair generated per second (N_{ehp}). It can be calculated by knowing the number of X-ray photon absorbed, X-ray energy and the energy required per electron hole pair. Since for thick GaAs, most of the X-ray flux are observed, N_{ehp} increases with X-ray energy. This explains the increasing signal magnitude with energy, though measured value shows some non-linearity at high X-ray energy, which indicates that the all the carriers generated by high energy X-ray are not collected by a low bias of 40V.

In summary, we have developed and characterized SI-GaAs based for hard X-ray detector operating in the energy range of 9 to 24 keV, which clearly outperforms Si based X-ray detectors. The results establish GaAs as a platform for compact, and fast detectors in this regime.

ACKNOWLEDGMENTS

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Exploring the Use of Piezoelectric Quartz Tuning Fork Transducers in Mid-IR gas Sensing for SF₆

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Abstract. We present the development of a compact and robust mid-infrared gas sensing system based on quartz-enhanced photoacoustic spectroscopy (QEPAS) employing a piezoelectric quartz tuning fork (QTF) transducer for the selective detection of sulfur hexafluoride (SF₆). The system utilizes a distributed feedback quantum cascade laser (QCL) operating at 10.6 μm , modulated for second harmonic (2f) wavelength modulation spectroscopy. A commercial ~ 32.7 kHz QTF with a custom acoustic detection module and micro-resonator tubes achieves efficient acoustic coupling. Under optimized low-pressure conditions (~ 225 Torr), the system achieved a minimum detection limit (MDL) of ~ 75 ppb with excellent signal-to-noise ratio. Compared with conventional microphone-based photoacoustic cells, the QTF-based approach offers higher immunity to environmental noise, compactness, and field-deployable capability. These results confirm the viability of MIR QEPAS for real-time, portable monitoring of greenhouse gases.

INTRODUCTION

Quartz tuning forks (QTFs), conventionally used in watches and frequency standards, have emerged as efficient piezoelectric sensors in photoacoustic gas sensing, especially in the QEPAS technique [1, 2]. Their high quality factor, small size, and low cost make them highly suitable for miniaturized optical detection platforms. QEPAS relies on the excitation of target gas molecules using a modulated laser beam. The resulting non-radiative relaxation produces localized pressure waves, which drive the QTF into resonance. The piezoelectric signal from the QTF correlates with the gas concentration [3]. Mid-infrared (MIR) QCLs, offering access to strong fundamental molecular absorption bands, provide excellent selectivity and sensitivity for trace gas detection. Integrating QTFs with MIR QCLs enables the development of rugged optical gas sensors suitable for environmental and industrial applications. This work reports on the development and optimization of a MIR QEPAS system for SF₆ detection using a commercial QTF, with emphasis on modulation parameters, and micro-resonator design.

PIEZO-ELECTRIC QUARTZ TUNING FORK CHARACTERISTICS

The electrical characteristics of the quartz tuning fork (QTF) were modeled as an equivalent LCR circuit [4], and its frequency response was characterized by performing a frequency sweep using a signal generator (Tektronix AFG3102C) (Fig. 1). A custom-built transimpedance amplifier was employed to convert the weak piezoelectric signals into measurable voltages with minimal noise. The commercial QTF is enclosed within a vacuum encapsulation; the cap was removed by cutting with a handheld cutter. The QTF consists of two prongs made of piezoelectric material, each approximately 4 mm in length and 0.58 mm in thickness, with a gap of about 300 μm between them (Fig. 2). Electrical connections were configured such that the QTF generates an electrical signal only when the prongs vibrate in opposite directions. This differential mode operation provides immunity to external acoustic noise, which generally moves both prongs in the same direction and thus does not contribute to the signal. Following the findings of Cao et al. [5], the excitation beam was focused at ~ 80 % of the prong length from the base to maximize acoustic coupling.

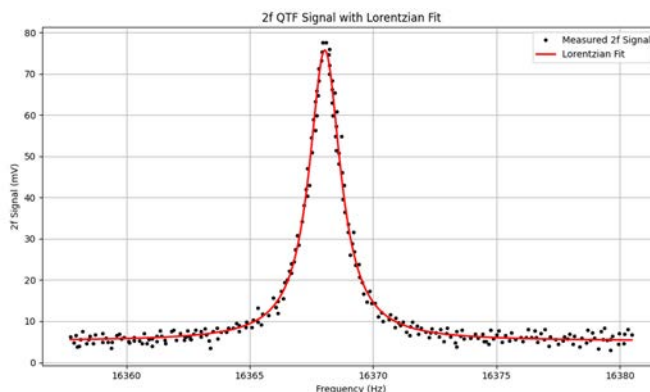


FIGURE 1. Frequency response of the QTF with a small SF₆ sample concentration. Axes: Frequency (Hz), 2f Signal (mV)

EXPERIMENTAL SETUP

A custom QEPAS setup was constructed using a DFB QCL (model HHL644, Alpes Lasers) emitting at 10.6 μm , corresponding to a strong SF₆ absorption line from the HITRAN database. The laser was sinusoidally modulated at half the QTF resonance frequency (~ 16.368 kHz) for 2f-WMS detection using an Anfattec 250 lock-in amplifier.

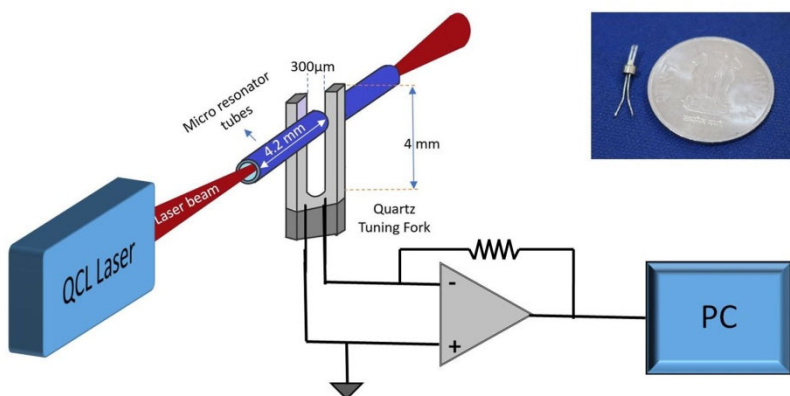


FIGURE 2. QCL beam focused between QTF prongs; inset: physical size comparison with a one-rupee coin.

The QTF (32.7 kHz) was housed within a custom-designed acoustic detection module featuring symmetric micro-resonator tubes to enhance pressure wave coupling (Fig. 2). This assembly was placed inside a photoacoustic cell equipped with ZnSe windows and gas inlet/outlet ports. Gas flow was regulated by a diaphragm pump and a vacuum controller to maintain stable low-pressure operation (~ 225 Torr). A 25 mm focal length germanium plano convex lens focused the 18 mW continuous-wave collimated laser beam into the 300 μm gap between the QTF prongs, producing a spot size of approximately 160 μm . Gas samples (certified 99.6 ppm SF₆ in nitrogen) and ambient air were alternately introduced through calibrated mass flow controllers (Sevenstar D07 series) for signal and background measurements during calibration.

RESULTS AND DISCUSSION

The QTF exhibited a sharp resonance at ~ 32.7 kHz, with a quality factor exceeding 15000 under vacuum conditions. The 2f-WMS signal demonstrated excellent stability and minimal background noise, confirming the effectiveness of the modulation and detection strategy. Fig. 3 shows the measured 2f-QEPAS signal for SF₆ (top) and ambient air (bottom).

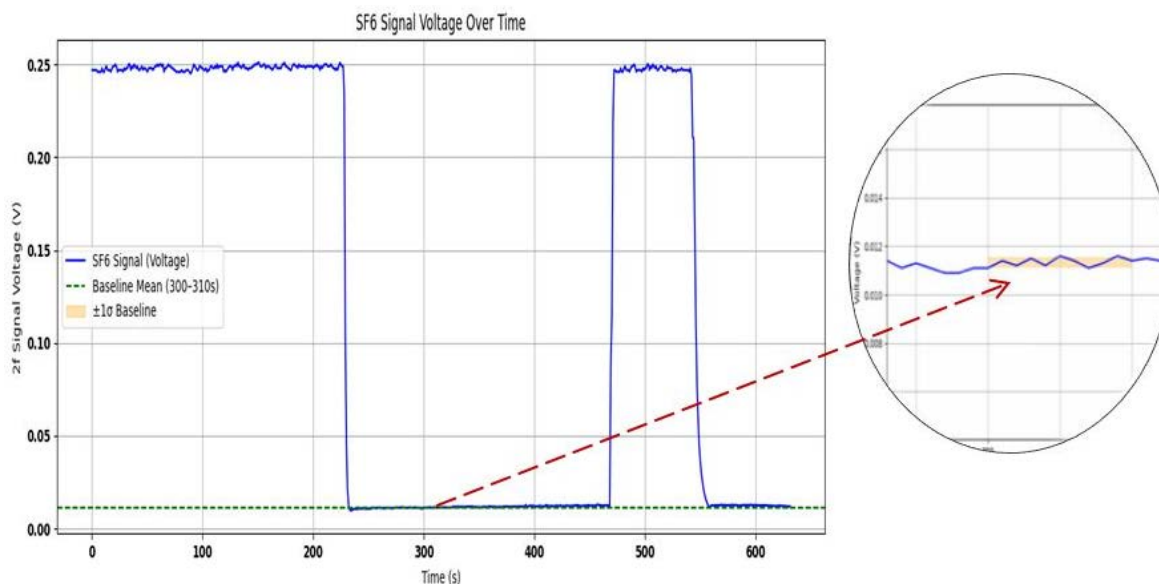


FIGURE 3.2f-QEPAS signal v/s time for SF₆ Sample (top) and ambient air (bottom); inset: 1 σ noise level (right).

Introduction of a certified 99.6 ppm SF₆ sample in nitrogen as the carrier gas resulted in a strong and well-resolved second harmonic (2f) signal. The amplitude of the signal exhibited a linear dependence on the SF₆ concentration [1], confirming the system's potential for quantitative analysis. Preliminary measurements demonstrated a minimum detection limit (MDL) of approximately 75 ppb. Notably, small fluctuations in the recorded signal were observed during repeated measurements, primarily attributed to the limited accuracy of the mass flow controllers (MFCs) used for gas sample introduction. Despite these minor variations, the signal-to-noise ratio remained sufficiently high to enable reliable trace detection. It is important to note that the 1 σ minimum detection limit (MDL) was ultimately constrained by the electronic noise of the acoustic detection module.

CONCLUSION

A compact MIR QEPAS sensor using a commercial QTF and DFB QCL achieved 75 ppb SF₆ detection with high stability and noise immunity. This study demonstrates the feasibility and effectiveness of using piezoelectric quartz tuning forks in MIR QEPAS setups for selective and sensitive trace detection of SF₆. With a compact design, low power requirements, and sensitivity in the sub-ppm range, the developed system holds promise for real-time, field-deployable applications in environmental monitoring and industrial leak detection. Future enhancements will include improved noise suppression; third-harmonic detection for improved laser locking and the use of custom-fabricated acoustic detection module for broader applicability across various gas species.

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Investigation Of The Optoelectronic Behaviour Of Erbium Sulfate Crystals

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Abstract. Erbium Sulfate crystals were synthesized by the slow evaporation solution growth method and were subsequently characterized to investigate their structural and optoelectrical properties. The X-ray diffraction analysis showed that the crystals possess a monoclinic structure with C2/c space group. The information that we gleaned from transmittance and reflectance spectra proved helpful in determining the refractive index, extinction coefficient and other parameters for these crystals. Furthermore, the important characteristics like band gap, nonlinear refractive index, optical electronegativity were evaluated for these crystals. These findings demonstrate the potential of Erbium Sulfate as a candidate for optoelectronic device applications.

INTRODUCTION

Rare earth elements (REEs), that include the lanthanide series as well as scandium and yttrium, have gained prominence in recent years because of their distinctive physical and chemical properties [1]. These distinguishing characteristics make them essential for a wide range of modern industrial applications. REEs are used in a wide range of high-tech disciplines, including electronics, optics, magnetics, ceramics, hydrogen storage, catalysis and battery technology [2]. Researchers have been very interested in alkali metal sulfates of the form M_2SO_4 (where $M = Li^+, Rb^+, Cs^+, Na^+, K^+$) because of their unique mechanical, electrical, and optical properties. Alkali rare earth sulfate (ARS) crystals in particular exhibit interesting optoelectronic properties and have been explored for possible applications in a variety of photonic devices including lasers, optical amplifiers and frequency converters. These crystals show the Nonlinear optical properties that play a key role in various areas such as photonics for communication, high-density data storage, processing and transmission of data and laser technology [3, 4]. The crystal structure has a major impact on optoelectrical properties of these crystals including, a high refractive index, wide optical band gap, and a high laser damage threshold [5]. This paper reports on the growth and characterization of Erbium Sulfate crystals, focusing on their structural and optoelectrical properties.

EXPERIMENTAL DETAILS

To obtain a saturated solution, analytical reagent (AR) grade Erbium sulfate octahydrate ($Er_2(SO_4)_3 \cdot 8H_2O$) was dissolved in double-distilled water and stirred continuously in a magnetic stirrer for about six hours. The prepared solution was then filtered in a beaker and covered with a perforated lid to keep out dust. The solution was left undisturbed at room temperature to enable gradual evaporation. Recrystallization process was used to improve the purity of the resulting crystals, producing light pink crystals. Additionally, the spin coating technique was used to grow a thin film of these crystals (FIGURE 1).

RESULTS AND DISCUSSION

This part comprises of four sections discussed below:

PXRD ANALYSIS

In FIGURE 2, the Powder X- ray diffraction analysis indicates that these crystals possess a monoclinic structure that pertain to C2/c space group with lattice parameters as $a = 13.461 \text{ \AA}$, $b = 6.672 \text{ \AA}$, $c = 18.162 \text{ \AA}$, $\beta = 101.90^\circ$, $Z = 4$.

TRANSMITTANCE AND REFLECTANCE



FIGURE 1. Crystal/ Thin film growth of Erbium sulfate

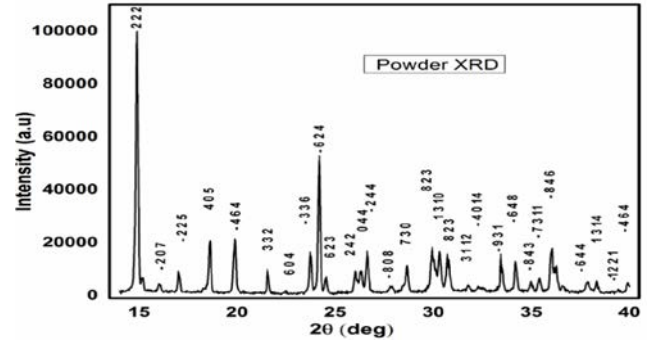


FIGURE 2. PXRD of Erbium sulfate

The crystals have a high transmittance of almost 71% at longer wavelengths as seen in FIGURE 3. The f-f electronic transitions of Er ions are responsible for the observed peaks, that could possibly result from structural defects/disorders.

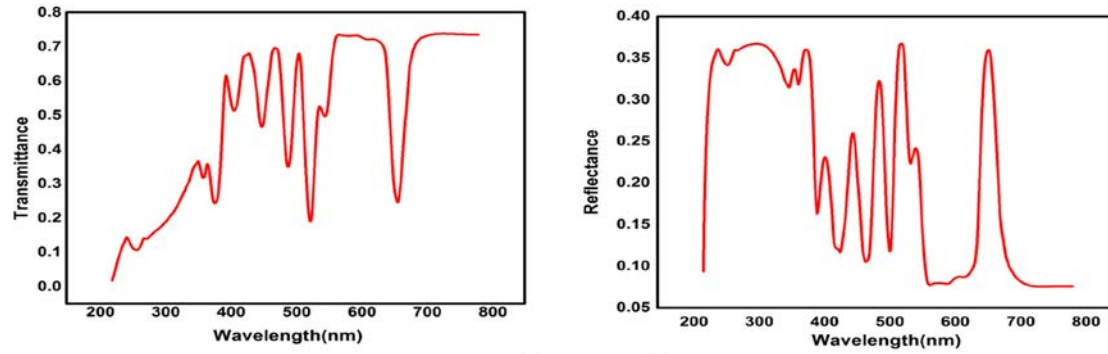


FIGURE 3. Transmittance and Reflectance spectra of Erbium Sulfate

ABSORBANCE SPECTRUM AND BAND GAP

The Tauc relation, that defines the relationship between the absorption coefficient (α) and photon energy ($h\nu$);

$$\frac{A \sqrt{h\nu - E_g}}{h\nu}$$

is used to calculate the band gap for direct band gap materials shown in FIGURE 4.

The wide band gap and strong optical transmittance exhibited by ES crystals projected them as promising material for optoelectronic applications.

NONLINEAR REFRACTIVE INDEX AND OPTICAL ELECTRONEGATIVITY

The refractive index (n) and the extinction coefficient (k) can be determined from $R(\lambda)$ and $T(\lambda)$ spectra by using the concept of reflectivity of light, given by the below relations;

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \text{ and } k = \frac{\alpha \lambda}{4\pi} \quad ; \text{ For insulating materials } k = 0.$$

Optical Electronegativity (η_{opt}) describes the bonding nature in materials and has applications in optoelectronics.

The relation between refractive index (n) and η_{opt} is given by;

$$\eta_{opt} = \left[\frac{A}{n} \right]^{\frac{1}{4}}$$

Where A is a dimensionless constant and is nearly equal to 25.54 for all materials. In semiconductors, bands are covalent in nature which results in smaller values of η_{opt} . On the other hand, in ionic crystals the ionic nature contributes to the larger value of η_{opt} . Thus these crystals are characterized with to the larger values of η_{opt} (around 1.954) and relatively smaller values of n (around 1.77).

The value of non-linear refractive index n_2 can be calculated by using the relation;

$$n_2^2 = \frac{12\pi\chi^3}{n_0}$$

Where χ^3 denotes optical nonlinear susceptibility and can be calculated by the relation;

$$\chi^3 = A_0 \left(\frac{n_0^2 - 1}{4\pi} \right)^4$$

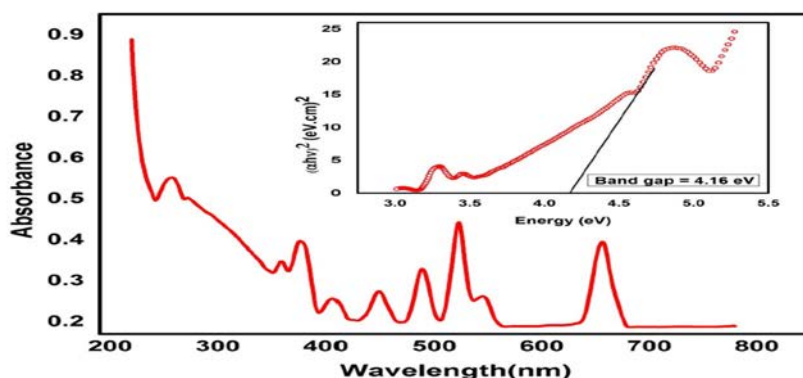


FIGURE 4. Absorbance spectrum and band gap of Erbium Sulfate

CONCLUSION

Erbium sulfate crystals were successfully grown using the slow evaporation method. Structural and optical investigations proved that the crystals have a large optical band gap of about 4.16 eV and a monoclinic structure with C2/c space group. The ionic character of these crystals is confirmed by the relatively high value of η_{opt} . The evaluated values of optical non-linear susceptibility χ^3 and non-linear refractive index n_2 suggest their potential for NLO behaviour. These crystals/thin films are ideal for use in optical interference filters, particularly long wave pass filters due to their relatively high refractive index and strong absorption in the short wavelength region.

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Evaluation of Third Order Nonlinear Optical Parameters of MXene by Z-scan Technique

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Abstract. MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) is synthesized through chemical etching technique from MAX phase precursor (Ti_3AlC_2) by removing “Al” using HF solution. The structure of MXene has been confirmed by X-Ray diffraction (XRD). The linear optical properties of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene have been investigated by UV-Visible spectroscopy. The non-linear optical parameters such as non-linear refractive index (n_2), absorption co-efficient (β) & Third Order Susceptibility ($\chi^{(3)}$) have been calculated using z-scan technique. The better value of Nonlinear Third Order susceptibility of MXene is due to Dielectric Confinement Effect.

INTRODUCTION

2D materials such as Graphene have attracted a lot of researchers with their exceptional properties which are not found in their bulk counterparts. Although, due to several limitations of Graphene such as zero band gap, inability in regulating the number of layers and presence of some intrinsic defects, its application is a bit difficult for future semiconductor devices [1]. Thus, there has been a great need to develop other 2D materials with built-in semiconductor properties. Among other 2D materials, MXenes exhibit remarkable potential for wide ranging applications due to their exceptional metal conductivity, high reducibility and electrochemical activity, ion exchange property, distinctive in-plane anisotropy, high surface area and appealing optical, mechanical, and thermal properties. Due to all these properties, MXenes and its composites have not only gained popularity as electrode materials in the energy storage industry [2-3], but they also exhibits significant promise in range of applications. MXenes are emerging 2D materials showing significant potential in nonlinear optical (NLO) applications. Their excellent NLO properties, like strong and broadband saturable absorption, arise from their unique electronic structures and high carrier density.

EXPERIMENTAL DETAILS

Materials and Methods

We have used parent precursor MAX phase as Ti_3AlC_2 (Sigma Aldrich), whose ‘Al’ element is to be removed using 48 wt. % HF (Qualigens) by chemical etching route. Precursor MAX phase (Ti_3AlC_2) was slowly added to Hydrofluoric and this reaction continued for 30 hours at constant temperature 35°C using magnetic stirrer. After the completion of reaction, the product is washed with DI and the acidic supernatant was removed using centrifugation till the pH reaches to 6-7. The filtrate was then dried at 80°C for 10 hours. This step is further proceeded by the molecular intercalation and the most popular intercalants used is dimethyl sulfoxide (DMSO; 99% extrapure) from SRL chemicals. After chemical etching and delamination followed by multiple washing steps, a stable MXene suspension is formed, which can be used to create solution-processed MXene films. MXene/PVA nanocomposite is synthesized by *in-situ* technique. Firstly, 0.5 wt. % solution of PVA (HIMEDIA, 99.999%) is prepared in DI water by constant stirring for 3 hours. MXene is added to PVA solution with magnetic stirring for 6 hours to form MXene/PVA nanocomposite. Then, thin-films were prepared onto the glass substrate by drop-casting method.

RESULTS AND DISCUSSION

X-ray Diffraction (XRD)

Fig. 1(a) and 1(b) displays the XRD diffractograph of MAX phase and synthesized MXene. The characteristic peaks of MAX phase (Ti_3AlC_2) are observed at $2\theta \approx 9.5^\circ$ (002), 21.5° (004), 38.72° (103), 40.9° (105), 45.01° , and 60.1° (110).

The disappearance or lowering of these peaks except (002) plane following chemical etching indicates the successful removal of Aluminum (Al) element from MAX phase. The broadening of (002) peak at 9.5 suggests that there is an increase in d-spacing of $Ti_3C_2T_x$ due to the delamination and termination groups (T_x) introduced during etching process [4]. These XRD pattern shows the changes of crystalline structure of powders in different stages. However, two distinct differences which were identified & noticed clearly are broadening, even split MXene peaks, with larger downshifts towards lower angles. In comparison with the intense peak of Ti_3AlC_2 at $2\theta = 38.72^\circ$, this peak has found to be lowered in XRD spectra of $Ti_3C_2T_x$ that confirms the removal of Al element. Quantum Confinement is the cause of broadening of peaks which also confirms the synthesis of MXene NSs similar to Graphene.

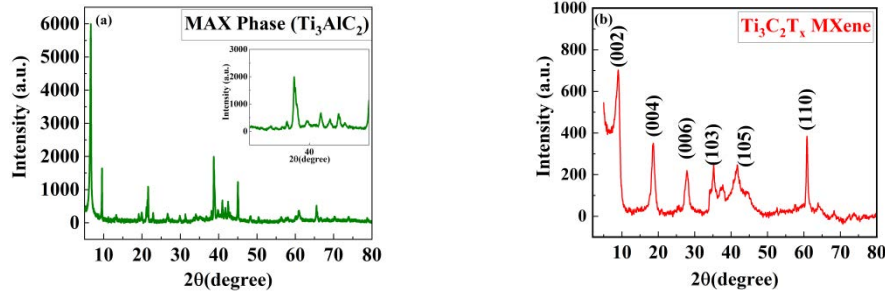


Figure 1. Represents the XRD spectra of (a) MAX phase and (b) as synthesized MXene.

UV-Vis Spectroscopy

The UV-Vis spectrum of $Ti_3C_2T_x$ MXene is shown in Figure 1(a). It shows three characteristics peaks at wave lengths of 260, 320, and 805 nm. The peak observed at 805 nm is attributed to the plasmonic properties of $Ti_3C_2T_x$ [3,5]. The absorption spectrum shows that the highest absorption occurs between 200 and 300 nm, indicating strong optical sensitivity of the synthesized MXene in the UV range. The optical bandgap is determined using the Tauc plot based on Tauc's equation.

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

where n is transition process number, whose value is dependent on the direct/indirect allowed/forbidden transitions, α is the absorption coefficient and A is constant. The inset of figure 1(a) shows $(\alpha h\nu)^2$ v/s $h\nu$ plot. Optical bandgap E_g is estimated by extrapolating its tangent up to energy axis and its value is 2.61 eV.

Z-Scan Technique

The Open Aperture (OA) Z-scan curve for MXene/PVA nanocomposite is presented in Figure 2(b). This Figure shows that the curve has rise around $z=0$, indicating the presence of Saturable Absorption (SA) in which absorption decreases considerably with increase in intensity. The sample shows SA behavior as a consequence of Pauli's blocking Effect [6]. The ground state depletes quickly and fails to repopulate under high incident intensity, leading to reduced absorption. This happens because excited-state absorption is less efficient than ground-state absorption. Pauli blocking also plays a role when the energy of a single photon exceeds the bandgap energy than E_g . The value of absorption coefficient β is calculated as 1.83×10^{-6} cm/W using relation

$$\beta = \frac{\lambda Z_r Q_0}{2 P_0 L_{eff}} \quad (2)$$

where λ is the wavelength of used laser light (632.8 nm), Z_r is the FWHM of Gaussian OA curve, Q_0 is Gaussian peak value, P_0 is the peak power of laser light, and L_{eff} is the effective thickness of sample.

The Closed Aperture (CA) z-scan curve for MXene/PVA nanocomposite is presented in Figure 2(c). The valley-peak configuration is observed, which indicates of a medium exhibiting positive nonlinear refraction. Nonlinear

absorption enhances peak and suppresses the valley in closed-aperture Z-scan curve. The non-linear refractive index n_2 in CA z-scan curve is calculated by using the equation as follows and its value is $5.09 \times 10^{-6} \text{ cm}^2/\text{W}$.

$$n_2 = \left| \frac{|\Delta\Phi_0|}{2\pi I_0 L_{eff}} \right| \quad (3)$$

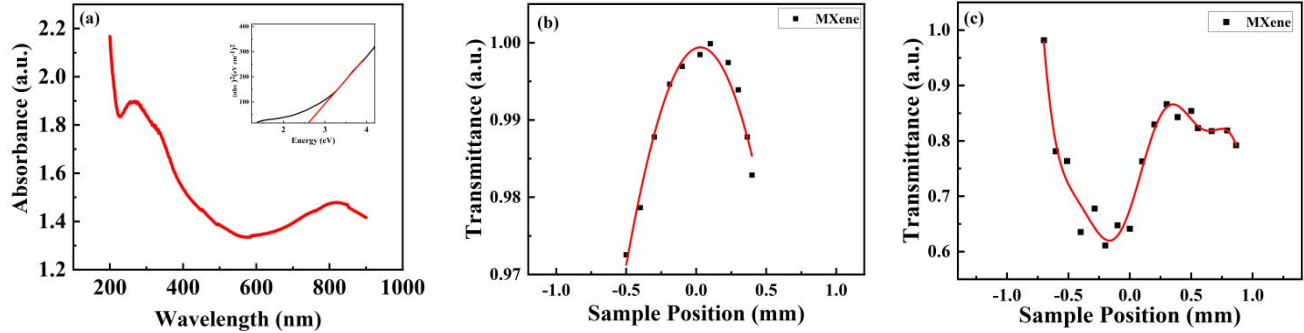


Figure 2. Represents the (a) Absorption spectra and inset shown Tauc Plot of MXene (b) Open Aperture (OA) and (c) Closed Aperture (CA) z-scan curves for MXene/PVA

The total third order nonlinear susceptibility is determined by using the equation

$$\chi^{(3)} = \sqrt{(\chi_R^{(3)})^2 + (\chi_{Im}^{(3)})^2} \quad (4)$$

The real $\chi_R^{(3)}$ and imaginary $\chi_{Im}^{(3)}$ part of $\chi^{(3)}$ has been calculated by using the values of β and n_2 as following

$$\chi_R^{(3)} = 2n_2 n^2 \epsilon_0 c \quad \text{and} \quad \chi_{Im}^{(3)} = n^2 \epsilon_0 c \beta / 3\pi \quad (5)$$

Where ϵ_0 is the permittivity of free space, c is the velocity of light in vacuum and n is linear refractive index. The calculated value of $\chi^{(3)}$ is $1.699 \times 10^{-10} \text{ cm}^2/\text{V}^2$ for MXene/PVA nanocomposite. The strong optical nonlinearity in MXene/PVA films is caused by changes on the material's surface and the PVA matrix when exposed to light. This effect is further increased by Dielectric Confinement, which plays an important role in increasing the nonlinearity of the nanocomposite.

CONCLUSION

In the present work, MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) has been synthesized within the polymer matrix. XRD results shows that “Al” element has been etched successfully. Z-scan technique is an effective tool for analyzing various nonlinear optical parameters such as n_2 , β and $\chi^{(3)}$. MXene/PVA nanocomposites exhibits enhanced nonlinearity and demonstrate Saturable absorption (SA) behavior.

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Enhancing Cu₂O/FTO Photodetector Performance and Spectral Selectivity through Carbon Dots

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Abstract. In this study, carbon dots (CDs) were prepared using a microwave-assisted method, and a Cu₂O/FTO sample was fabricated using an electrochemical deposition method. Further, a CD/Cu₂O/FTO photodetector was prepared by incorporating the carbon dots by the drop casting method. The I-V characteristics of Cu₂O/FTO and CD/Cu₂O/FTO samples have been studied, and it was found that CD/Cu₂O/FTO shows better responsivity with 0.039 A/W and a Detectivity of 0.5×10^{10} Jones at 632 nm. This work explores the addition of carbon dots to Cu₂O/FTO photodetectors, which facilitates charge separation and extended light absorption, resulting in the improvement of the spectral selectivity of visible light photodetectors.

INTRODUCTION

Cuprous oxide (Cu₂O) is a promising photodetector material due to its direct bandgap (~2.17 eV), strong absorption, p-type conductivity, low toxicity, and low cost. However, its performance is limited by carrier recombination and narrow spectral response, which can be improved through doping and nanoscale engineering [1], [2]. Carbon dots (CDs) are promising nanomaterials with tunable optical properties and high stability, capable of enhancing semiconductor device performance. However, their effect on Cu₂O-based photodetectors remains unclear [3]. This study investigates the effect of carbon dot incorporation on the spectral selectivity and photodetection performance of Cu₂O/FTO devices. The fabricated CD/Cu₂O/FTO photodetectors were characterized to evaluate improvements in optoelectronic response.

EXPERIMENTAL

Photodetector Fabrication Process

Cu₂O thin films were fabricated on FTO substrates through electrochemical deposition using a conventional three-electrode configuration with an Ag/AgCl reference electrode and a platinum mesh counter electrode operated via a BioLogic SP-150e workstation. Before deposition, the substrates were ultrasonically cleaned, and the films were deposited from a CuSO₄-lactic acid electrolyte adjusted to pH 12 at an applied potential of -0.4 V for 15 minutes, achieving a charge density of 0.68 C·cm⁻².

Microwave-assisted synthesis of Carbon Dots (M-CDs):

A homogeneous precursor solution was prepared by dissolving 2 g of urea and 1 g of D-glucose in 20 mL of double-distilled water. The resulting transparent solution was then subjected to microwave irradiation for 15 minutes using a Sharp R-219 T (W) microwave oven operating at 2450 MHz. When the treatment starts in the oven, all the water evaporates, leaving an off-white precipitate. This precipitate is subsequently burned, and the ultimate result is M-NCD. Mix this product with 50 mL of distilled water and sonicate it. During post-treatment,

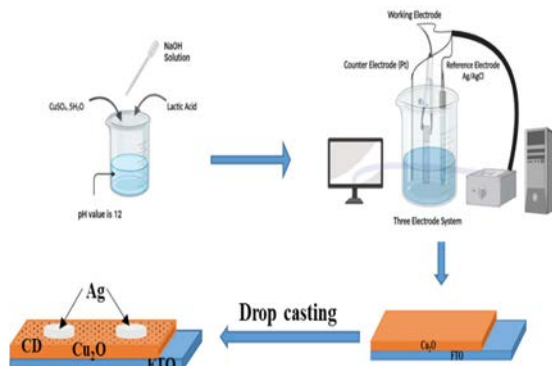


FIGURE 1. Systematic diagram of sample preparation.

the solution was initially centrifuged and then filtered through a 0.43 μm membrane to remove larger particles.[4]. Prior to applying the carbon dot solution (20 μL) to the substrate using the drop casting technique, we first deposited Cu_2O on FTO using the electrochemical deposition method. The photoactive layer with a firm mark was covered with a thermally evaporated silver (Ag) electrode on CD/ Cu_2O . Test devices for Metal-Semiconductor-Metal (MSM) planar structured photodetectors are finally constructed. The photoactive area remained consistent at 0.7 cm^2 for every sample.

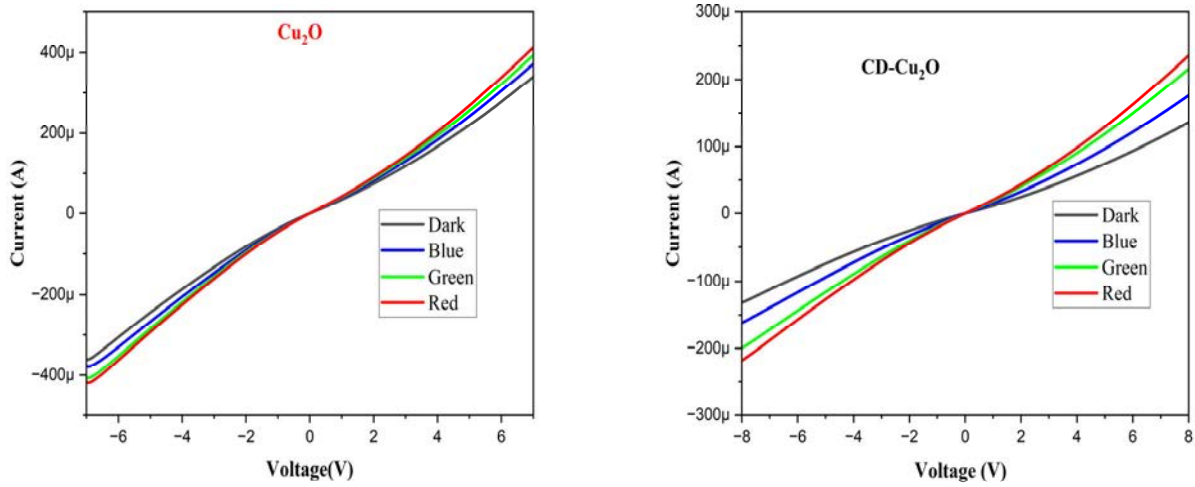


FIGURE 2. I-V characteristics of Cu_2O and CD- Cu_2O for different wavelengths of the visible light source.

RESULT AND DISCUSSION

The I-V characteristics of the $\text{Cu}_2\text{O}/\text{FTO}$ and CD/ $\text{Cu}_2\text{O}/\text{FTO}$ test devices are displayed in Figure 2 at bias voltage ranges from -7 to +7 V under various light illumination wavelengths. The Ag/photoactive layer interface exhibits Schottky-type behavior because the work function of Ag (4.3 eV) is lower than that of Cu_2O (4.84 eV), which is suitable for forming a Schottky junction with a p-type semiconductor. When exposed to visible light, photon absorption promotes electrons from the valence band to the conduction band, creating electron-hole pairs that contribute to the photocurrent generation[5], [6]. The photocurrent (I_{ph}), which is defined as $I_{ph} = I_L - I_D$, is created when these free electrons are subsequently trapped at the electrode. When the various light wavelengths are illuminated, the photocurrent is found to be 376, 405, and 416 μA for the $\text{Cu}_2\text{O}/\text{FTO}$ sample at 462 nm, 532 nm, and 632 nm, and 30, 69, and 85 μA for the CD/ $\text{Cu}_2\text{O}/\text{FTO}$ sample. The responsivity (R), detectivity (D), and external quantum efficiency (EQE) are the three key features to measure the performance of a photodetector. At lower optical density, a better photo directivity requires higher R, D, and EQE. The photocurrent (I_{ph}) generated per unit power of the incident light on the photodetector effective area (A) at a specific wavelength of illuminating light is used to calculate the responsivity and is given by

$$\text{Responsivity (R)} = \frac{I_{ph}}{P_{in}A} \text{ A/W where } I_{ph} = I_{light} - I_{dark} \quad (1)$$

Where I_{ph} denotes photocurrent, I_{light} and I_{dark} are currents achieved from the device under light and dark conditions, P_{in} is the input power, and A is the photoactive area.

Detectivity measures a device's ability to detect faint light signals, with the primary source of noise being shot noise from the dark current. It is given by

$$\text{Detectivity (D)} = \frac{R\sqrt{A}}{\sqrt{(2qI_{dark})}} \text{ Jones} \quad (2)$$

Where q is the charge of an electron, and I_{dark} is the dark current.

The efficiency of a photodetector in transforming photons into electric current is described by its External Quantum Efficiency (EQE) at a particular wavelength of the illuminated light source.

$$\text{External Quantum Efficiency (EQE)} = \frac{hcR}{q\lambda} \quad (3)$$

Where h is Planck's constant, c is the velocity of light.

The R, D, and EQE of $\text{Cu}_2\text{O}/\text{FTO}$ and CD/ $\text{Cu}_2\text{O}/\text{FTO}$ samples were calculated by using the above equations and are

mentioned in the table [7]. And measured at a power density of 3.1 mW/cm^2 for different wavelengths of visible light. The CD/Cu₂O/FTO photodetector showed better responsivity, detectivity, and EQE performance under different wavelengths of visible light compared to Cu₂O/FTO. It is also observed that the dark current decreases compared to Cu₂O/FTO due to the incorporation of carbon dots on Cu₂O/FTO photodetector.

TABLE 1. The calculated characteristics of the Cu₂O/FTO and CD/Cu₂O/FTO photodetectors at different wavelengths.

Wavelength (λ in nm)	Photocurrent(I_{ph}) (μA)		Responsivity(R) (A/W)		EQE (%)		Detectivity (D) (10^{10} Jones)	
	Cu ₂ O/FTO	CD/ Cu ₂ O/FTO	Cu ₂ O/FTO	CD/ Cu ₂ O/FTO	Cu ₂ O/FTO	CD/Cu ₂ O /FTO	Cu ₂ O/FTO	CD/ Cu ₂ O/FTO
462	376	30	0.007	0.013	1.88	3.49	0.09	0.16
532	405	69	0.02	0.031	4.66	7.23	0.2	0.4
632	416	85	0.026	0.039	5.10	8.17	0.33	0.5

CONCLUSION

Successfully fabricated a CD/Cu₂O/FTO heterostructure photodetector through electrochemical and microwave-assisted synthesis. The resulting CD/Cu₂O/FTO device has a responsivity of 0.039 AW^{-1} and a detectivity of 0.5×10^{10} Jones at 632 nm, with a detection band. These findings confirm that the device has good, excellent visible light selectivity, effectively mitigating the detrimental effects of UV absorption. This investigation provides a foundation for improving the spectral selectivity of VLPDs. Future studies can focus on optimizing the materials and fabrication processes to enhance device performance further and explore new applications.

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Analysis of Temperature Induced Effects on Mid-Infrared Spectra of Astromixtures

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Abstract. The detection and analysis of astromolecules is not trivial. Various factors like conditions of Interstellar medium (ISM), molecular properties, observational techniques and instrumentation etc. can affect the detection and analysis of molecules present in space. The several conditions of ISM include density and temperature, radiation field, presence of dust grains and turbulence. Since the acquisition of mid infrared (IR) spectra has speeded up the detection of complex astromolecules under variable conditions existing in stellar and planetary atmospheres, we have explored the temperature induced changes in the IR spectra of pure molecules and mixtures, with the help of peak feature analysis of IR modes. Isolation of prominent modes and quantification of changes in IR modes have been carried out using relative intensity estimates. The differences in IR peaks of pure molecules compared to the mixed astromolecules have been quantified. Temperature not only induces peak centre shifts, but qualitative changes too. Machine learning analysis has been done with the help of clustering and principal component analysis. Testing of few machine learning algorithms has been carried out for higher accuracy in astromolecule detection from IR spectra.

INTRODUCTION

There is a plethora of molecules in the solar system as well as interstellar medium (ISM) which are often in the ice phase ranging from simple to complex. Many molecules have been discovered through several ground based and space-based telescopes but the most common from them is the water ice. As a proof of the chemical complexity present in the ISM, Glycolaldehyde (CH_2OHCHO) has been found in the ISM. Reduced alcohol of glycolaldehyde, ethylene glycol (EG), was subsequently identified towards the Sgr B2 (N-LMH) in the ISM using several millimetre-wave transitions of the lowest conformer and EG was later observed in the hot core of Orion, towards NGC 1333-IRAS2A, towards the intermediate-mass protostar NGC 7129 FIRS 2 and in the MM1 core of NGC63341 [1-3]. EG has been detected in around seven comets in different proportions along with carbonaceous meteorites. A large amount of methanol was also found in those comets. This is important since laboratory analogue experiments have shown that methanol rich ices can easily synthesize EG upon energetic processing of mixture of H_2O and CH_3OH ices and also via the barrierless reaction of two hydroxymethyl radicals (CH_2OH) proving a route to EG synthesis under astronomical conditions [4-5]. Over 300 astromolecules have been discovered so far – Comets, interstellar space, protostars, protoplanetary disk, asteroids, exoplanets. Major tools – MIRI and NIR spectra of JWST, ALMA, NOEMA (have shown the presence of water and complex organic molecules)

RESULTS

Very often, it becomes cumbersome to isolate specific molecular modes in IR spectra of mixed species. This impedes the detection of astromolecules through a simple search process in IR spectra. Figure 1 demonstrates how two vibrational modes of CH_3OH change in pure and mixed state in $\text{H}_2\text{O}+\text{CO}+\text{CH}_3\text{OH}+\text{NH}_3$ mixture, at various temperatures – 120K, 100K, 50K and 10K [6]. In addition to peak center shift, a change in peak width (FWHM) is observed. Figure 2 shows the consolidated changes occurring in the IR modes of pure CH_3OH and $\text{H}_2\text{O}+\text{CO}+\text{CH}_3\text{OH}+\text{NH}_3$ mixture with respect to temperature in the form of cluster plots, which makes it easy to visualize the changes through dimensional reduction techniques. These cluster plots are plotted with FWHM vs. the peak center, for the pure and mixed astromolecules at the four different temperatures examined.

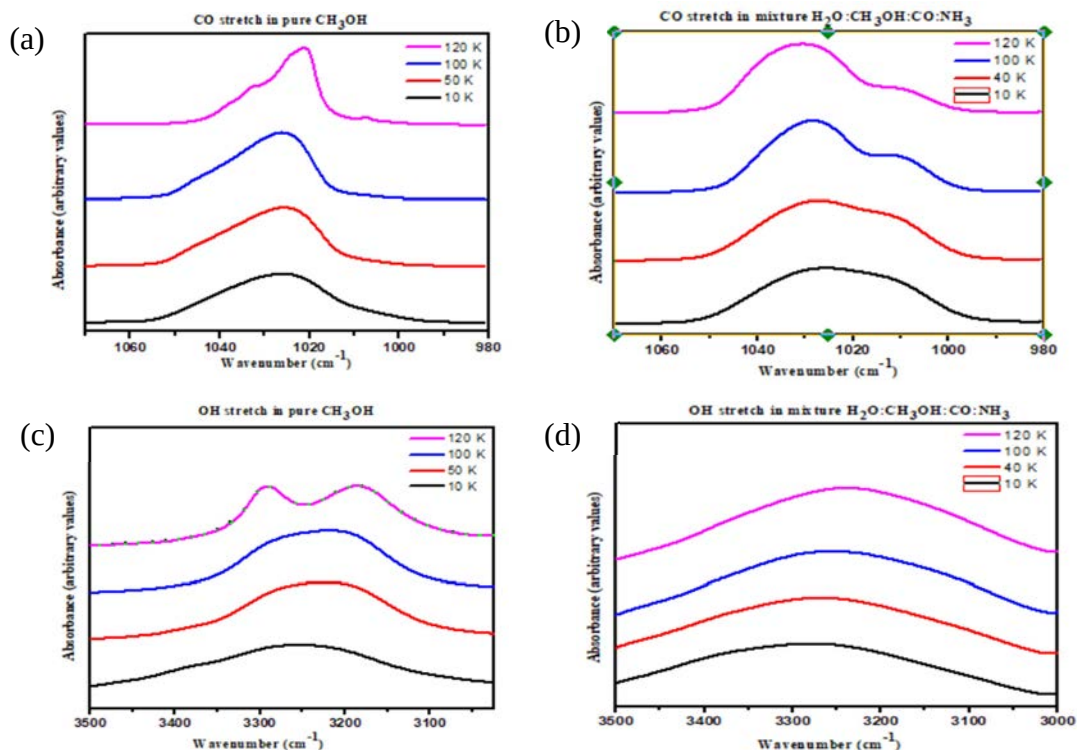


FIGURE 1. (a) C-O stretching mode in IR spectra of pure methanol (CH_3OH) at different temperatures. (b) C-O stretching mode in IR spectra of $\text{CH}_3\text{OH}+\text{H}_2\text{O}+\text{CO}+\text{NH}_3$ mixture at various temperatures. (c) O-H stretching mode in IR spectra of pure methanol (CH_3OH) at different temperatures. (d) O-H stretching mode in IR spectra of $\text{CH}_3\text{OH}+\text{H}_2\text{O}+\text{CO}+\text{NH}_3$ mixture at various temperatures.

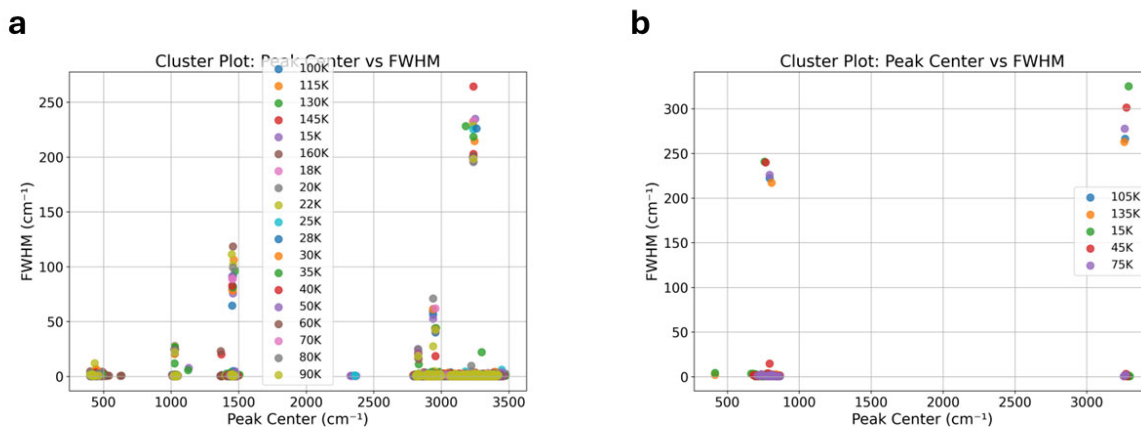


FIGURE 2. (a) FWHM vs. peak center of all modes in IR spectra of pure methanol (CH_3OH) at different temperatures. (b) FWHM vs. peak center of all modes in IR spectra of $\text{CH}_3\text{OH}+\text{H}_2\text{O}+\text{CO}+\text{NH}_3$ mixture at various temperatures.

TABLE 1. Molecular IR modes in pure astromolecules.

Molecule	Mode	Wavenumber(cm^{-1})	Molecule	Mode	Wavenumber(cm^{-1})
Pure H_2O	OH stretching	3260	Pure CH_3OH	OH stretching	3178
	H-O-H	810		CH asymmetric	2948
	liberation			stretching	
Pure CO	C=O	2137		CO symmetric	2823
Pure CO_2	stretching			stretching	
	C=O	2344		CO stretching	1024
	stretching		Pure NH_3	NH stretching	3363
				NH_3 umbrella	1072
				NH_3 diffraction	1633

CONCLUSIONS

We demonstrate the pronounced change in IR spectra of astromolecules in the pure state and mixed state with other astromolecules, and with respect to temperature as well. These changes have been quantified with not only IR mode peak feature analysis, but machine learning algorithms too. This work would be useful for spectral detection of molecules from IR spectra obtained from different regions of space, and for estimating the conditions prevailing in those atmospheres.

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Deep-UV Surface-Enhanced Resonance Raman Scattering via GLAD-Fabricated Aluminum Nanorod Arrays

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Abstract. Surface-enhanced Raman scattering (SERS) amplifies inherently weak Raman signals through localized surface plasmon resonance (LSPR) generated in metallic nanostructures. Conventional silver and gold-based SERS substrates work efficiently under visible or near-infrared (NIR) excitation but show limited performance in the deep ultraviolet (DUV) region. Aluminum (Al), with its broadband plasmonic response spanning DUV to NIR, offers a viable alternative for UV-active SERS applications. In this study, highly ordered, anisotropic Al nanorod arrays were synthesized via the glancing angle deposition (GLAD) technique, enabling fine control over nanorod alignment, inter-rod spacing, and structural morphology, which are critical factors for tailoring plasmonic hotspot characteristics. The nanorods were deposited on glass substrates via electron beam evaporation and evaluated using a 266 nm excitation source. The fabricated arrays enabled sensitive and reproducible detection of adenine at a concentration of 0.1 mM, with strong signal-to-noise ratios and minimal background interference. This work demonstrates the potential of GLAD-engineered Al nanorod arrays as efficient, scalable, and cost-effective substrates for DUV-SERS-based molecular detection.

INTRODUCTION

Surface-enhanced Raman scattering (SERS) is an extremely sensitive spectroscopic technique that strengthens weak Raman signals through electromagnetic (EM) enhancement driven by localized surface plasmon resonance (LSPR) in metallic nanostructures. EM enhancements typically range from 10^4 to 10^8 , with additional chemical enhancement via charge transfer contributing up to 10^2 to 10^6 [1]. Since Raman scattering efficiency scales with the fourth power of the excitation frequency (ω^4), ultraviolet (UV) and deep-ultraviolet (DUV) excitation further boost signal intensity. DUV excitation also reduces fluorescence background, enhancing signal-to-noise ratio [2]. When the excitation overlaps with a molecule's electronic absorption, resonant Raman scattering (RRS) occurs, significantly amplifying the signal. This makes DUV-resonance Raman (DUV-RR) especially effective for detecting biomolecules like DNA and proteins, which strongly absorb in the DUV region [3]. Integrating SERS with deep-UV resonance Raman (DUV-RR) gives rise to deep-UV surface-enhanced resonance Raman scattering (DUV-SERRS), enabling exceptional sensitivity and molecular selectivity. However, conventional SERS substrates such as Ag and Au suffer from interband damping in the UV region, which diminishes their performance. [4]. Aluminum (Al) has emerged as a promising alternative due to its strong plasmonic response from DUV to NIR, low absorption below 200 nm, and cost-effectiveness. While other UV-active metals have been explored, Al remains the most practical [5]. A key challenge, however, is fabricating uniform Al nanostructures. Glancing angle deposition (GLAD) offers a scalable, low-cost method to produce vertically aligned Al nanorods with tunable morphology for optimized hotspot formation [6]. In this study, Al nanorod arrays were fabricated via GLAD using e-beam evaporation and evaluated under 266 nm excitation for detecting 0.1 mM adenine. The substrates exhibited strong enhancement, high reproducibility, and low background, establishing their potential for ultrasensitive DUV-SERS-based biosensing.

EXPERIMENTAL

The glass slides were cleaned with a soap solution, then sequentially ultrasonicated in acetone, isopropyl alcohol (IPA), and deionized (DI) water. Aluminum nanorods (Al NRs) were then fabricated using the electron beam glancing angle deposition (e-beam GLAD) technique, as shown in Fig. 1(a). Al pellets were loaded into a crucible, and a cleaned glass substrate was positioned at an 85° inclination relative to the incoming vapor flux. Once a base pressure of 4×10^{-6} mbar was attained, the e-beam source was initiated to evaporate Al, allowing its controlled deposition onto the substrate. During deposition, maintained at $\sim 1.1 \times 10^{-5}$ mbar, Al atoms formed isolated nucleation sites that acted as growth centers. Larger islands captured more atoms due to a geometric shadowing effect and limited surface mobility

of adatoms. This anisotropic growth resulted in vertically aligned, rod-like columnar Al structures typical of the GLAD process [7].

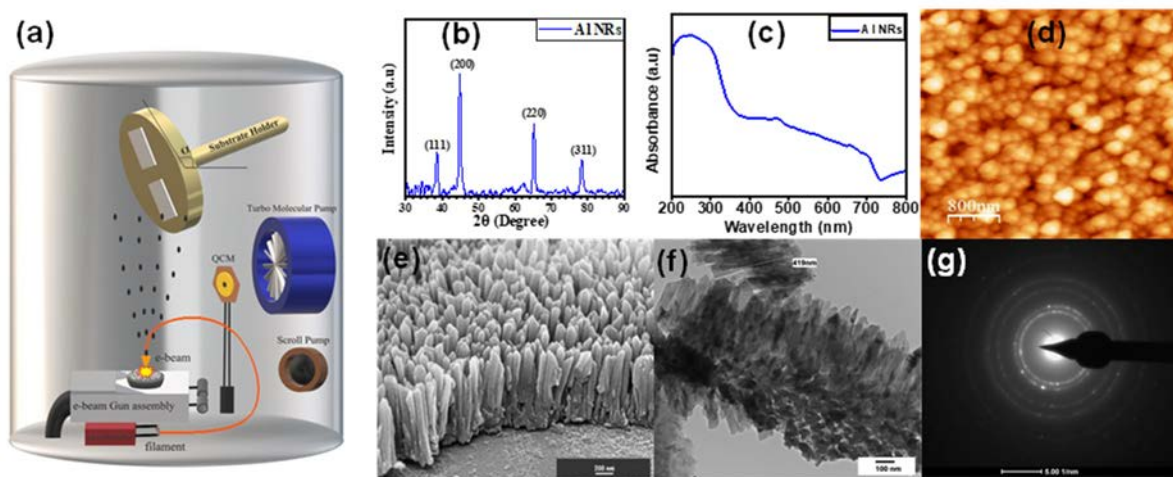


FIGURE 1. (a) Formation of Al NRs via e-beam GLAD. (b) XRD pattern, (c) Absorbance spectrum, (d) AFM image, (e) FESEM view, (f) HRTEM image, (g) SAED pattern of Al NRs.

RESULTS AND DISCUSSION

The crystal structure of the Al nanorods was verified by X-ray diffraction (Fig. 1(b)), with diffraction peaks at 38.5° , 44.7° , 65.1° , and 78.2° , indexed to the (111), (200), (220), and (311) planes of face-centered cubic (FCC) Al (JCPDS No. 04-0787). The UV-vis absorbance spectrum (Fig. 1(c)) displayed a prominent peak at 260 nm, corresponding to localized surface plasmon resonance (LSPR), governed through nanorods' size and aspect ratio. Atomic force microscopy (AFM, Fig. 1(d)) revealed a uniform columnar surface, while FESEM images (Fig. 1(e)) confirmed the vertical alignment of the Al NRs. HRTEM analysis (Fig. 1(f)) showed an average nanorod diameter of ~ 75 nm. The SAED pattern (Fig. 1(g)) indicated the polycrystalline nature of the Al NRs.

DEEP UV- SIMULATIONS AND SERS

Three-dimensional finite-difference time-domain (FDTD) simulations of Al nanorods were performed to investigate the electromagnetic field distribution across the nanostructure and to elucidate the origin of DUV-SERS enhancement [8]. The simulation model, shown in Fig. 1(e-f), consists of Al nanorods with a length of 450 nm and a diameter of 75 nm, designed to replicate the experimental geometry. The nanorods are arranged in a 4×3 array with a 20 nm spacing in both the x- and y-directions on a SiO_2 substrate. As depicted in Fig. 2(a), the top-view electric field distribution under normal incidence of a 266 nm plane wave exhibits strong field confinement within the gaps between adjacent nanorods, resulting from plasmonic coupling. The side-view in Fig. 2(b) further shows significant field enhancement at the nanorod interfaces due to coupled surface plasmon oscillations, which underpins the electromagnetic contribution to DUV-SERS enhancement. The deep-UV SERS spectrum of adenine, acquired using a 266 nm excitation source, is illustrated in Fig. 2(c). Adenine molecules adsorbed on GLAD-fabricated Al nanorods (NRs) exhibit significantly enhanced Raman signals compared to those on bare glass. As shown in Fig. 2(d) [9], the 1200 cm^{-1} band corresponds to C-H in-plane bending and purine ring deformation, while the 1325 cm^{-1} peak arises from C-N stretching and ring breathing. Bands at 1453 and 1608 cm^{-1} are attributed to N-H bending & C=N stretching, respectively, with peaks at 2644 and 2780 cm^{-1} likely due to overtone or combination modes. The enhanced bands at 1316 and 1467 cm^{-1} indicate charge transfer from Al to the LUMO of adenine under UV excitation. This metal-to-molecule charge transfer selectively boosts high-frequency modes, confirming strong plasmonic activity of Al NRs for sensitive, label-free DUV SERS detection.

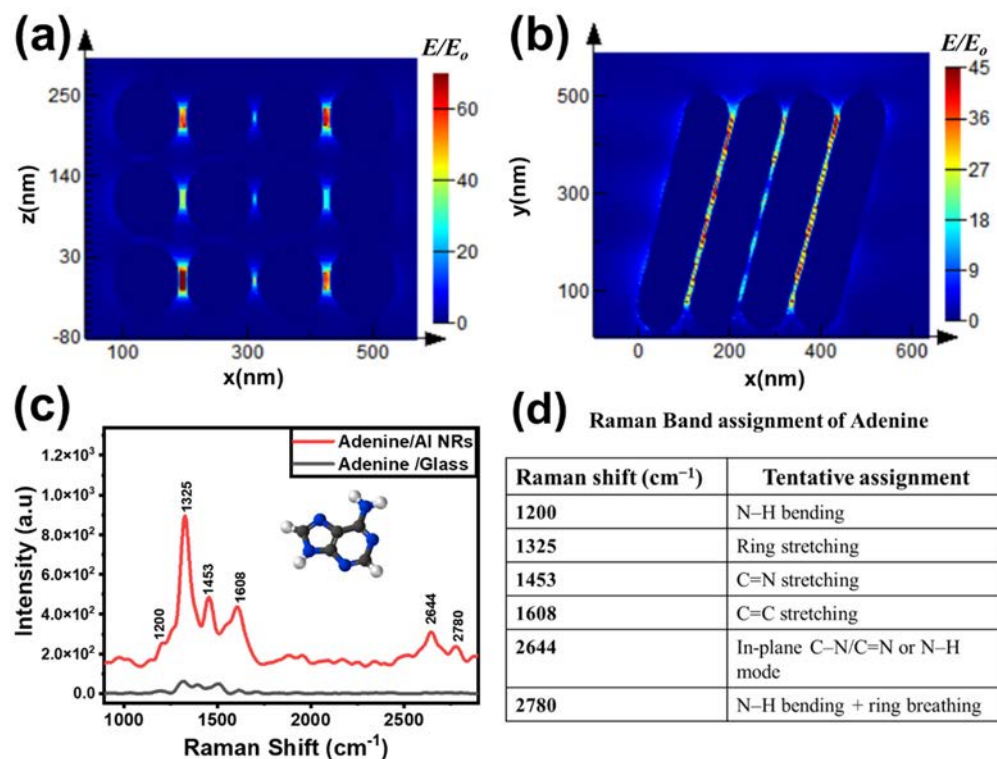


FIGURE 2. Deep UV-FDTD simulation of Al NRs: (a) Side view, (b) Top View. (c) Deep UV-SERS Spectra of Adenine. (d) Raman Band assignment of Adenine.

CONCLUSION

In conclusion, GLAD-fabricated Al nanorod arrays exhibited strong DUV-SERS performance under 266 nm excitation, enabling sensitive and label-free detection of adenine. The substrate showed excellent enhancement, reproducibility, and low background, highlighting its promise for deep-UV SERS biosensing.

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Percolation threshold of Fe / CoFeB films on MgO: A comparative study using *in situ* resistance variation

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Abstract: In the present work, Fe and CoFeB films are examined *in situ* for investigating the percolation threshold of both the magnetic films on MgO. Thus resistance variation approach was followed *in situ* while depositing Fe and CoFeB films on the deposited MgO film. The structural quality and thickness of deposited magnetic film was ensured using X-ray reflectivity. The variation of resistance and rate of change of resistance with depositing film thickness indicates the Volmer-Weber growth for both the films. However, percolation threshold is observed to be higher for CoFeB film as compared to Fe which is due to low wettability of CoFeB on MgO. The results are important and directional in view of modification of growth process on MgO, which may further improve the interface dominating phenomena.

INTRODUCTION

Fe/MgO and CoFeB/MgO are potential systems of current interest [1-4] playing an important role in development of novel spintronic devices exhibiting large interfacial perpendicular magnetic anisotropy (PMA), low spin transfer torque, low switching current and high tunnel magnetoresistance (TMR). These properties have significant implications in view of magnetic tunnel junctions with applicability in high density data storage and low power consumption. The interfaces of ferromagnetic layers with oxide layer like MgO, which exhibits high spin filter effect, are crucial in controlling the functional properties [5, 6]. For example recent studies on Fe/MgO show the role of interfaces in modulating the interfacial magnetic anisotropy and Gilbert damping constant [6]. Similarly the engineering of interfaces in CoFeB/MgO systems may also lead to control Domain wall dynamics [5].

It has been observed that growth mechanism of magnetic films on MgO decides the interfacial properties and hence the TMR [7]. For example literature studies report precise stacking of MgO layer on Fe (001) film [8], because of small lattice mismatch and relatively low surface free energy of MgO. However there is concern while depositing Fe or CoFeB film on MgO as it follows Volmer-Weber growth reflecting poor wettability of Fe / CoFeB on MgO [9, 10]. Therefore it is important to know about the percolation thickness of Fe and CoFeB films on MgO i.e. the thickness of transition from insulating to conductive state when there is a continuous path for electrical conduction.

In the present work, resistance variation has been observed *in situ* while depositing Fe and CoFeB films on MgO film. The results were compared to elucidate the percolation threshold in both the cases.

EXPERIMENTAL

MgO films were deposited on Si (001) substrates using e-beam evaporation setup [11]. Subsequently silver contacts were deposited on diagonally opposite ends of MgO film by masking the film in remaining area. The deposited structure was mounted in an ultra-high vacuum (UHV) chamber equipped with facility of ion-beam sputtering and *in situ* four probe resistivity measurement. Being hygroscopic, MgO film was annealed at 150°C in UHV conditions to remove the possible contamination or water vapors adsorbed on the surface of MgO film. The base pressure of the chamber prior to deposition was 2×10^{-7} mbar. Deposition of Fe and CoFeB films was carried out separately on treated MgO film, using sputtering of Ar ion beam (at 500 eV) on commercially purchased targets of Fe and CoFeB (purity > 99.95%). A piece of polished Si substrate was mounted nearby to MgO film to elucidate the thickness of deposited

magnetic film and to calibrate the thickness in resistance measurements. The measurements of resistance with increasing film thickness were done using four-probe technique at room temperature with constant current source and high precision digital multimeter of Keithley. X-ray reflectivity measurements were done post-deposition at UGC-DAE CSR, Indore using Bruker's D8 diffractometer fitted with a Göbel mirror on the incident beam side in order to obtain a parallel monochromatic beam of Cu $K\alpha$ radiation.

RESULTS AND DISCUSSION

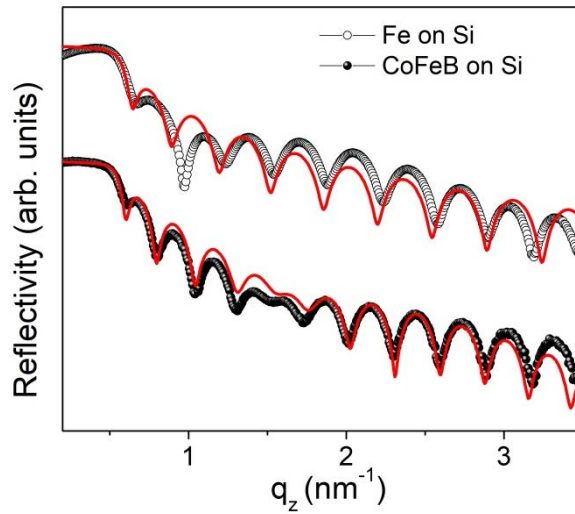


Figure 1: X-ray reflectivity of Fe and CoFeB films deposited on adjacent Si substrates. The continuous curve represents the best fit to experimental data. Different curves are displaced vertically with respect to each other for easy viewing.

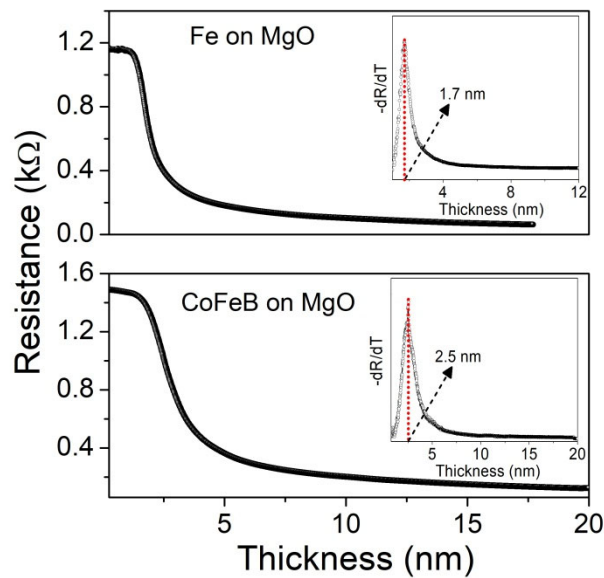


Figure 2: Resistance (R) as a function of film thickness (T) of Fe and CoFeB film deposited on MgO film. Inset shows the rate of change of resistance $-(dR/dT)$ as a function of film thickness.

Figure 1 shows the X-ray reflectivity (XRR) of Fe and CoFeB films deposited on adjacent Si substrates. Experimental data was fitted using Parratt's formalism. The continuous curve represents the best fit to experimental. Thickness as calculated from fitting of XRR data comes out to be $\sim 20 \pm 0.1$ nm for CoFeB and 18 ± 0.1 nm for Fe. Low surface and substrate roughness (< 0.5 nm), as obtained from XRR fitting ensures the deposition of good quality samples. The data is best fitted with 3% reduced electron density than the standard values, which is possibly due surface oxidation in absence of capping layer. Thicknesses as obtained from fitting of XRR data were further implemented to calibrate the thickness axis in *in situ* resistance results.

Figure 2 shows the variation of resistance between silver contacts deposited on MgO film, while Fe and CoFeB films were deposited *in situ*. For both the cases, one may note that at low film thickness the resistance is constant which decreases rapidly beyond certain thickness and becomes constant at higher film thickness. Qualitatively one may note that the change of resistance with film thickness is varying at slow rate for CoFeB film compared to Fe film. For quantitative analysis inset of the Figure 2 depicts the variation of rate of change of resistance ($-dR/dT$) with film thickness. For Fe film the peak value of ($-dR/dT$) is obtained around 1.7 nm film thickness, and becomes constant beyond 4 nm film thickness. However, CoFeB film exhibits a peak value of ($-dR/dT$) around 2.5 nm film thickness and becomes constant beyond 7.5 nm film thickness.

Such variation of resistance can be understood in view of growth behavior of Fe and CoFeB films on MgO. Both the films exhibit Volmer-Weber growth on MgO because of low surface free energy of MgO (1.1 J/m^2). At low film thickness growth is in form of islands which are well separated from each other and are inhibiting the flow of current from one end to other. Beyond this, hopping conduction takes place across the islands, thereby reducing the resistance at slow rate. With further increase in thickness, coalescence of islands takes place and resistance decreases rapidly. The peak in the variation of resistance with film thickness signals percolation threshold, which is observed to be at 1.7 nm for Fe and at 2.5 nm for CoFeB on MgO. In fact, for Fe film, the result agrees with earlier studies of Fe film on MgO (001) [12]. The higher percolation threshold for CoFeB film is attributed to poor wettability of CoFeB on MgO as reported in literature studies [13, 14], which can be improved by introducing additional layers at the interface. Such behavior of magnetic films on MgO plays an important role in modification of interfacial PMA.

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The Role of Substrate Orientation On Uniform Growth Of TiO₂ Nanorods

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Abstract. A highly ordered, vertically oriented TiO₂ nanorods array is successfully synthesized on a fluorine doped tin oxide (FTO) conducting substrate with a facile and cost-effective synthesis using hydrothermal method. The effect of different preparation conditions on the growth morphology of TiO₂ nanorods was investigated. Field emission scanning electron microscopy results demonstrate large scale nanorods grown on the FTO substrate. The nanorods are well aligned at growth condition of FTO conducting surface facing downwards and kept at an angle of 45° for 60 min growth time. From cross sectional image of TiO₂ nanorods, we have analyzed the length of the nanorods and is found to an average of 1.6 μm. The X-ray diffraction results reveals that only the rutile phase is present. These results indicates that well oriented and single phase TiO₂ nanorods have been successfully grown.

INTRODUCTION

The titanium dioxide is a wide bandgap semiconductor and have attracted much attention owing to their excellent properties such as high oxidation power, excellent electronic and optical properties, long term chemical stability and non-toxicity [1-4]. Crystallite TiO₂ has three polymorphs such as anatase, rutile and brookite. The rutile phase is more thermodynamically stable and it has direct bandgap and high refractive index, making suitable for various applications like photodetectors, optical coatings and photoelectrochemical cells [5-6]. One dimensional TiO₂ nanorods offers enhanced surface to volume ratio, unidirectional charge transport pathways and reduced grain boundaries which helps in charge separation and transport characteristics. The highly oriented vertical nanorods are more advantageous in optoelectronic applications for unidirectional charge carriers flow and also provide higher absorption rate due to increased surface to volume ratio. The growth of highly oriented vertical nanorods is also bit challenging. In this study, our aim was to prepare the highly oriented TiO₂ nanorods and study the effect of preparation conditions.

EXPERIMENTAL PROCEDURE

The TiO₂ nanorods were grown using hydrothermal synthesis process. At first, the 1:1 ratio of distilled water (DI) and HCl are taken for sonication. After that 0.5 ml of TiO₂ precursor TTIP (Titanium Tetraisopropoxide) is added and sonicated. The resultant solution is poured into the Teflon lined autoclave and the FTO substrate is kept inside the autoclave. Finally sealed autoclave is taken for the hydrothermal reaction which was carried out at 180 °C for an hour. The synthesized TiO₂ film is washed with DI water and kept for drying.

The structural analysis was carried out using X-ray diffraction and the vibrational modes were estimated using Raman characterization. The UV absorption spectroscopy was carried out to determine the bandgap of the prepared film. The microstructure analysis was studied using Field Emission Scanning Electron Microscopy (FESEM). XPS analysis were also carried out to estimate the binding energies of the constituent elements.

RESULTS AND DISCUSSIONS

Microstructure analysis

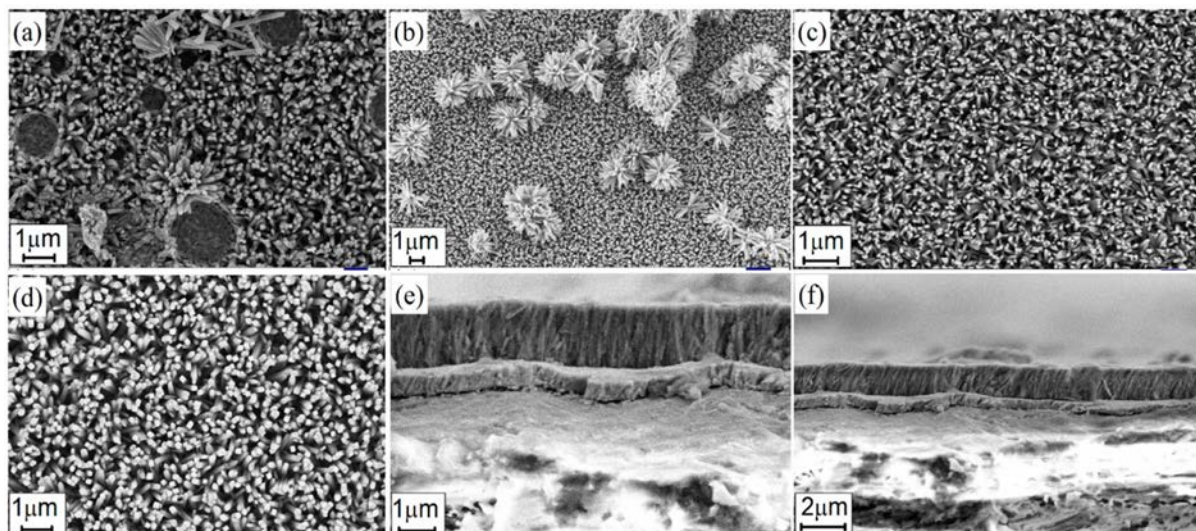


FIGURE 1. Surface morphology of (a) trial 1, (b) trial 2, (c) trial 3 and (d) trail 4 of TiO₂ nanorods. Cross sectional image of (e) and (f) trail 4 with different magnification.

The TiO₂ nanorods preparation was carried out in different conditions and their surface morphology was shown above. The Fig. 1(a) is the trial 1 where the FTO substrate was kept horizontally to the bottom surface and the conducting surface is facing upwards with growth time 60 min. In this type of preparation, we observed some pits around the nanorods. Fig. 1(b) is the trial 2, where the FTO substrate is inclined at an angle of 45° and conducting surface is facing upwards. In this trial 2, we have observed the nanorods growth along with nano flowers for growth time of 60 min. Fig. 1(c) is the trial 3, where the growth time is restricted to 45 min and the conducting surface of the substrate is facing downside with 45° inclination. In this we got only the nanorods but not highly vertically oriented. The trial 4 in Fig. 1(d), the conducting surface is facing downwards at angle of 45° and the growth time is 60 min. In this trail, highly oriented nanorods have been observed which is evidenced from the Fig. 1(d). This trial 4 sample is chosen for further characterizations. The Fig. 1(e) and Fig. 1(f) show the cross-sectional view of the TiO₂ nanorods with resolution of 1 μm and 2 μm, respectively. The length of the TiO₂ nanorods were found to be 1.6 μm.

Structural and Optical Properties

The Figure 2(a) shows the X-ray diffraction of TiO₂ nanorods on FTO substrate. The diffraction peaks observed at 36.12°, 54.40°, 62.91°, 69.08° and 69.89° are well consistent with rutile phase of TiO₂, which are indexed to (101), (211), (002), (301) and (112) crystal planes respectively (JCPDS card no. 21-1272). Fig. 2(b) shows the Raman characterization of TiO₂ nanorods. The peaks observed at 608 cm⁻¹, 440 cm⁻¹ and 237 cm⁻¹ are attributed to A_{1g}, E_g and multiphonon Raman vibrational modes of rutile phase of TiO₂. Fig. 2(c) display the UV absorption spectroscopy of TiO₂ nanorods. The bandgap estimation was estimated using Tauc's plot and was found to be 3.11 eV, as shown in Fig. 2(d).

XPS analysis

The XPS analysis was carried out to understand the binding energies of the elements of TiO₂ film. The high resolution spectra of Ti 2p and O 1s spectra is shown in Fig. 2(e) and Fig. 2(f) respectively. The obtained binding energies are found to be 458.91 eV for Ti 2p_{3/2}, the values are in agreement with the reported values [5]. The O 1s spectra shows the peak for O-H around 532 eV is due to hydrolysis process used in sample preparation.

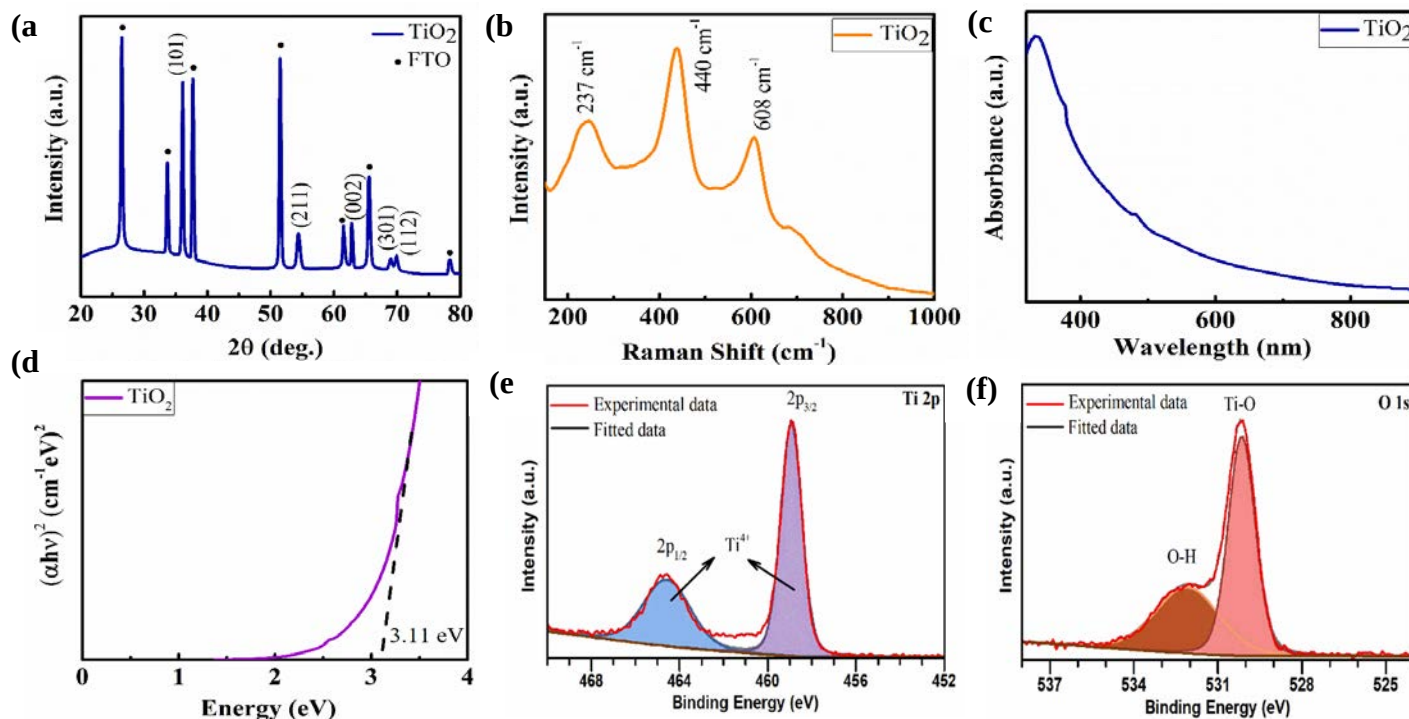


FIGURE 2. TiO₂ nanorods of (a) X-ray diffraction analysis, (b) Raman characterization, (c) UV absorption spectroscopy and (d) Tauc's plot. XPS plot of (e) Ti and (f) O.

Conclusions

The effects of substrate orientation and growth time on the TiO₂ nanorods growth is carried out, using a simple and cost effective hydrothermal synthesis method. It is observed that the 60 min growth and conducting side of FTO facing downwards at an angle of 45° substrate orientation yield highly vertical and uniform distribution of TiO₂ nanorods. The successful growth of highly oriented vertical TiO₂ nanorods has been achieved which is more advantageous for applications in the development of optoelectronic devices.

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Fabrication of Nanopatterned Flexible AuNPs@Grating@PDMS film for SERS Applications

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Abstract. Here, we report the development and evaluation of flexible polymeric film-based Surface-enhanced Raman Spectroscopy (SERS) plasmonic substrates comprised of pristine PDMS, AuNPs-embedded PDMS (AuNPs@PDMS), and AuNPs-embedded patterned PDMS (AuNPs@grating@PDMS). The substrates were produced using a simple curing process. The maximum SERS enhancement achieved was on AuNPs@grating@PDMS substrate owing to the dual advantages of periodic nanostructures at grating level and additional plasmonic hotspots due to embedding of AuNPs. We observed that AuNPs@PDMS exhibited some moderate enhancement due to the presence of AuNPs whereas pristine PDMS did not yield significant signal as expected. The findings will be important for understanding the strong SERS enhancement observed on these substrates as they demonstrate the requirement of surface nanostructuring and resulting availability of nanoparticles to achieve such an enhancement. The method shows a low-cost, tunable, and scalable way to produce efficient SERS substrates.

INTRODUCTION

The detection of trace targets has become prevalent by using the surface-enhanced Raman scattering (SERS) technology. Its performance depends on active substrates producing "hot spots" via localized surface plasmon resonance (LSPR) that greatly amplify the Raman signals. Flexible substrates like polydimethylsiloxane (PDMS) have gained attention due to their flexibility, optical transparency, and minimal Raman signal interference, making them ideal for SERS applications [1,2].

This study presents the investigation of the SERS performance of three different flexible substrates designed to explore the synergistic effects of plasmonic nanostructures and substrate morphology in enhancing Raman signals. The comparative analysis involves the SERS measurements on pristine PDMS, PDMS infused with gold nanoparticles (AuNPs), and nanostructured PDMS substrates featuring DVD-grating-replicated patterns combined with AuNPs integration.

EXPERIMENTAL SECTION

AuNPs were synthesized using the sodium citrate reduction method [2]. PDMS solution was prepared by mixing a pre-polymer base with a curing agent using an elastomer kit. The mixture was stirred thoroughly and then poured into a petri dish to form a flexible pristine PDMS film (Fig. 1). The colloidal AuNPs solution was incorporated into the PDMS mixture and mixed thoroughly. This AuNPs-infused mixture was poured onto a glass Petri dish to obtain the AuNP-embedded PDMS (AuNPs@PDMS) flexible film (Fig. 1). Also, the AuNPs-infused mixture was poured onto a DVD to transfer its nanostructure, creating a flexible AuNPs@grating@PDMS film (Fig. 1). All the prepared samples were then heated to 80°C for 2 hr to ensure proper cross-linking of the PDMS, resulting in the desired hardness and stiffness. After curing, the PDMS substrates were carefully peeled away as shown in Fig. 1.

UV-Visible absorption spectra were recorded using a Shimadzu UV-2600 spectrophotometer. An optical microscope (OLYMPUS BX51) was employed to observe the surface morphology of the substrates. SERS measurements were carried out with a LabRAM HR-UV-Open micro-Raman spectrometer (HORIBA Scientific,

France) using a 532 nm, 1 mW laser, 0.75 NA objective, and $50\times$ lens with 1 s acquisition time. Structural analysis was performed using a high-resolution X-ray diffractometer (HRXRD, Rigaku SmartLab II)

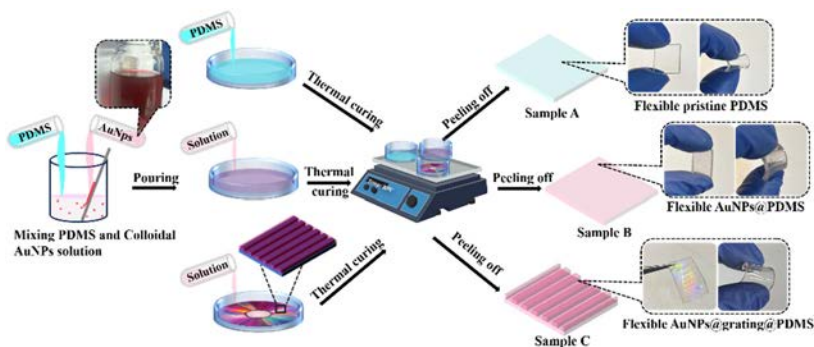


FIGURE 1. Schematic illustration of the fabrication process of flexible PDMS Polymeric SERS substrate by thermal curing.

RESULTS AND DISCUSSION

When colloidal AuNPs solution and PDMS was mixed, the NPs did not have enough energy and time to aggregate and the colour was preserved (composites became pink in colour, see Fig. 1). Fig. 2(a) shows an optical microscopic picture of PDMS with incorporation of AuNPs. This picture shows that bubbles/voids, together with the AuNPs, are well dispersed and randomly oriented in PDMS. The diameter of the exhibited structures is on the micrometer scale, which surpasses that of AuNPs, likely attributable to the amalgamation of voids and the development of microbubbles in the liquid phase during the thermal drying process in the oven [3]. These phenomena result in the creation of microporous materials and an increased surface roughness.

XRD technique was used to analyze the structure of pristine PDMS and AuNPs@PDMS film (Fig. 2(b)). The diffraction peak of pristine PDMS appeared at $2\theta \approx 12^\circ$, corresponding to the reflection plane (101). In contrast, the AuNPs@PDMS film exhibited the characteristic peak of PDMS along with an additional peak at $2\theta \approx 45^\circ$ corresponding to the (200) crystal planes of face-centred cubic (FCC) gold [4]. This confirms the presence of crystalline AuNPs in the sample. These results indicated that the PDMS contributes to diffuse scattering rather than discrete Bragg peaks in the XRD spectrum because it is an elastomeric polymer with flexible chains and an amorphous shape, and the addition of AuNPs did not change the bulk properties of the PDMS.

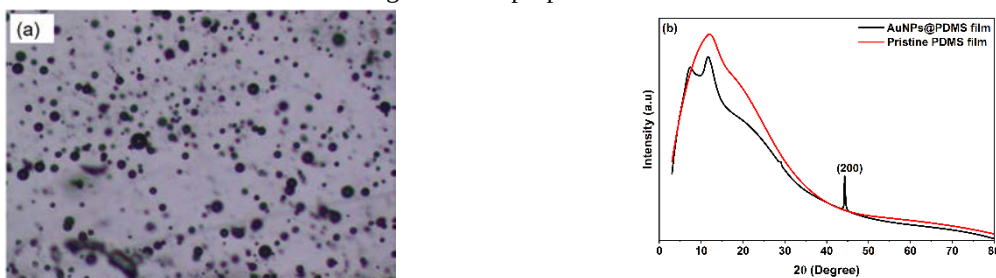


FIGURE 2. (a) Optical image of AuNPs-embedded PDMS film; (b) XRD pattern of PDMS and AuNPs-embedded PDMS films.

UV-Vis spectroscopy was utilized to confirm the incorporation of AuNPs in PDMS by detecting their characteristic surface plasmon resonance (SPR) peak. Fig. 3(a) shows the optical absorbance test result of colloidal AuNPs, AuNPs@PDMS film and AuNPs@grating@PDMS film. Colloidal AuNPs showed a sharp absorbance peak at 527 nm, and the broadness of the peak shows the presence of different NPs than spheres [1,3,4]. AuNPs@PDMS film showed a broader SPR peak than AuNPs sample. This broadening is due to the increase in the local refractive index around the AuNPs introduced by the PDMS [3,4]. The distribution of AuNPs in a specific pattern may be the reason for AuNPs@grating@PDMS film showed a broader SPR peak than AuNPs and AuNPs@PDMS film [1-4]. Also, the absorbance of AuNPs in a patterned PDMS is indeed dependent on the number of AuNPs present. Specifically, the intensity of the SPR peak increases with a higher concentration of AuNPs. Absorbance results showed less intense SPR peaks for AuNPs@PDMS and AuNPs@grating@PDMS films because of the incorporation of small amount of

colloidal AuNPs solution in the PDMS mixture. Briefly, this result indicates the presence of the AuNPs on the PDMS film. Broadness and shift in the peaks of all three samples related to the change in refractive index (surrounding medium) around the AuNPs, the number of AuNPs in PDMS and the distribution arrangement of AuNPs in the linear structure of the DVD.

SERS efficiency of all three distinct flexible films was evaluated using *Rhodamine 6G* (R6G) as a Raman probe. Raman and SERS spectra of R6G on bare Si substrate, AuNPs, and AuNPs@PDMS and AuNPs@grating@PDMS films are presented in Fig. 3(b), showing the enhancement of Raman signals. Among these polymeric samples, AuNPs@grating@PDMS films demonstrate a more significant enhancement in Raman signals due to the incorporation of AuNPs and the grating structure of DVD. The most prominent Raman bands, exhibiting strong scattering intensities at 610, 771, 1361, 1506, 1571, and 1648 cm^{-1} , are associated with xanthene/ phenyl ring deformation, out-of-plane bending motion of hydrogen atoms in the xanthene ring, respectively. 1361, 1506, 1571, and 1648 cm^{-1} to C–C stretching vibrations in the xanthene/phenyl ring of the R6G molecule. These modes align well with previously reported Raman spectra of R6G [1,2] and with the Raman spectra (Fig. 3(b)). Furthermore, we identified key factors contributing to the high-quality SERS spectra. No signal enhancement was expected due to the absence of AuNPs/grating structure in the pristine PDMS film. The embedded AuNPs may have been located too deep within the PDMS films, which limits their interaction with R6G molecules and thereby weakens the SERS effect in AuNPs@PDMS film and AuNPs@grating@PDMS film. Furthermore, low NPs density, nonuniform distribution, and poor surface adsorption of R6G likely contributed to the diminished signal. The use of a high R6G concentration may also have resulted in strong fluorescence, which can overshadow the weak Raman signals and increase spectral noise.

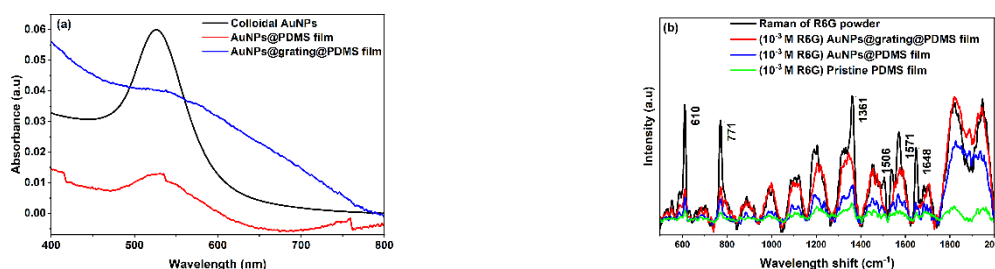


FIGURE 3. (a) Absorbance spectrum of AuNPs, AuNPs-embedded PDMS film and AuNPs-embedded patterned PDMS film; (b) SERS and Raman spectra of R6G on PDMS, AuNPs-embedded PDMS and AuNPs-embedded patterned PDMS films showing the enhancement.

CONCLUSIONS

We investigated the SERS performance of flexible PDMS Polymeric films, including pristine PDMS, AuNPs-embedded PDMS (AuNPs@PDMS), and AuNPs-embedded patterned PDMS (AuNPs@grating@PDMS). AuNPs@grating@PDMS exhibited the highest SERS enhancement, highlighting the synergistic effect of both the grating structure and plasmonic nanoparticles. AuNPs@PDMS, containing only AuNPs, showed moderate enhancement, while pristine PDMS, lacking both nanostructure and AuNPs, produced the weakest signal. These results demonstrate that the incorporation of nanoscale structural features, along with surface accessible AuNPs, significantly improves SERS sensitivity.

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Influence of Structural Evolution on Magnetic and Electrical Response of $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ Thin Film

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Abstract: In this study, $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ (NCFO) thin film is deposited onto Pt/Si (111) substrates using the pulsed laser deposition (PLD) technique to study the influence of structural evolution on magnetic and electrical leakage characteristics. The deposited films exhibited the formation of a single-phase spinel structure, with dense packed grains with an average surface roughness of approximately 3 nm. Magnetic hysteresis measurements exhibited soft ferromagnetic behavior with a coercivity of 27 Oe, saturation magnetization of 302 emu/cc, and remnant magnetization of 10 emu/cc. Leakage current measurements revealed low leakage density ($\sim 3.51 \times 10^{-5}$ A/cm²), with conduction dominated by Ohmic behavior at low fields and a transition to space charge limited conduction (SCLC) at higher fields. These results highlight the strong correlation between microstructural features and functional properties, offering insight into the design of NCFO thin films for advanced electronic applications.

INTRODUCTION

Spinel ferrite thin films have attracted significant attention due to their remarkable magnetic, electrical, and multifunctional properties, making them promising candidates for advanced electronic and spintronic applications [1]. Among them, $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ (NCFO) exhibits excellent chemical stability, soft ferromagnetic behavior, and tunable electrical characteristics. The functional properties of NCFO thin films are strongly influenced by their structural evolution, microstructure, and cation distribution. Therefore, understanding the correlation between structural features and magnetic as well as electrical responses is essential for optimizing device performance. In this work, NCFO thin films are deposited on Pt/Si (111) substrates using the pulsed laser deposition (PLD) technique. Detailed investigations of the structural, morphological, magnetic, and leakage conduction properties are carried out. The obtained results reveal that the dense microstructure and improved crystallinity significantly influence the magnetic softness and leakage current behavior of the films. These findings provide valuable insight into the design of ferrite-based thin films for multifunctional electronic applications.

RESULTS AND DISCUSSION

Structural Analysis

The $\text{Ni}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ (NCFO) thin film forms a single-phase cubic spinel structure with an $\text{Fd}\bar{3}\text{m}$ space group, as confirmed by Rietveld-refined XRD analysis shown in **Fig. 1(a)**. Raman spectroscopy further validates phase purity and reveals crucial insights into the phonon modes as illustrated in **Fig. 1(b)**. The Raman active modes, $\text{A}_{1\text{g}}$, E_{g} , and $3\text{T}_{2\text{g}}$, arise from the motion of oxygen, tetrahedral (A-site), and octahedral (B-site) ions. Specifically, $\text{A}_{1\text{g}}$ modes, observed above 600 cm^{-1} , indicate symmetric stretching of oxygen in the A-site void, while E_{g} and $3\text{T}_{2\text{g}}$ modes, below 600 cm^{-1} , represent symmetric and antisymmetric bending in the B-site void. A distinct shoulder-like feature at 690 cm^{-1} is attributed to inhomogeneous cation distribution within the mixed spinel ferrite, a characteristic previously reported for spinel ferrite [2].

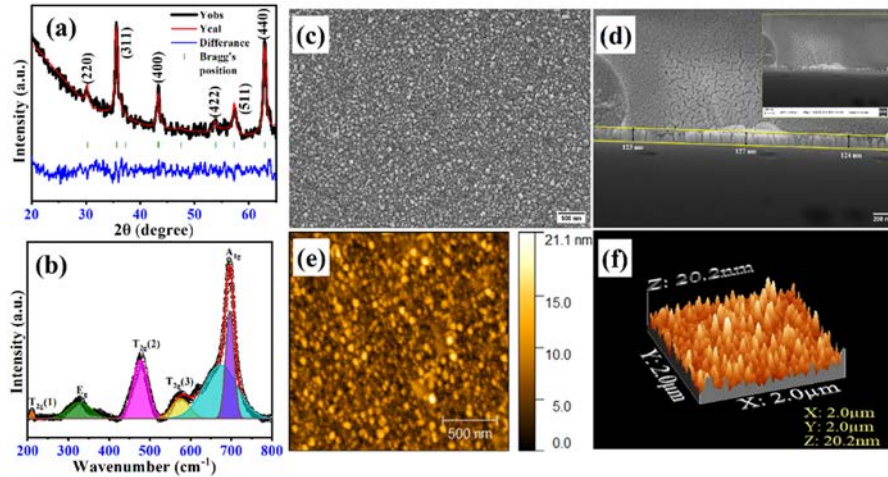


FIGURE 1(a) Rietveld-refined XRD pattern, (b) Raman spectra, (c) FESEM images (d) cross-sectional views, (e-f) detailed 2D and 3D perspectives of the surface topography of the deposited NCFO thin film.

The surface morphology of the films is examined using field emission scanning electron microscopy (FESEM), as shown in **Fig. 1(c)**. It revealed a dense and homogeneous microstructure. This microstructural uniformity is attributed to sufficient atomic mobility at the high annealing temperature of 700 °C, which enables atoms to occupy energetically favorable lattice positions. Cross-sectional FESEM imaging, shown in **Fig. 1(d)**, is used to determine the film thickness, which exhibiting an estimated thickness of approximately 125 nm. The average grain size is determined using ImageJ software, and it is found to be approximately 45 nm. Atomic force microscopy (AFM) analyzes the surface topography and grain growth behavior over a $2\ \mu\text{m} \times 2\ \mu\text{m}$ scan area. **Fig. 1(e-f)** presents the 2D and 3D AFM images, revealing well-distributed grains and surface uniformity. The root mean square (RMS) surface roughness, calculated using Gwyddion software, is 2.53 nm, indicating a relatively smooth and compact film surface.

Magnetic Properties and Leakage Current Density

The magnetic properties of the prepared NCFO thin film is investigated at room temperature, revealing a soft ferromagnetic behavior, as shown in **Fig. 2(a)**. The film exhibits a well-defined saturation magnetization ($M_s = 302\ \text{emu/cc}$), with a low coercive field ($H_c = 27\ \text{Oe}$) and low remanent magnetization ($M_r = 10\ \text{emu/cc}$). To gain deeper insight into the magnetic behavior, the high-field region of the M–H curve is further analyzed using the law of approach to saturation (LAP), as presented in **Fig. 2(b)**. The extracted magnetic parameters collectively confirm the soft ferromagnetic nature of the NCFO thin film. These results indicate high crystallinity and a homogeneous microstructure, which play a critical role in magnetic softness. The low coercivity suggests minimal domain wall pinning, likely due to the uniform grain distribution and dense microstructural packing, as supported by structural and morphological analyses. The favorable cation distribution of Ni^{2+} and Co^{2+} ions between tetrahedral (A) and octahedral (B) sites in the spinel lattice enhances superexchange interactions, contributing to the soft magnetic response. The presence of Co^{2+} not only increases magnetic anisotropy and thermal stability but also supports magnetic softness by maintaining low coercivity. The dense microstructure may facilitate easier domain wall motion, further reducing magnetic losses. The room temperature leakage current density (J–E) characteristics for the NCFO thin film is illustrated in **Fig. 2(c)**. The leakage current density curve is not symmetric for positive and negative electric fields. At a particular applied field of 645 kV/cm, the leakage current density for NCFO thin film is $2.2 \times 10^{-5}\ \text{A/cm}^2$. To gain insight into the dominant conduction mechanism, the positive-bias region of the J–E curve is analyzed using various conduction models [3].

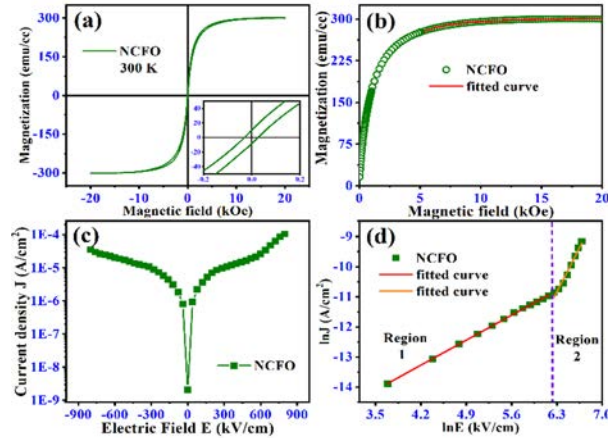


FIGURE 2 (a) M-H loop, (b) LAP fit, (c) Leakage current vs. electric field, (d) Ohmic and space charge limited conduction (SCLC) mechanism.

As shown in **Fig. 2(d)**, the $\log(J)$ – $\log(E)$ plot is well-fitted with two linear regions, each corresponding to a different power-law dependence, suggesting different dominant mechanisms across the electric field range. In the low-field region, the slope (s_1) is close to 1, which indicates Ohmic conduction, where the current density is linearly proportional to the applied electric field. In this regime, thermally generated free carriers dominate the current transport, and the intrinsic conductivity of the material limits the current. The low leakage in this region reflects the good insulating nature and uniform microstructure of the NCFO film. In the high-field region, the slope (s_2) increases significantly to 4.63, suggesting that space charge limited conduction (SCLC) becomes dominant. Specifically, the slope greater than 2 implies the occurrence of a trap-filled limit (TFL) regime. In SCLC, the current is governed by the injection of charge carriers from the electrode into the dielectric film. Therefore, the abrupt increase in current with field (as reflected in $s_2 = 4.63$) is attributed to the saturation of trap states, which are often associated with oxygen vacancies or cation disorder in the spinel lattice. Such behavior underscores the importance of trap dynamics in controlling leakage current in ferrite thin films. The presence of Ni^{2+} and Co^{2+} ions may influence trap formation through local structural distortion or charge compensation effects. The relatively low leakage current and well-defined conduction transition suggest a dense microstructure and good film quality, consistent with the observed structural and morphological results.

In summary, high-quality NCFO thin films are successfully deposited on Pt/Si (111) substrates using the PLD technique. Structural and morphological analyses confirmed the formation of a single-phase spinel structure with dense and uniform microstructure. The films exhibited soft ferromagnetic behavior with low coercivity and enhanced magnetic response, both strongly influenced by improved crystallinity and a favorable cation distribution. Leakage current analysis revealed a low leakage density, with a transition from Ohmic conduction at low electric fields to space-charge-limited conduction at higher fields. The observed correlation between microstructural evolution and functional properties highlights the potential of NCFO thin films for advanced multifunctional electronic applications.

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Mixed Langmuir Monolayers of 8CB and BHAB

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Abstract. The 8CB molecule (4-cyano-4-n-octylbiphenyl) belongs to a class of liquid crystal compounds designed for specific uses in technologies such as liquid crystal displays, biosensors, and other photosensitive devices. Most of these applications involve thin films of mixtures of liquid crystal and photoactive molecules. Hence, it is important to study the properties of 8CB monolayer in the presence of photoactive molecules. In this work we have studied the quasi-2D phases exhibited by the monolayer films of mixtures of 4,4'-Bis (heptyloxy) azobenzene (BHAB) and 8CB at the air-water interface and analyzed the surface pressure–area per molecule isotherms for understanding the thermodynamic stability of the mixed monolayer.

INTRODUCTION

The study of the 8CB monolayer (4-cyano-4-n-octylbiphenyl) is important to understand the behavior and unique properties of liquid crystals at interfaces essential for a wide range of technological applications. For devices like organic light-emitting diodes (OLEDs), sensors, and liquid crystal displays (LCDs) studies, it is essential to study the molecular interactions, self-assembly, and phase behavior of the ultra-thin films[1]. The variety of ordered structures of the thin films varies with temperature, surface pressure, and the substrate[2]. The study of the 8CB monolayer in the presence of photoactive molecules such as BHAB molecules helps in understanding the effect of rigid core molecules on the self-assembly of the 8CB molecule. The studies on the effect of the BHAB molecules on the 8CB monolayers are important to design the next-generation materials for low-cost, flexible, and efficient organic devices[3, 4, 5].

EXPERIMENTAL SECTION

Surface manometry is a technique for studying phase transition phenomena in Langmuir monolayers[6,7]. In this technique, surface pressure (π) is measured as a function of inverse of the surface density, which corresponds to the area per molecule (A_m) in the Langmuir monolayer. The surface pressure is obtained by calculating the difference between water–air interfacial tension in the absence of a monolayer (γ_0) and when a monolayer is present at the air-water interface ($\pi = \gamma_0 - \gamma$)[8]. To preserve a steady temperature of the sub phase, water is circulated in the Langmuir trough with the help of a water circulator. The Langmuir trough (Apex Instruments) is placed on a granite slab to reduce the effects of vibrations, and it is rinsed with high purity de-ionised water prior to each experiment. The trough is initially cleaned with distilled water and wiped with chloroform-soaked tissue paper and again rinsed with de-ionised water. We can form an 8CB monolayer at the air-water interface by injecting a certain number of molecules using a Hamilton syringe and compressing the monolayer by moving barriers to study the variation of surface pressure with respect to the area per molecule.

RESULTS AND DISCUSSION

Figure 1 shows the $\pi - A_m$ isotherm for the monolayers of mixtures of BHAB and 8CB molecules for different mole fraction of BHAB in the monolayer ($\chi_{BHAB} = 0.1, 0.2$, and 0.3). The monolayer with $\chi_{BHAB} = 0.1$, exhibits a gaseous phase for A_m is greater than the $64 \text{ \AA}^2$. For $64 \text{ \AA}^2 > A_m > 60 \text{ \AA}^2$, the monolayer exhibits liquid expanded phase. The monolayer collapses at area per molecule of $40 \text{ \AA}^2$ and 14 mN/m surface pressure. The monolayer with $\chi_{BHAB} = 0.2$, exhibits gaseous phase for A_m greater than the $62 \text{ \AA}^2$. For $62 \text{ \AA}^2 > A_m > 60 \text{ \AA}^2$, the monolayer exhibits a liquid expanded phase. The monolayer collapses at an area per molecule of $34 \text{ \AA}^2$ and 16 mN/m surface pressure. The monolayer with $\chi_{BHAB} = 0.3$ exhibits gaseous phase for A_m is greater than the $54 \text{ \AA}^2$. For $52 \text{ \AA}^2 > A_m > 42 \text{ \AA}^2$

the monolayer exhibits liquid expanded phase. The condensed phase exhibit between area of the $52 \text{ \AA}^2 > A_m > 34 \text{ \AA}^2$. The monolayer collapses at an area per molecule of $28 \text{ \AA}^2$ and 17 mN/m surface pressure.

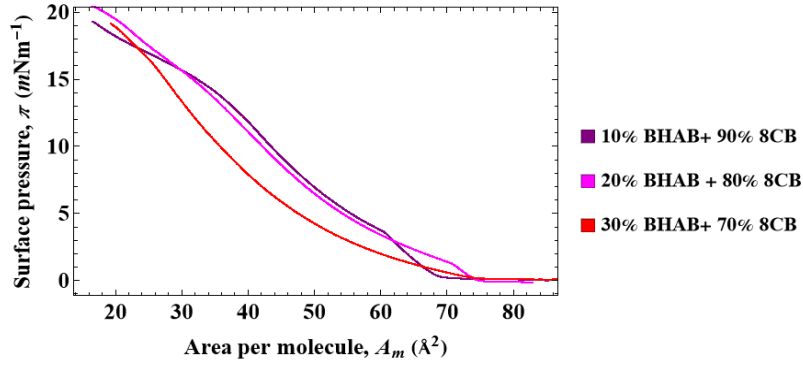


FIGURE 1: Plot of $\pi - A_m$ isotherm obtained at 21°C for different mole fractions of BHAB in 8CB mixed monolayers.

The miscibility of molecules in the Langmuir monolayer at the air-water interface can be studied by calculating the excess area occupied by the molecules in the **binary monolayer**. For a perfectly miscible monolayer the total area of the monolayer at a given surface pressure will be sum of area per molecules of pure monolayers at that surface pressure. For an ideal two-component system, the additive principle calculates the average area per molecule A_{ideal} occupied at a given surface pressure.

$$A_{ideal} = \chi_{8CB} A_{8CB} + \chi_{BHAB} A_{BHAB} \quad (1)$$

Here, A_{8CB} and A_{BHAB} are the average molecular areas occupied by 8CB and BHAB molecules at pressure π , and χ_{8CB} and χ_{BHAB} are the respective molar fractions of 8CB and BHAB. If the mixed monolayer has molecules mutually interacting with each other, then the actual area occupied by the monolayer (A_{mix}) can be either less or more than the A_{ideal} . The excess area is then given by,

$$A_{ex} = A_{ideal} - \chi_{8CB} A_{8CB} - \chi_{BHAB} A_{BHAB} \quad (2)$$

Figure 2a shows variation of the excess area A_{ex} for different mole fractions of the BHAB and for varied surface pressures. For all the surface pressures, the excess area obtained is positive. For the mixed monolayers with 20% mole fraction of BHAB, the excess area is maximum. The positive excess area corresponds to the repulsive interaction between 8CB and BHAB molecules. From Figure 2a, it can also be observed that the excess area decreases as we increase the surface pressure from 2 to 17 mN/m . The change in the Gibbs' free energy per mole in the mixed monolayers can be obtained by using the expression,

$$\delta G_{ex} = N_A (A_{ideal} - \chi_{BHAB} A_{BHAB} - \chi_{8CB} A_{8CB}) d\pi \quad (3)$$

Figure 2b shows the excess free energy δG_{ex} for the binary monolayer at a specified surface pressure calculated by using Equation 3. It is evident that δG_{ex} is positive for all the mixed monolayers studied. The positive δG_{ex} indicates the repulsive interaction between the components of the mixtures. All curves show peaks around $\chi_{BHAB} = 0.2$, representing non-ideal behavior. Repulsive interactions are more significant in this composition. For higher χ_{BHAB} δG_{ex} decreases, indicating that the interactions become less pronounced for the relative composition of BHAB $\chi_{BHAB} > 0.3$. The components in the mixture repel more than they attract, showing the positive deviation of δG_{ex} . As the surface pressure increases, the molecules come closer to each other increasing the potency of the repulsive interactions. The figure (2b) shows an increase in the Gibbs free energy as surface pressure increases[9]. The Gibbs free energy of the system (G) is given by $G = H - TS$, where H is the enthalpy, T is the temperature, and S is the entropy. Compressing the monolayer, the energy associated with the system due to the work done against the repulsive forces, thus increasing the enthalpy (H). Compression also reduces entropy (S) because the molecules have fewer

configurations. The increase in enthalpy and the decrease in entropy contribute to a substantial increase in Gibbs energy.

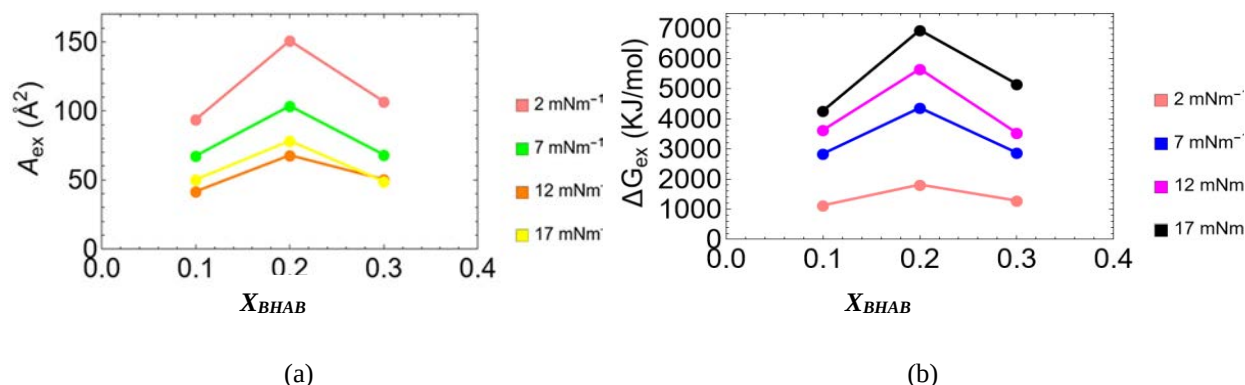


FIGURE 2: Figure shows the plot of variation of excess area (figure 2a) and Gibbs free energy (figure 2b) as a function of different mole fraction of BHAB in 8CB for different surface pressures values- 2,7,12 and 17mN/m .

To conclude, the study of the monolayers and changing concentration of photoactive molecule BHAB in the 8CB monolayer shows important findings into molecular interactions at the interface between air and water. The excess area in the $\pi - A_m$ isotherms decreases with increasing surface pressure, showing stronger molecular packing and enhanced miscibility between molecules. The monolayer progressive stabilization due to the effect of molecular interactions and reduced entropy system suggests increased Gibbs free energy with increasing surface pressure. These studies show the important role of molecular compositions and surface pressure in modifying monolayer properties for possible applications in photo-responsive systems.

ACKNOWLEDGMENTS

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Effect of Ag-Doped V_2O_5 as an Electron Transport Layer (ETL) on PM6 Polymer Thin Films for Organic Solar Cell Applications

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Abstract. In this study, a thin film of silver vanadium oxide (Ag- V_2O_5) was deposited onto a PM6 polymer thin film using radio frequency (RF) sputtering to evaluate its potential as an electron transport layer (ETL) in organic solar cells. Following the deposition, a series of characterization techniques were employed to investigate the structural, optical, and electrical properties of the resulting composite films. UV-Visible spectroscopy revealed a shift in the absorption spectra of the PM6 polymer, indicating strong interaction between the Ag- V_2O_5 layer and the underlying polymer PM6. Photoluminescence (PL) spectroscopy showed an increase in PL intensity upon the addition of Ag- V_2O_5 , indicating reduced non-radiative quenching and suggesting modifications in exciton dynamics at the interface. Raman spectroscopy further confirmed shifts in the characteristic vibrational modes of PM6, supporting the presence of molecular interactions and potential structural modifications resulting from the incorporation of Ag- V_2O_5 . Scanning Electron Microscopy (SEM) revealed the presence of embedded silver nanoparticles within the polymer matrix, which may contribute to enhanced charge transport pathways. Atomic Force Microscopy (AFM) analysis provided insights into changes in surface roughness and topography induced by the Ag- V_2O_5 layer. Collectively, these results suggest that Ag- V_2O_5 may serve as an effective electron transport layer, significantly improving the optoelectronic properties and performance of polymer-based organic solar cells.

INTRODUCTION

Organic solar cells (OSCs) are an attractive photovoltaic technology due to their low fabrication cost, flexibility, and tunable optoelectronic properties [1,2]. Among the active donor materials, PM6 is widely used for its strong absorption and high hole mobility [3]. However, device efficiency is often limited by poor charge transport and recombination losses at the interfaces [4]. To overcome these issues, interfacial engineering using metal oxides like vanadium pentoxide (V_2O_5) has been explored, as they can function as an effective charge transport layer due to their suitable energy levels and transparency [5]. Incorporating metallic nanoparticles, such as silver (Ag), can further enhance charge transport by introducing conductive pathways and plasmonic effects [6,7]. In this work, we investigate a composite Ag- V_2O_5 thin film deposited on PM6 thin film via RF sputtering, aiming to improve charge transport and overall device performance. A range of characterization techniques—including UV-Vis, PL, Raman, SEM, and AFM—were used to analyze the structural, optical, and morphological changes. Electrical measurements revealed improved carrier mobility, indicating that Ag- V_2O_5 can serve as an effective charge transport layer in polymer-based OSCs.

RESULTS AND DISCUSSION

From FIGURE 1a it was found that with addition of Ag- V_2O_5 absorbance spectra is broadened and also absorbance is increased and from FIGURE 1b increase in PL spectra convey that there is decrease in non radiative recombination which reduces the voltage loss in organic solar cells. FIGURE 2a it was found there is decrease in PM6 mode suggesting there is an interaction between PM6 and Ag- V_2O_5 and further is confirmed by FESEM image in FIGURE 2b showing the presence of silver nanoparticles. FIGURE 3a and FIGURE 3b show that there

is increased roughness with addition of $\text{Ag-V}_2\text{O}_5$. Increased roughness provide more surface area for charges to flow which help in improvement of organic solar cell.

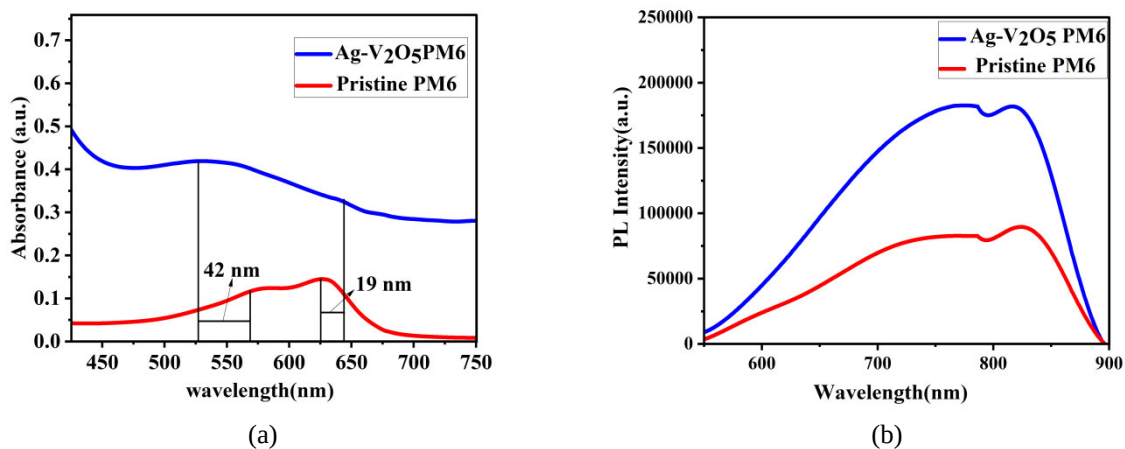


FIGURE 1. Enhancement in optical properties of PM6 by coating $\text{Ag-V}_2\text{O}_5$ thin film

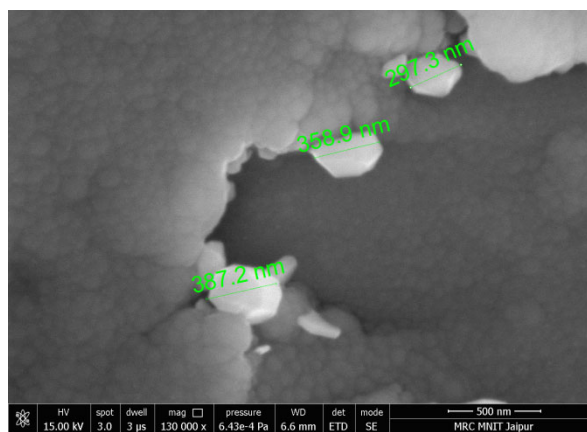
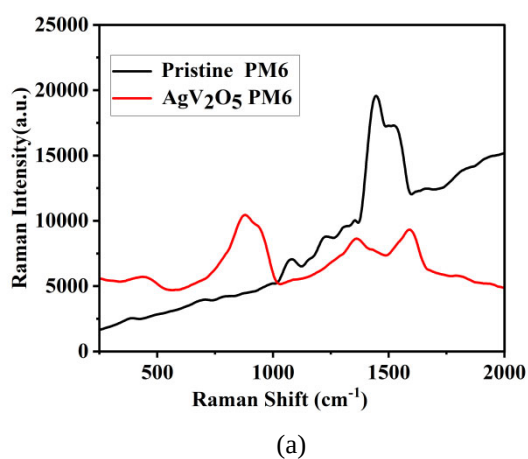


FIGURE 2. Change in structural properties of PM6 by coating $\text{Ag-V}_2\text{O}_5$ thin film

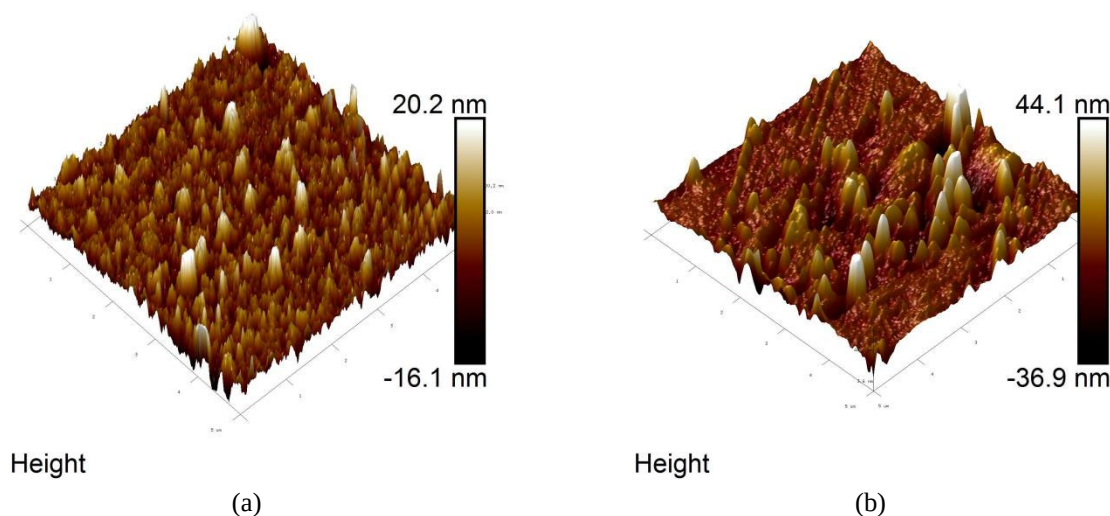


FIGURE 3 Change in morphology of (a) PM6 thin film (b) by making Ag-V₂O₅ thin film on it using AFM images.

CONCLUSION

In summary, this study demonstrates the successful integration of a silver vanadium oxide (Ag-V₂O₅) thin film onto a PM6 polymer layer using RF sputtering, with the goal of enhancing the performance of polymer-based organic solar cells. The comprehensive characterization revealed significant improvements in the structural, optical, and electrical properties of the composite system. UV-Visible spectroscopy and photoluminescence analysis indicated strong interfacial interactions and reduced non-radiative losses, while Raman spectroscopy confirmed molecular-level changes in the PM6 polymer upon Ag-V₂O₅ incorporation. SEM and AFM analyses highlighted morphological modifications, including the presence of embedded Ag nanoparticles and altered surface topography, both of which are conducive to improved charge transport. These findings underscore the potential of Ag-V₂O₅ composite films in advancing the efficiency and functionality of next-generation organic solar cells through interfacial engineering.

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Investigating the Photoelectrochemical Performance of PLD Synthesized MoO₃ Vertical Nanowires

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Abstract - Vertically aligned α - MoO₃ nanowires were synthesized on FTO substrates using pulsed laser deposition (PLD) under optimized conditions. The as-deposited film was utilised to investigate its photoelectrochemical properties. Structural and morphological characterizations confirmed phase purity and high aspect ratio, which contributed to enhanced light absorption and charge carrier transport. The nanowire electrodes exhibited a photocurrent density of 2.06 mA/cm² and a solar-to-hydrogen (STH) efficiency of 2.5%. Mott-Schottky analysis indicated p-type behavior, while EIS and stability tests confirmed efficient charge transfer and good photostability. These findings demonstrate the potential of MoO₃ nanowires as efficient photoelectrodes for solar-driven water splitting.

INTRODUCTION

Solar-driven water splitting for hydrogen generation is considered a promising technology for future sustainable energy systems. Among various approaches, photoelectrochemical (PEC) water splitting is an efficient method to produce hydrogen fuel using sunlight and water¹. The fundamental mechanism of PEC involves efficient light absorption, charge carrier production, separation, and transport to facilitate the redox reactions². Transition metal oxides have emerged as viable alternatives for PEC water splitting applications owing to their chemical stability, abundance, and tunable electrical properties³. Nanostructuring these oxides into different morphologies has been shown to significantly enhance their PEC performance⁴. This improvement is primarily attributed to increased surface area, enhanced light absorption, reduced hole diffusion length, and improved charge-carrier separation and collection. Molybdenum trioxide (MoO₃), a wide band gap (>2.8 eV) material, exists in two stable crystalline phases: orthorhombic α - MoO₃ and monoclinic β - MoO₃. Both phases exhibit unique physical and chemical properties, making MoO₃ suitable for a range of functional applications⁵.

In this study, we fabricated vertically aligned α - MoO₃ nanowires using pulsed laser deposition (PLD) under optimized substrate temperature and oxygen pressure conditions. The structural, morphological, and compositional characterizations were performed using X-ray diffraction (XRD), Raman spectroscopy, field-emission scanning electron microscopy (FE-SEM), and energy-dispersive X-ray spectroscopy (EDX). Following the successful synthesis of these high-aspect-ratio vertical nanowires, we systematically investigated their photoelectrochemical water-splitting performance using photocurrent measurements, Mott-Schottky analysis, electrochemical impedance spectroscopy (EIS), and continuous ON-OFF cycling measurements.

EXPERIMENTAL

Vertically aligned MoO₃ nanowires were fabricated using a PLD system with a KrF excimer laser (wavelength = 248 nm, energy = 60 mJ per pulse, pulse width = 20 ns, repetition rate = 5 Hz). The deposition was carried out on an FTO substrate maintained at 500 °C under an oxygen pressure of 5×10^{-2} mbar, with a total of 5000 laser pulses. The resulting nanowire film was thoroughly studied using XRD, Raman spectroscopy, FE-SEM, and EDX to investigate its phase composition, crystallinity, chemical properties, morphology, and stoichiometry. The PEC measurements were conducted in a three-electrode photoelectrochemical cell configuration, utilizing a Platinum wire as the counter electrode, Ag/AgCl as the reference electrode and the MoO₃ nanowires film deposited on FTO as our working electrode. These electrodes were immersed in 0.5 M Na₂SO₄ electrolyte solution. A 150 W xenon arc lamp was used as the UV-Visible

light source, and all measurements were carried out using a scanning potentiostat system obtained from Autolab, Netherlands.

RESULTS AND DISCUSSION

The structural property of the as synthesized MoO₃ nanowires was investigated using XRD analysis, the XRD pattern (Figure 1A) confirmed the crystal structure with the diffraction peaks corresponding to the orthorhombic α - MoO₃ (JCPDS card # 05-0508)⁶. The prominent (0k0) peaks indicate the layered and anisotropy corresponding to α - MoO₃. Figure 1B shows the observed Raman spectra for the nanowire film. The characteristic peaks observed correspond to α - MoO₃ phase⁷. The narrow range of observed vibrational peaks suggests a well-defined and ordered structure. Additionally, the absence of peaks associated with other MoO₃ phases confirm the phase purity. FE-SEM images (Figure 1C) reveal a dense array of vertically aligned ultrathin nanowires, each exhibiting a remarkably small diameter (see inset of Figure 1C) and considerable length resulting in nanowires with a very high aspect ratio and significant inter-wire spacing, both of which contribute to enhanced photoelectrochemical performance. The EDX spectra (Figure 1D) confirm the presence of only Mo and O elements, with no detectable impurities.

Photoconductivity refers to an enhancement in the electrical conductivity of a material upon exposure to light. When the material absorbs light, it generates additional free electrons and holes, thereby enhancing its overall conductivity. The photocurrent density is determined by subtracting the dark current from the light current in the linear sweep voltammogram, ranging from -1V to 1V, with a constant scan rate of 20 mV/sec at an electrolyte pH of 6.8 was found to be 2.06 mA/cm² at -1 V vs Ag/AgCl (Figure 2A). The vertical nanowire structure enhances light absorption, therefore increasing the generation of electron-hole pairs. As a result, an increased amount of charge carriers reach the MoO₃ electrode, contributing to the enhanced photocurrent observed. The solar-to-hydrogen (STH) efficiency (η_{STH}) of the MoO₃ nanowire-based electrodes was calculated using the formula

$$\eta_{STH} = \frac{j_{sc} * 1.23V * \eta_F}{P_{total}} \quad (1)$$

where $j_{sc}(\frac{mA}{cm^2})$ is the photocurrent density, $P_{total}(\frac{mW}{cm^2})$ is the incident light power density, and η_F represents the Faradaic efficiency, assumed to be 1. Based on this calculation, STH efficiency (η_{STH}) was found to be 2.5%. Mott-Schottky measurements were carried out on the MoO₃ nanowire-based electrodes to determine the conductivity type of the material (Figure 2B). While MoO₃ is typically an n-type semiconductor, the observed negative slope in the Mott-Schottky plot indicates p-type conductivity. This unexpected p-type behavior may be attributed to the formation of an inversion layer near the surface of the nanowires, likely caused by a high concentration of oxygen vacancies in the high-aspect-ratio structures⁸. Figure 2C presents the Nyquist plot derived from the electrochemical impedance spectroscopy (EIS) measurements of MoO₃ nanowires film. The plot shows the imaginary component of impedance as a function of the real component, providing insight into the interfacial charge-transfer mechanism with the shape of the Nyquist arc giving valuable information about the reaction kinetics occurring at the working electrode under light illumination. A smaller arc radius in the plot indicates lower charge transfer resistance, suggesting more efficient charge transport across the interface⁹. The photostability of the MoO₃ nanowire samples was evaluated under chopped light ON/OFF illumination at a bias potential of 0.3 V vs Ag/AgCl for 400 seconds, as shown in Figure 2D. The plot clearly demonstrates the generation of photocurrent upon light exposure. The photocurrent response remains relatively stable throughout the duration, with only a minor baseline shift, indicating good photostability of the MoO₃ nanowires in the aqueous electrolyte.

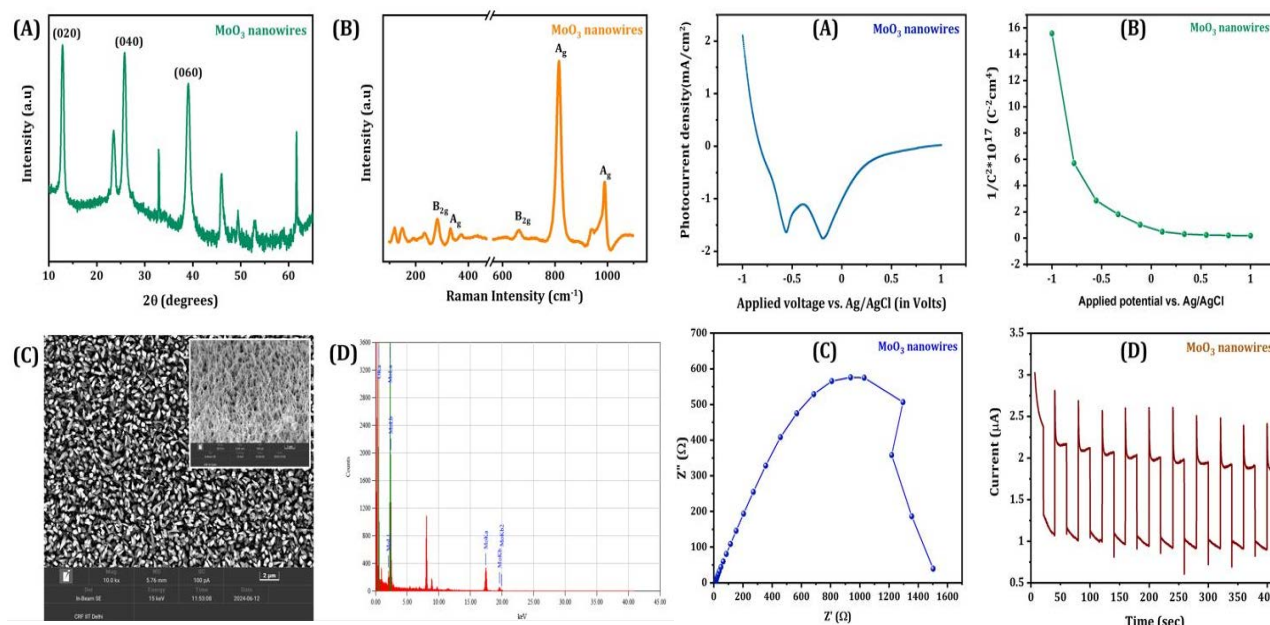


Figure 1: (A) XRD and (B) Raman Spectra of PLD synthesized MoO₃ nanowires, (C) FESEM images depicting the vertically aligned ultrathin MoO₃ nanowires, (D) EDX spectra of the synthesized MoO₃ nanowires.

Figure 2: (A) Photocurrent density of MoO₃ nanowires, (B) Mott Schottky plot under dark conditions, (C) EIS spectra in presence of light, and (D) photocurrent variation under on-off illumination cycles.

CONCLUSION

Vertically aligned α – MoO₃ nanowires were successfully synthesized using pulsed laser deposition. Structural and elemental analyses confirmed phase purity, high aspect ratio, and stoichiometry. The nanowire electrodes showed enhanced photocurrent and an STH efficiency of 2.5%. Mott-Schottky and EIS measurements indicated p-type behavior and efficient charge transfer respectively. These results highlight the potential of MoO₃ nanowires for stable and efficient solar water splitting.

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Room Temperature Non-Volatile Resistive Switching Properties of Vanadium Oxide Thin Film

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Abstract: We report fabrication and characterization of a VO₂-based metal–oxide–semiconductor (MOS) device exhibiting non-volatile resistive switching behaviour. The devices fabricated on *n*-type Si(100) substrates by depositing VO₂ thin film using rf magnetron sputtering exhibit resistive switching with an ON/OFF current ratio of above 10². X-ray photoelectron spectroscopy (XPS) reveals the presence of V⁴⁺ and V³⁺ associated oxygen vacancies responsible for conductive filament formation. Room temperature *I*–*V* measurements show a sharp transition from high to the low resistance state (LRS) at around –7 V followed by a RESET to the high resistance state (HRS) in positive cycle confirming non-volatile and reversible switching. These findings highlight the importance of oxygen vacancy dynamics and vanadium redox chemistry enabling resistive switching in VO₂-based non-volatile memory devices.

INTRODUCTION

Resistive switching (RS) refers to the reversible change in the resistance state of a dielectric or semiconducting material under an applied electric field. This phenomenon underlies the working principle of resistive random-access memory (ReRAM), a promising next generation non-volatile memory technology [1]. ReRAM devices offer advantages such as fast switching speed, low power consumption, simple metal–insulator–metal (MIM) structure, and high scalability making them attractive candidates for integration in future memory and neuromorphic systems [2]. A variety of metal oxides namely, TiO₂ [3], HfO₂ [4], ZnO [5] etc. have been extensively investigated for their resistive switching properties. Among them, vanadium dioxide (VO₂) stands out due to its unique electrical and structural characteristics. VO₂ exhibits a thermally induced insulator-to-metal transition (IMT) near 68 °C [6] and a rich spectrum of oxidation states (V³⁺, V⁴⁺, V⁵⁺) making it highly responsive to electric fields and redox activity [7]. These features make VO₂ a compelling material for resistive memory applications where oxygen vacancy dynamics and valence state modulation play a crucial role in filamentary switching mechanisms. In this study, we explore the resistive switching behaviour of VO₂ thin films at room temperature deposited using rf magnetron sputtering on *n*-type Si (100) substrates and on the top, Ag metal electrode was deposited and patterned to get MOS structure. X-ray photoelectron spectroscopy (XPS) was performed on VO₂ films at room temperature to identify the chemical composition and oxidation states of vanadium and oxygen whereas room temperature current–voltage (*I*–*V*) measurements were carried out to evaluate the device's switching performance.

EXPERIMENTAL SECTION

An *n*-type Si (100) wafer with a resistivity ranging from 0.1 – 0.5 Ω·cm cut into substrates of 1 cm² area was used for VO₂ thin film deposition. The substrates were cleaned using a standard protocol to remove surface contaminants. Initially, the samples were ultrasonically cleaned in acetone for 5 minutes followed by a 5-minute ultrasonic bath in 2-propanol. The substrates were then rinsed with deionized (DI) water and dried using a nitrogen gun. Hydrofluoric (HF) acid was then used to remove the native silicon oxide layer and cleaned by DI water. The cleaned substrates were immediately loaded into a radio frequency (RF) magnetron sputtering system. The chamber was evacuated to a base pressure of 9.0×10^{–6} mTorr. VO₂ thin films were deposited at room temperature for 12 minutes using an rf power of 45 W. The working pressure during deposition was maintained at 5 mTorr using programming throttle valve and high-purity argon (Ar) was used as the sputtering gas. Substrate rotation was set to 30 rpm to ensure uniform film coverage. The sample was used for XPS study. Afterwards, silver (Ag) metal was deposited using an electron beam evaporation system and patterned to get top electrodes. The chamber base pressure was 5×10^{–8} mB with source voltage

of 5.8 kV and an emission current of 30 mA. The Ag film was deposited over a period of 15 minutes. XPS was performed at room temperature to investigate the chemical composition and oxidation states of the VO₂ thin films. In addition, room temperature *I*-*V* measurements were carried out to evaluate the electrical characteristics of the VO₂ films.

RESULT AND DISCUSSION

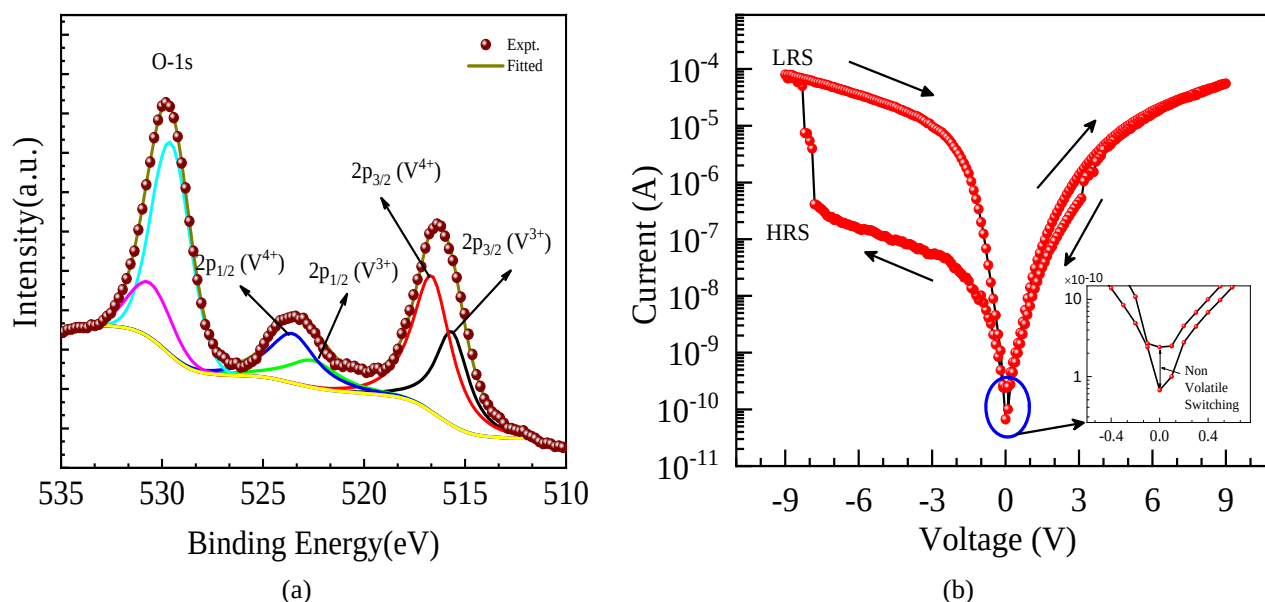


FIGURE 1. (a) De-convoluted XPS spectra for V-2p_{3/2}, V-2p_{1/2} and O-1s, (b) Non-volatile and digital memristive switching characteristics of VO₂ thin film at room temperature.

XPS analysis was performed at room temperature to identify the oxidation states of vanadium and the presence of lattice and non-lattice oxygen in the film. Charge correction was done by referencing the C 1s peak for C-C bonding at 284.6 eV [8]. The spectra were deconvoluted using CasaXPS software applying Shirley background model and GL(30) fitting function for O-1s and GL(90) for V-2p states [9]. An Al K_α x-ray source (1486.7 eV) was used with the pass energy set to 20 eV. Fig. 1(a) shows the deconvoluted V 2p spectrum at room temperature. Two oxidation states, V⁴⁺ and V³⁺ are clearly identified. The V 2p_{3/2} peak appears at 515.64 eV for V³⁺ and 516.64 eV for V⁴⁺, while the corresponding V 2p_{1/2} peaks are located at 522.54 eV for V³⁺ and 523.64 eV for V⁴⁺ [10]. The observed energy separation of ~ 7 eV between the 2p_{3/2} and 2p_{1/2} components is consistent with standard spin-orbit splitting in vanadium oxides. During curve fitting, the area ratio between V 2p_{3/2} and V 2p_{1/2} peaks was maintained at 2:1 [9]. The presence of V³⁺ suggests the existence of oxygen vacancies as this lower oxidation state typically arises from the partial reduction of vanadium in oxygen deficient environments. The O 1s spectrum shows two distinct peaks at 529.56 attributed to lattice oxygen (O²⁻) and 530.58 eV corresponding to non-lattice oxygen possibly originated from hydroxyl groups, surface adsorbates or oxygen-deficient regions [11]. These findings collectively indicate that the film contains a significant concentration of oxygen vacancies due to the presence of V³⁺ and non-lattice oxygen components.

Fig. 1(b) displays the *I*-*V* characteristics of the MOS device measured at room temperature (RT). The curve exhibits a prominent hysteresis loop indicative of a non-volatile resistive switching behaviour. As the voltage is swept from 0 V to -10 V, the current initially remains low corresponding to the high resistance state (HRS). Around -7 V, a sudden increase in current by nearly three orders of magnitude is observed marking the transition to low resistance state (LRS). This abrupt change is attributed to the activation and migration of oxygen vacancies. Upon reversing the voltage sweep from -10 V to 0 V, the device maintains the LRS confirming the non-volatile nature of the transition at room temperature. During the positive voltage sweep, a reverse transition from LRS back to HRS is observed indicating a reset process. The resulting loop reflects clear unipolar switching behaviour with distinct paths during the set and reset operations. This resistive switching behaviour characterized by stable LRS and HRS states and strong

hysteresis demonstrates the potential of the device for non-volatile memory applications, where oxygen vacancy dynamics and vanadium redox reactions play a key role.

CONCLUSION

In this study, we demonstrate that the VO₂-based MOS device exhibits well-defined unipolar set/reset switching behaviour with an ON/OFF current ratio of approximately more than 10² order along with non-volatile nature. The *I*–*V* characteristics at room temperature reveal a sharp transition from the HRS to LRS at around –7 V attributing to the formation of conductive filaments facilitated by oxygen vacancy migration and clustering. The device retains its LRS even after the removal of the external bias confirming non-volatile switching behaviour. The RESET process, observed during the positive voltage sweep disrupts the conductive path gradually bringing the device back to HRS.

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Highly Optimized Ag Nanohelix Array for Enhanced SERS-based Biosensing

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Abstract. We have fabricated and optimized silver nanohelices (AgNHs) using the glancing angle deposition technique for enhanced SERS performance. The ability of these nanohelices has been investigated using 2-di(4-pyridyl)ethylene (BPE) as the Raman probe. A 2-fold SERS enhancement has been obtained for these substrates in comparison with conventional silver nanorods. The limit of detection (LOD) of BPE using AgNHs has been obtained as 10^{-15} M. Further, these substrates are employed to enhance the SERS signal of lab cultured biologically significant bacteria (*P. aeruginosa*). The formation of high-density ‘hotspots’ among the AgNHs arrays, along with increased surface area, provides better binding sites and hence entrapment, increasing the net effective contact area between the bacteria and the plasmonic metal surface.

INTRODUCTION

Recent significant advances in Surface enhanced Raman spectroscopy (SERS) have created the possibility to detect biomolecules in small numbers (or even single molecules), expanding its practical applications.[1]. Glancing angle deposition (GLAD) is a stable and effective physical vapor deposition technique for the fabrication of nanostructures.[2] SERS substrate fabricated using this technique possesses high sensitivity and reproducibility with less than 10% batch-to-batch variation.[3] GLAD fabricated Ag SERS substrates have been successfully employed for diagnosis, molecular fingerprinting, and studying viruses and bacteria, and other bioanalytes, suggesting that the SERS platform is suitable for the detection of biomaterials. *Pseudomonas aeruginosa* is a pathogen that colonizes the damaged sites prone to infection, such as surgical wounds, burns, and the respiratory tract. *P. aeruginosa* is also highly resistant to antibiotics, which may lead to severe pulmonary infections in immunocompromised patients.[4] Successful treatment of such an infection requires rapid and accurate identification of the pathogens. In this work, we have fabricated helical silver SERS substrates using the GLAD technique. With precise control over the parameters, GLAD can easily create highly uniform and reproducible helical nanostructures with a large surface area, enhancing their SERS performance for biodetection and sensing. The work reports direct and label-free SERS detection of 2-di(4-pyridyl)ethylene (BPE) using GLAD-fabricated silver chiral nanohelical substrates (AgNHs) grown directly over glass. These AgNH substrates increase the number of ‘hotspots’, providing better entrapment for the bacteria *P. aeruginosa* onto the AgNHs, giving rise to an enhancement in the SERS signal.

EXPERIMENTAL

To create the chiral Ag nanostructures, a 20 nm Ti film was deposited over a set of 1×1 cm² cleaned glass slides. The glass substrates were then mounted in the thermal deposition chamber. The chamber was constantly maintained at a pressure of 2×10^{-6} Torr, and silver powder was thermally evaporated to obtain AgNHs. The substrate holder was tilted at an angle of 85° and then uniformly rotated clockwise azimuthally at a constant speed using a stepper motor to control the coil diameter and the helix angle. The rotational speed was kept at 5 rpm throughout the deposition, forming 5-6 turns of AgNHs. The entire deposition was carried out in a class 100/1000 clean room, and fabricated AgNHs SERS substrates were finally packed with N₂ gas to enhance their performance and longevity. These AgNHs SERS substrates were further characterized by XRD, Uv-Vis spectroscopy, and FESEM followed by their FDTD Lumerical simulations. The SERS measurements were further taken using ASSURX Raman spectrometer, TSI Inc., USA, with 785 nm laser excitation. The laser power was kept at 20 mW, the laser spot size was 5 μm, and the integration time was 20-30 s, respectively.

RESULTS AND DISCUSSION

The morphology of the as-prepared AgNHs was studied using scanning electron microscopy (SEM) (Zeiss SEM EVO 18 special edition) (Figure 1(a)). Figure 1(b) shows the SEM image of a single nanohelice with 5-6 turns, having an average height of ~ 800 nm, a pitch of ~ 150 nm, and a diameter of ~ 70 nm. The XRD pattern of the Ag SERS substrates was obtained with a Rigaku Ultima 1V diffractometer equipped with $\text{CuK}\alpha$ ($1.54\text{\AA}$) radiation scanned in 2θ range 30° to 80° indicating the polycrystalline nature of the nanohelices (Figure 1(c)). The UV-Vis absorbance spectra of the chiral silver structures were measured by a Perkin Lambda UV-Vis-NIR spectrometer in the wavelength range between 400 and 800 nm. The plasmonic peak of the AgNHs was obtained at around nm (Figure 1(d)). FDTD simulations were carried out to study the local field enhancement ($|E_{\text{local}}/E_0|$) for the nanostructures (Figure 1(e-f)). The plane wave source was used for the simulation.

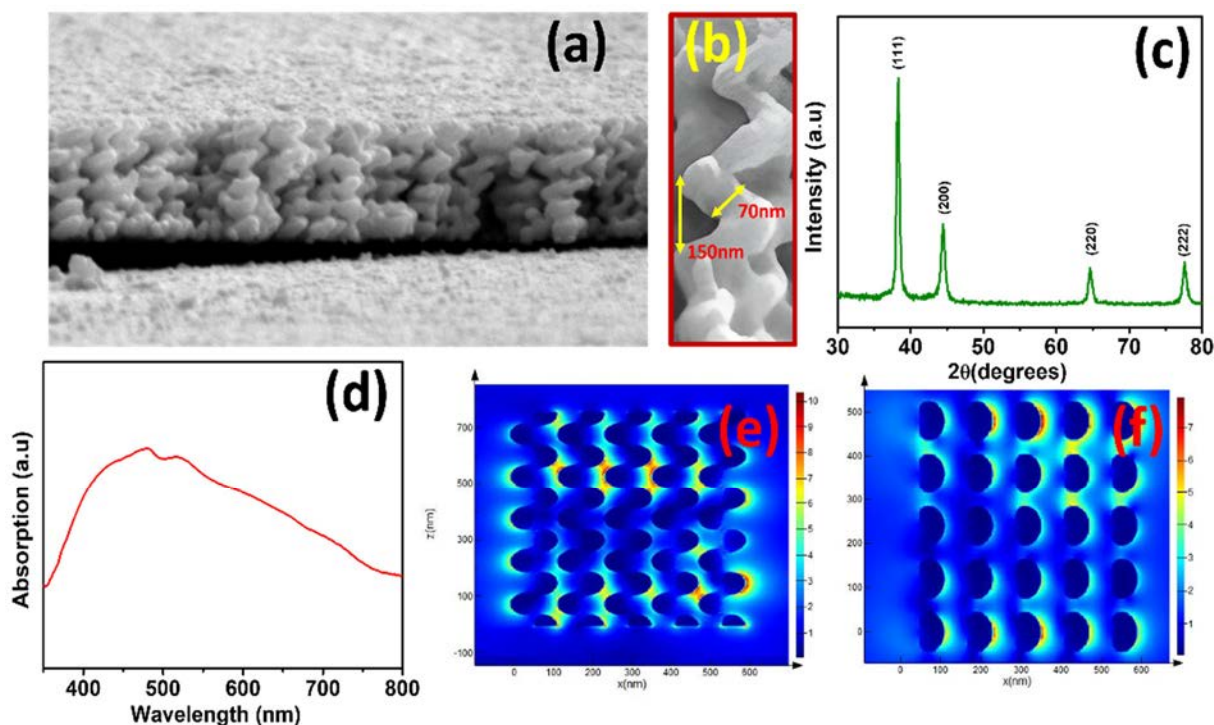


FIGURE 1. (a) FESEM image of AgNHs (b) Zoomed FESEM image of single helix, (c) XRD of AgNHs (d) UV-Vis data showing absorption spectra of AgNHs (e) Side view (Y-Z), and (f) top view (X-Y) of FDTD simulation results of AgNHs

To find the SERS response of these substrates, $5\mu\text{L}$ of 1mM 1,2-di (4-pyridyl)ethylene (BPE) was dropcast over the AgNHs, and the SERS enhancement factor was calculated as 10^9 . A 2-fold enhancement was obtained for the BPE using AgNHs in comparison to conventional Ag nanorods (AgNRs)[5]. (Figure 2(a)). To obtain the limit of detection (LOD) of the probe molecule, a concentration-dependent SERS study was performed, and the LOD of BPE was obtained as 10^{-15} M for AgNHs. Further, to access the capability of these substrates for biodetection, the SERS signal for lab-cultured *P. aeruginosa* was obtained. The MTCC 2453 strain was used. Cultures were grown on agar plates of Luria broth (LB)[6]. Figure 2 (b) shows the comparison of SERS spectra of *P. aeruginosa* obtained using AgNHs SERS substrates with respect to AgNRs SERS substrates. A 2-fold enhancement was obtained for AgNHs in comparison to AgNRs, establishing the higher detection ability of AgNHs in comparison to conventional AgNRs SERS substrates. This may be attributed to enhanced localized hot spots and larger surface area of these substrates, hence providing the analytes with increased binding sites with enhanced plasmonic performance.

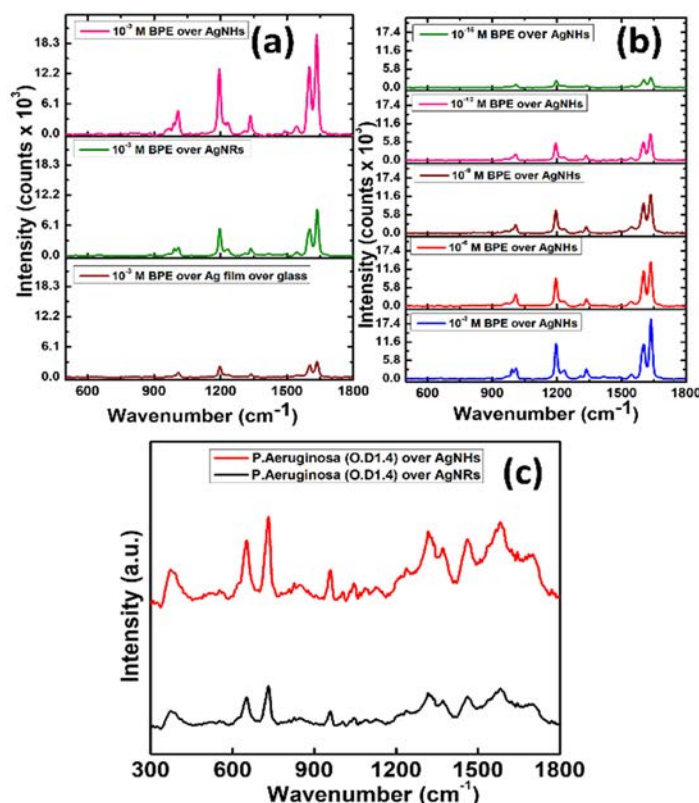


FIGURE 2. (a) Comparison of BPE over AGNHs, AgNRs, and Ag film substrates (b) Concentration-dependent SERS spectra of BPE over AgNHs (c) Comparison of SERS spectra of P.aeruginosa over AgNRs and AgNHs

CONCLUSION

We have fabricated and optimized silver AgNHs for maximum SERS enhancement using the GLAD method. Characterization and FDTD simulations have been performed for the AgNHs to study and verify their morphological and optical properties. SERS spectra have been obtained for the probe molecule BPE, and the AgNHs substrates are found to provide 2-fold enhancement in comparison to conventional AgNRs substrates. The capability of these AgNHs substrates is further studied for bacterial detection using lab-cultured *P. aeruginosa* bacteria. Therefore, the proposed highly optimized AgNHs SERS substrates can be employed for vast applications in biodetection, drug delivery, and early disease diagnosis, along with the chemical, biomedical, and industrial fields.

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Influence of Annealing Temperature on Structural, Optical, and Dielectric Properties of PLD-grown $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ Thin Films

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Abstract. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST) thin films were deposited on n-type Si and quartz substrates using the pulsed laser deposition (PLD) technique. Post-deposition annealing was performed at various temperatures, to optimize the structural and functional characteristics of the films. X-ray diffraction analysis verified the formation of a single-phase cubic perovskite structure. Field emission scanning electron microscope showed a densely packed microstructure, while optical measurements indicated a wide band gap. The dielectric constant measured across varying temperatures remained stable for the film annealed at 700°C. These findings highlight a significant influence of annealing temperature on both structural and dielectric characteristics, confirming the material's potential for use in advanced capacitor technologies.

INTRODUCTION

Barium strontium titanate (BST) is a well-known ferroelectric material that belongs to the family of perovskite oxides and has garnered significant attention due to its tunable dielectric properties, high permittivity, and low dielectric loss [1]. Among its compositions, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ is highly attractive for its applications in tunable microwave devices, dynamic random-access memories (DRAMs), and energy storage capacitors [2]. In recent years, extensive research has focused on BST thin films due to their excellent functional properties and the ability to tailor properties via compositional modification, and deposition environment.

The structural and functional properties of BST are sensitive to various factors, including composition, film thickness, deposition method, post-deposition treatments, and substrate type, which necessitate careful control during fabrication [3]. Pulsed laser deposition (PLD) has emerged as a promising technique for fabricating high-quality BST thin films, owing to its ability to maintain stoichiometry, and enable fine control over growth conditions [4]. Furthermore, post-deposition annealing plays a crucial role in enhancing crystallinity, which directly influences the dielectric performance[5]. Understanding the effect of annealing on BST thin films is therefore essential for optimizing their functionality in capacitors and other electronic applications.

EXPERIMENTAL DETAILS

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST) ceramic target (1" diameter) has been prepared by solid-state reaction using barium carbonate (BaCO_3), strontium carbonate (SrCO_3), and titanium oxide (TiO_2) (Sigma-Aldrich, 99.99%). BST thin films were deposited onto n-type silicon and quartz substrates using with pulsed laser deposition technique. The deposition chamber was evacuated to a base pressure of 1×10^{-6} mbar, and oxygen gas at 20sccm is purged through a mass flow controller into the deposition chamber. The target-to-substrate distance is kept at 5cm, and deposition was done for 30min by maintaining substrate temperature of 300°C at an ambient pressure of 1×10^{-2} mbar. Post-deposition, films were annealed at 600 °C, 700°C, and 800°C for 1hour.

The phase and crystallinity of as-deposited BST thin films were verified by using the X-ray diffractometer (TTRAX III, Rigaku corporation, Japan) with Cu-K α radiation of wavelength ($\lambda = 1.5406\text{\AA}$). The surface morphology of the deposited BST thin films was observed using a field emission scanning electron microscope (JSM-7610F, JEOL) and optical measurements using an Agilent Cary UV-Vis spectrophotometer. For frequency- and temperature-

dependent dielectric measurements, the Wayne Kerr 4300 series LCR meter was used over frequencies from 100Hz to 1MHz and the temperatures ranging from 25 °C to 250°C.

RESULTS AND DISCUSSIONS

Structural Analysis

The X-ray diffraction (XRD) patterns of the BST thin films annealed at 600 °C, 700 °C, and 800 °C are shown in the Fig. 1. All three patterns exhibited a cubic perovskite structure without any additional secondary phase. The XRD pattern obtained matches with JCPDS data card number 00-039-1395 of cubic $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ with Pm-3m space group. With increase in the annealing temperature, the intensity and sharpness of the diffraction peaks improved significantly, suggesting enhanced crystallinity at higher temperatures. The magnified view of the (101) peak on the right side of the figure clearly shows a peak shift towards higher angles and narrowing of the peak with increasing annealing temperature. The XRD results confirm the successful crystallization and phase formation of the material upon thermal treatment, with optimum structural quality observed at 800 °C.

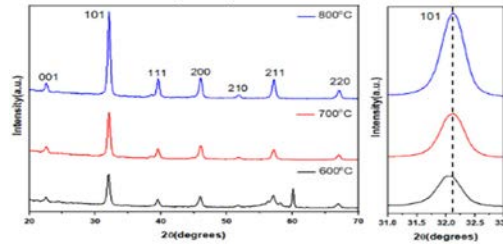


FIGURE 1. XRD spectra of BST thin films annealed at different temperatures

Optical properties

The transmittance spectra of BST thin films annealed at 600 °C, 700 °C, and 800 °C are shown in the Fig. 2(a). All films exhibit high transparency in the visible range, and with a sharp absorption edge occurring below 300 nm. However, the film annealed at 700 °C shows the highest transmittance. Assuming a direct allowed electronic transition, Tauc plots, Fig. 2(b), $(\alpha h\nu)^2$ versus $h\nu$ were constructed to determine the optical band gap energy. The calculated band gap values were found to be 4.24 eV (600°C), 4.33 eV (700°C), and 4.28 eV (800°C).

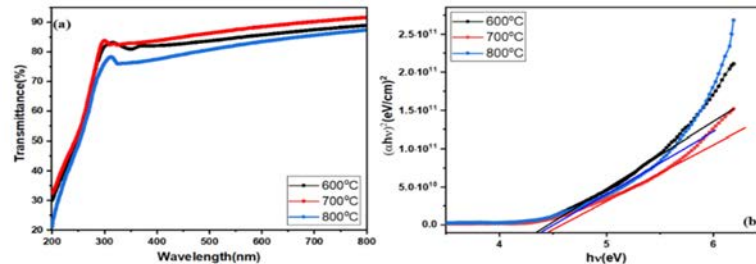


FIGURE 2. (a) Transmittance spectrum (b) Tauc plots of BST thin films annealed at different temperatures.

Microstructural Analysis

The FESEM images of 1μm, BST thin films annealed at different temperatures, recorded at 1μm magnification, are shown in Fig. 3. All the films exhibited spherical grain structure with a homogeneous surface morphology. The presence of closely packed grains, including some larger clusters and grain coalescence, can be observed. The grain sizes measured using the ImageJ software were found to be 18.20nm, 28.65nm, and 26.36nm for the films annealed at 600 °C, 700 °C, and 800°C, respectively.

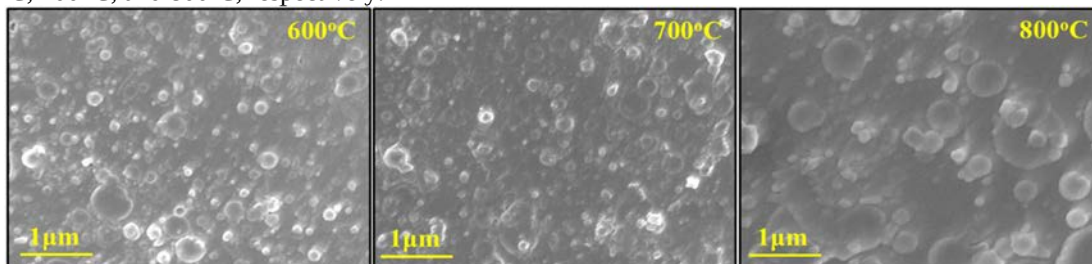


FIGURE 3. FESEM images of BST thin films annealed at different temperatures.

Dielectric properties

The variation of dielectric constant with temperature at a frequency of 1MHz, for BST thin films annealed at 600 °C, 700 °C, and 800 °C, is shown in Fig. 4(a). All three films displayed a gradual increase in the dielectric constant with increase in the temperature. The results indicate that 700°C is an optimal annealing temperature for BST thin films in terms of dielectric performance and temperature stability, whereas the other two samples highlight the temperature sensitivity. The variation of dielectric loss($\tan \delta$) with temperature is shown in Fig. 4(b). The film annealed at 700°C demonstrates the stable loss behavior, maintaining a nearly constant value across the entire temperature range. The film annealed at 600°C exhibited a high loss, and the one at 800°C exhibited a very low $\tan \delta$ at low to moderate temperatures, indicating excellent dielectric loss behavior initially, but raised sharply with an increase in temperature.

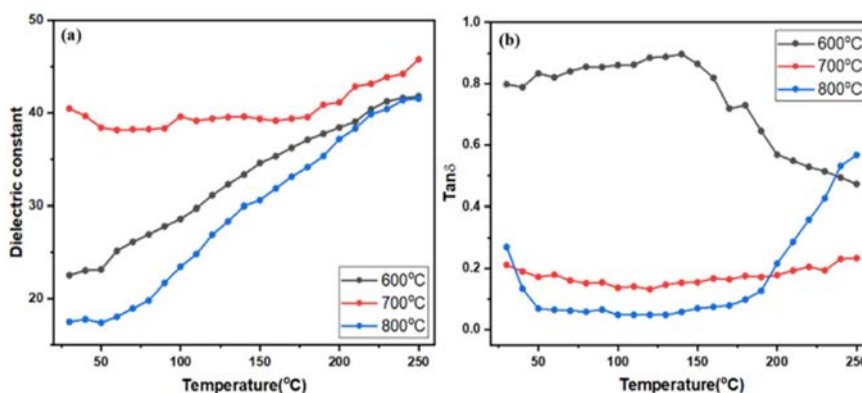


FIGURE 4. (a) Dielectric constant (b) Dielectric loss versus temperature of BST thin films annealed at different temperatures at frequency 1MHz.

CONCLUSION

BST thin films deposited using the pulsed laser deposition method were annealed at three different temperatures. The XRD pattern of all deposited BST thin films confirms a cubic perovskite structure, with the space group Pm-3m. The film annealed at 700°C exhibited an average grain size of 28.65nm and showed a wide band gap energy of 43.33eV, confirming its strong insulating nature. The same film showed a stable dielectric constant and low dielectric loss. These findings highlight the importance of optimizing annealing conditions to achieve high-performance BST thin films, which are significant for specific applications such as capacitors, energy storage, and optoelectronic devices.

ACKNOWLEDGMENTS

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One-step NiO/Ni Nano Heterostructures Formation in Microwave Synthesis and Enhanced Ammonia Gas Sensing Response

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Abstract: p-type semiconducting nickel oxide (NiO) and its heterostructures have been used for gas sensing due to their interesting properties, which are tunable by different strategies. This study presents gas sensing studies on NiO/Ni nano heterostructures formed through one step microwave synthesis and comparison with the conventional annealing process. X-Ray diffraction characterization confirms the NiO/Ni heterostructures with a large Ni phase fraction in the microwave route compared to the conventional annealing process. Moreover, heterostructure thin films are formed on silicon substrates with two point electrodes for gas sensing studies, where the changes in the resistance are monitored by exposing to different gas concentrations (acetone, ethanol, methanol, ammonia, and propanol). The highest gas selectivity and enhanced sensing response for ammonia is obtained for microwave processed NiO/Ni heterostructures. This is attributed to the NiO/Ni (semiconductor-metal) nano heterostructure phenomena, catalytic activity and enhanced charge transfer due to high Ni fraction.

INTRODUCTION

Nickel oxide (NiO) is a wide band gap (~3.6 eV) semiconductor that exhibits p-type conductivity and possesses very good electrical, magnetic, catalytic, gas sensing, and electrochemical properties[1]. NiO nanostructures, such as nanotetrahedra, nanosheets, hollow microspheres, and composites significantly boost surface area and facilitate gas–solid interactions[2]. The sol-gel technique is widely employed to prepare nanostructured NiO, which enables fine control over composition, porosity, particle size, and surface morphology. However, sol-gel derived gel powders require an annealing step at high temperatures to obtain crystalline structures, which need to be precisely controlled to obtain reproducible results[3]. Microwave synthesis has been emerged as a greener, faster alternative to conventional heating in processing NiO nanostructures. The unique volumetric and selective heating effect enables rapid nucleation, reduced synthesis times, and high purity metal oxides with controlled morphology. Compared to conventional heating or hydrothermal methods, microwave heating delivers energy locally to the precursors, yielding uniform nanostructures with enhanced surface defects beneficial for gas adsorption[4]. This work presents a comparative study of NiO/Ni nano heterostructures formed in a single step microwave process from the Ni precursor gel and conventional annealing of the gel powders. Moreover, gas sensing studies have shown high ammonia selectivity and enhanced response by NiO/Ni heterostructures. The study highlights the direct formation of NiO/Ni heterostructures, the role of metallic Ni incorporation, and the processing method on the material's structural and functional properties.

MATERIAL AND METHODS

The Ni precursor gel was prepared via a citrate-assisted sol–gel technique. The analytical grade of Nickel nitrate hexahydrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and citric acid ($\text{C}_6\text{H}_8\text{O}_7$) were utilized as the metal precursor and complexing agent, respectively, without any further purification. Deionized water was consistently employed in the synthesis process. The molar ratio of the nickel nitrate and citric acid was 1:1 (N:C). A required amount of nickel nitrate was dispersed in deionized H_2O and stirred at 80 °C for 60 minutes on a hot plate to ensure complete dissolution. Subsequently, a solution of citric acid was added dropwise to the hot solution under continuous stirring. The temperature was then increased to 130 °C to facilitate gel formation. The resulting gel was maintained at this temperature and kept dry for 12 hours. Finally, the dried gel was calcined at 500 °C and 800 °C for 3 hours in a muffle

furnace to obtain the desired oxide material. For microwave synthesis, the Ni precursor gel formed at 130°C is aged for 12 h at room temperature and treated with a microwave setup (Model-RG34L2R) operated at 700 W for 10 minutes.

CHARACTERIZATION

The crystal structure as well as phase purity of the obtained samples were characterized by powder X-Ray Diffraction analysis (XRD, PANalytical X'pert³ with Cu K_α source ($\lambda = 1.54 \text{ \AA}$). The sensor was designed on a silicon wafer with silver painted two point electrodes separated by 2 mm. Thin films were formed by drop casting the NiO/Ni powders dispersed in ethanol, followed by annealing at 200°C. Gas sensing tests of the films were performed by measuring the change in their electrical resistance using a Keithley DMM6500 electrometer under controlled exposure to various gas concentrations (300, 400, 500, 600, 700 ppm).

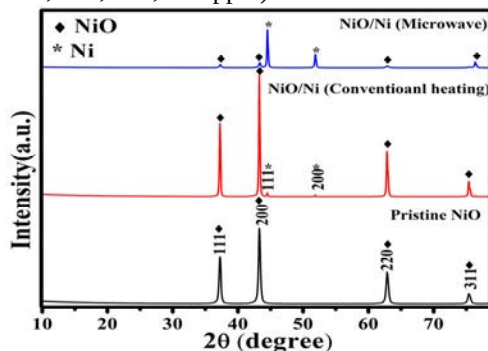


FIGURE 1. X-ray diffraction results of pristine NiO formed in conventional heating at 800°C. Direct NiO/Ni heterostructures formed in the conventional heating at 500°C and microwave processing at 700 W (10min)

RESULTS AND DISCUSSION

NiO/Ni heterostructures are obtained in conventional annealing at 500°C and microwave processing as explained in the materials and methods. The XRD patterns are shown in Fig.1 for both the methods. The XRD analysis confirms the formation of NiO phase (JCPDS:04-0835) and Ni metal (JCPDS:04-850) peaks. Ni phase is minute in the conventional heating (at 500°C) and pure NiO phase is obtained at 800°C annealing of Ni precursor gel. Whereas, the microwave processing of the Ni-precursor gel resulted in a large Ni fraction giving the NiO/Ni heterostructures. Where, nucleation of Ni or NiO takes place rapidly upon each other thus resulting in the heterostructures growth. The crystal size (by Scherrer relation) of NiO and Ni found to be 23 nm and 35 nm respectively for the microwave processed samples. Whereas, phase fraction of the Ni is 0.75 and NiO is 0.25 as analysed by taking the XRD peak intensities into account. The microwave single step process resulted in NiO/Ni heterostructures with high Ni phase fraction. Rapid and local high heating temperatures in microwave synthesis promote the localized reduction of Ni²⁺ and formation of metallic Ni along with Ni oxidation (NiO formation). In contrast, conventional heating offers slower, more slow thermal decomposition, favouring NiO formation.

SENSING CHARACTERISTICS AND MECHANISM

The gas sensing response is defined as

$$\text{response (\%)} = \frac{|R_a - R_g|}{R_a} \times 100 \quad (1)$$

where R_a represents the resistance of the sensing sample in normal atmospheric conditions without interacting to the target gas and R_g is the changed resistance after exposure to the gas. The NH₃ sensing response curves of NiO/Ni films of conventional heated and microwave processed samples are shown in Fig.2. The NiO/Ni heterostructures formed in microwave single step has shown large response towards ammonia (NH₃) gas. This is attributed to the high metallic Ni fraction, more defects within NiO and Ni due to surface active sites, promoting catalytic interaction and fast electron transfer by the metallic phase. This resulted in high NH₃ selectivity, large response, and conductivity. When

a p-type NiO semiconductor is interacted with air, oxygen molecules are adsorbed onto its sample surface and undergo chemisorption by capturing electrons from the NiO, which increases the hole concentration near the surface and thereby reduces the sensor's resistance. In contrast, when exposed to ammonia (NH_3), the NH_3 molecules react with the adsorbed oxygen, which results in releasing electrons to the NiO surface ($2\text{NH}_3 + 3\text{O}_2^-(\text{ads}) \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 6\text{e}^-$). This electron donation reduces the hole concentration near the sample surface, resulting in an increase in the resistance[5]. The sensitivity and selectivity of the microwave processed NiO/Ni sample is shown in Fig.2 (e), and Fig.2(f), respectively. The ammonia detection has shown the highest response compared to other target gases studied.

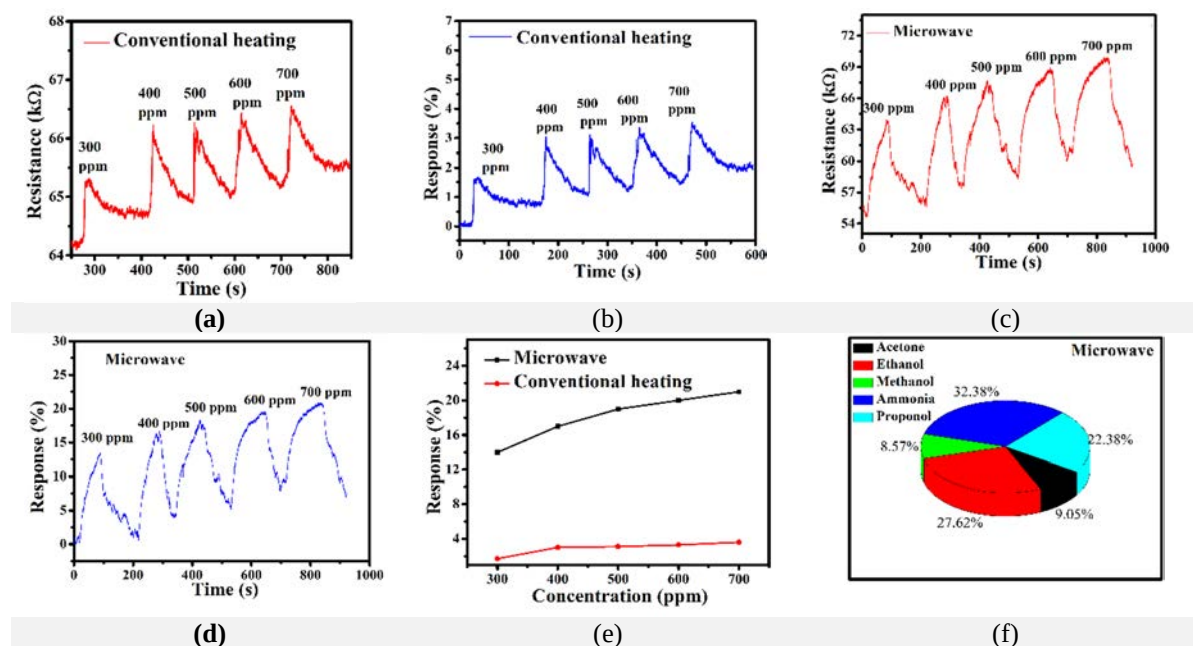


FIGURE 2. Ammonia gas sensing (a) resistance, and (b) response plots of by the NiO/Ni heterostructures from conventional heating, (c) resistance, and (d) response plots for microwave processed NiO/Ni samples at varying gas concentration. (e) Sensitivity plots and (f) gas selectivity results for the microwave processed sample.

CONCLUSION

The study demonstrates the direct formation of NiO/Ni nano heterostructures in a microwave one step synthesis. XRD analysis confirms the presence of a high phase fraction of Ni in the microwave process. This enhanced the ammonia sensing response due to increased NiO/Ni heterostructure mechanism and improved charge transfer dynamics. These findings establish that microwave processing of the Ni-gel results in direct NiO/Ni heterostructure formation, which enhances the gas sensing characteristics.

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Fractal Surface Engineering of NiO Thin Films for Enhanced Ag/NiO/FTO Schottky Diode Properties

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Abstract. This study investigates the influence of mono-fractal surface morphology on the electrical feature of NiO thin films in Ag/NiO/FTO Schottky diodes. Atomic force microscopy analysis and the correlation function were utilized to compute the fractal dimension D_f of the NiO surfaces, which varied from 2.15 to 2.32. A higher D_f , indicating increased surface complexity and roughness, was found to enhance light scattering and carrier collection. Correspondingly, Schottky diodes with higher D_f value exhibited the improvement of electrical performance, with increased forward current and decreased the ideality factor (η decreasing from 3.2 to 2.3). These results clearly demonstrate that fractal surface engineering via the height–height correlation assessment is a powerful approach to optimize the performance of metal oxide-based electronic and optoelectronic devices.

INTRODUCTION

Nickel oxide (NiO) is a widely used as a p-type semiconductor known for its optical transparency, excellent optical absorption, chemical-thermal stability. Its application in optoelectronics devices have gained significant interest due to its ability to improve interface characteristics and charge transport phenomenon. Recent investigations reflect that designed device performance is impacted not only by the thickness, composition but also significantly by the surface roughness of films [1]. Particularly, *fractal surface behavior* usually characterized by roughness plays an essential role. This surface complexity is typically quantified by the **fractal dimension** (D_f) are calculated via height–height correlation function using captured atomic force microscopy (AFM) images [2]. In Schottky diodes, principle variable including leakage current, ideality factor (η), and barrier potential height are very sensitive to the interface behavior of heterojunction. The complex surfaces usually introduce interface states and barrier inhomogeneities, which altering the transport phenomenon[3]. In this work, NiO thin films are grown onto FTO substrates using magnetron sputtering and assessed to determine their fractal dimension (D_f). These values were then correlated with the electrical behavior of Ag/NiO/FTO Schottky diodes.

EXPERIMENTAL DETAILS

Firstly, the FTO substrate, having an area of 4 cm², was cleaned with acetone for 10 minutes. Subsequently, a Ni target was employed as the source material to deposit the film onto Si substrates. Deposition parameters were varied across the samples, including the magnetrons power, set at 45 W and argon flow rate, in order to control grain size. Gas flow rates were adjusted using the digital MKS flowmeters, and 40 sccm of argon gas was introduced into the chamber to generate plasma. The chamber pressure was adjusted at 3.5×10^{-3} Torr throughout the deposition procedure. The NiO films were deposited for 5-minutes, 10-minutes and 20-minutes, respectively. Surface topology were analyzed using AFM (NOVA 18 Research) is employed for NiO surface analysis, whereas electrical measurements are conducted with a Keithley digital source meter (Model 2450).

RESULTS AND DISCUSSION

To obtain a better understanding of grain distribution, scaling behavior and surface properties of NiO thin films on FTO substrate, AFM was used to measure the important parameters of the surface such as the average roughness (R_a) and root mean square roughness (R_q). The AFM was operated in the non-contact mode and the scan size was 5 μm x 5 μm . Fig 1(a-c) shows three-dimensional AFM images of the NiO films, where the growth of the grains is shown with time of deposition. Moreover, the pictures demonstrate the development of island-like features which grow

laterally and vertically with the increase of the time of deposition. The longer the time of deposition, the larger the island features on the films resulting in a greater height variation between the peaks and valleys. The AFM data were processed to obtain the surface roughness parameters (R_a and R_q) with the help of the standard relations [4]: $R_a = \langle |z(i,j) - \langle z(i,j) \rangle| \rangle$, and $R_q = \sqrt{\langle |z(i,j) - \langle z(i,j) \rangle|^2 \rangle}$. The values of R_a and R_q obtained are 27 to 33 nm and 34 to 42 nm respectively with sample depositions of 5 to 20 minutes long. This tendency shows that with the growth of the deposition time the morphology of the surface becomes more non-uniform and rougher. It should be noted, however, that surface roughness is not a sufficient characteristic to completely describe the complex morphological features and irregularities of the films since it is a scale-dependent characteristic.

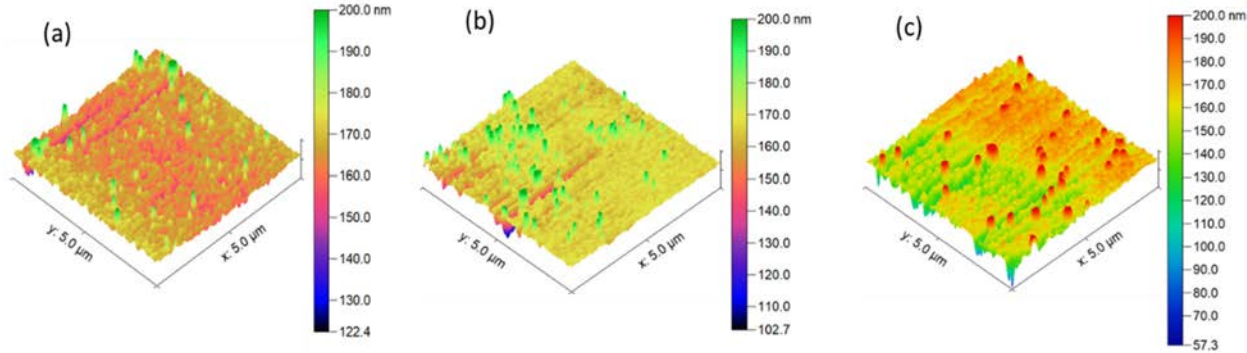


FIGURE 1. AFM topological images, (a) 5 minute, (b) 10 minute, (c) 20 minute of NiO thin film

In order to counter this shortcoming scale-invariant techniques are necessary to characterize surface features more accurately. In this respect, the height correlation function was used to identify the fractal parameters of the films. The correlation function, $K(r)$, which is used in the AFM data, is determined as [5], $K(r) = \frac{1}{N(N-m)}$. $K(r)$ gives a better understanding of the self-affinity as well as the mound-like structure of the surface. It obeys a scaling law that is provided by, $K(r) = \begin{cases} 2R_{rms}^2, & \text{for } r \gg \xi \\ r^{2\alpha}, & \text{for } r \ll \xi \end{cases}$. where, α represent the roughness exponent or local (small-scale) surface irregularity. The log-log plot of $K(r)$ versus r has two different regimes, as illustrated in Fig 2: (I) at larger r , the function levels off to approximately $2R_q$ and (II) at smaller r , it has a dependence of a power-law $K(r) \sim r^{2\alpha}$. The slope of the linear part of the log-log plot gives α value. The extracted value of α are 0.91, 0.85, and 0.78, respectively for all sample, and it can be determined that the surface irregularity increases gradually with the deposition time. Moreover, the fractal dimension D_f are calculated using $D_f = 3 - \alpha$. The corresponding D_f values are 2.10, 2.14, and 2.19 for deposition times of 5, 10, and 20 minutes, respectively. The lowest deposited time give smoother surface. On the contrary, the highest deposition time indicating more roughness and surface complexity.

The schematic diagram of the Ag/NiO/FTO fabricated device is presented in Figure 3(a), consisting of several layers as follows: (a) NiO layer serves as the active absorbing layer, and (b) silver (Ag) layers serve as the top contacts layer, respectively. Figure 3(b) shows the semi-logarithmic ($\ln I-V$) measurement of the Ag/NiO/FTO diode under the illuminated conditions, recorded over an applied external voltage variation of -1 V to $+1$ V. The important parameters that include ideality factor (η), leakage current (I_0), and potential barrier height (ϕ_b) are calculated in Thermionic Emission (TE) model to determine the electrical performance of the diode. The I-V characteristics were studied with the help of the TE model, which is described by the following equation [6], $I = I_0 \left[\exp\left(\frac{qV}{\eta kT}\right) - 1 \right]$. The η and I_0 values are determined as the gradient and intercept of the semi-logarithmic ($\ln I-V$) plot by the following equations, $\eta = \frac{q}{kT \cdot \text{slope}}$ and $I_0 = -\frac{y\text{-intercept}}{\eta kT/q}$. The values of the η obtained are 3.20, 2.57 and 2.33 for fabricated Ag/NiO/FTO device. The device that has a 20 minutes deposition time exhibits the least η and largest fractal dimension (D_f) i.e. surface roughness meaning the greater the complexity of the surface, the higher the light absorption capacity at the junction and the lowest the carrier recombination. This, on the other hand, enhances the performance of the designed diode by the reduction of the deviations of the ideal behavior. The values of barrier height (ϕ_b) were further determined as 0.73 eV, 0.78 eV and 0.86 eV for 5 minutes, 10 minutes and 20 min respectively. The observed growth of ϕ_b as a result of increasing surface roughness can be explained by the increased D_f . With an increase in D_f the surface is more intricate, rough and inhomogeneous; more carrier trapping sites are observed and the band bending increases. This causes an increase in the possible barrier to carrier transport through the junction.

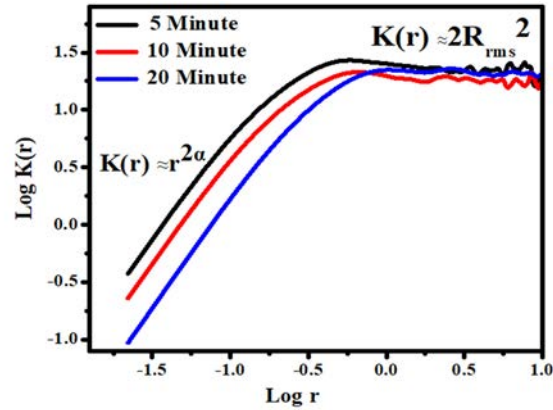


FIGURE 2. Height-height correlation plot of NiOx Film

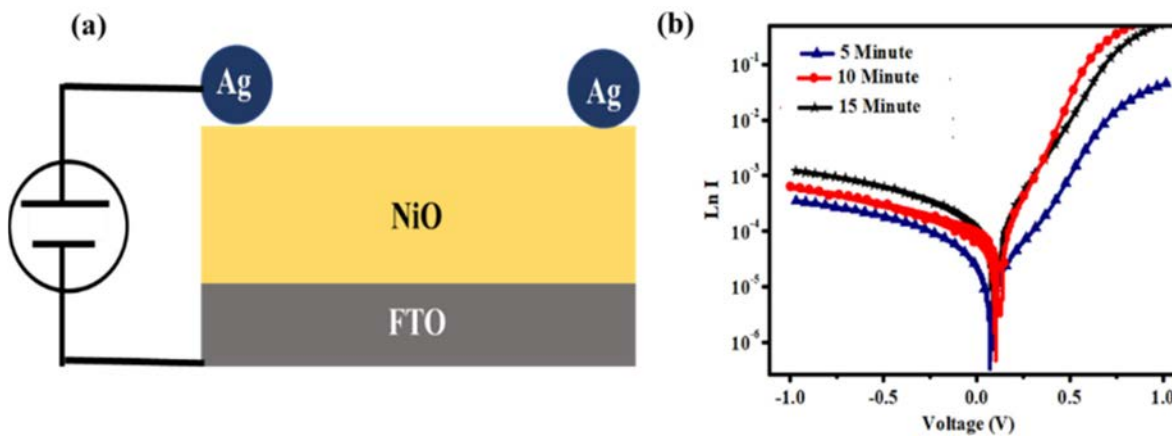


FIGURE 3. (a) schematic illustration of the Ag/NiO/FTO device, (b) Ln I-V plot of the Ag/NiO/FTO diode

CONCLUSION

This work demonstrates a clear correlation between deposition time, surface roughness and Ag/NiO/FTO fabricated diode performance in NiO-based thin films. AFM assessment revealed that increasing the deposition time from 5 to 20 minutes led to higher surface roughness and fractal dimension ($D_f = 2.10$ to 2.19), suggesting complex, irregular and rough surface features. Electrical assessment of Ag/NiO/FTO Schottky diodes exhibited to the improved diode performance with increasing D_f , suggested by the minimized ideality factor from 3.20 to 2.33 and increased barrier potential height from 0.73 eV to 0.86 eV. The enhanced diode behavior is clearly attributed to increased surface roughness and surface complexity, which gives an excellent light absorption and stronger band bending at the fabricated junction, thus minimizing the recombination and improving carrier transport.

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Structural Analysis of Sputtered MoS₂ Film Leading To The Superlubricity

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Abstract: Molybdenum disulfide (MoS₂) is a popular solid lubricant widely utilized in tribological applications due to its lamellar structure and low shear resistance. The covalently bonded S-Mo-S layers are held together by weak van der Waals forces in molybdenum disulfide. This weak bonding facilitates easy shear between basal planes, enabling low friction during sliding. This study focused on the growth of pure MoS₂ thin films on silicon substrates using sputtering techniques under controlled vacuum conditions. Structural characterization was performed by using X-ray diffraction (XRD) and Raman spectroscopy to assess crystallinity and phase purity. The XRD patterns confirmed the hexagonal-MoS₂ (h-MoS₂) phase with preferential (002) orientation, indicating alignment of the basal planes parallel to the substrate, an essential feature for controlling the tribological performance or friction energy dissipation, while Raman spectra confirmed good structural integrity and characteristic of well-ordered h-MoS₂ having its two prominent E_{2g} and A_{1g} modes. The integrity and orientation of these crystalline planes play a critical role in reducing friction by promoting interlayer slippage. This study highlights the significance of structural ordering and phase purity in tailoring MoS₂ as an effective solid lubricant in ambient conditions.

INTRODUCTION

Friction is an undesirable phenomenon in industrial and aerospace contact interfaces, leading to significant energy consumption during friction and wear, which can ultimately lead to equipment failure [1]. Solid lubricants are essential for reducing friction and wear in mechanical systems where liquid lubrication is ineffective [2]. Transition metal dichalcogenides (TMDs), a new class of materials, exhibit excellent lubricity due to their layered structure. Diamond-like-carbon, graphene, sputtered MoS₂, composite coating of MoS₂, and tungsten disulfide (WS₂) have been extensively employed due to their ability to provide low friction even in dry or vacuum conditions [2–6]. The mechanisms stemming from the atomistic nature of the materials in contact and from long-range dispersive interactions are complex and not yet fully understood. The superior lubricating behaviour of 2D MoS₂ is inherently related to its crystal structure, which facilitates easy shear between layers, not only good lubricity, but also is environmentally friendly [7, 8].

MoS₂ typically crystallizes in the hexagonal 2H phase, which consists of stacked S-Mo-S layers held together by weak van der Waals forces. In a trigonal prismatic coordination, each Mo atom is covalently bonded to six S atoms, forming tightly bound layers. However, the bonding between adjacent layers is significantly weaker, allowing them to slide over one another with minimal resistance. This anisotropic bonding, with strong in-plane and weak out-of-plane bonding, is the fundamental reason for MoS₂'s low shear strength and excellent lubrication properties. The ability of layers to slip under mechanical stress is the core mechanism behind their reduced coefficient of friction, and friction completely disappears when the solid surface is completely clean, a phenomenon called superlubricity. The presence of superlubricity depends on the lattice commensurability of a contact surface; it's either commensurability or incommensurability, shown in **FIGURE 1(a,b)** [3, 9–12].

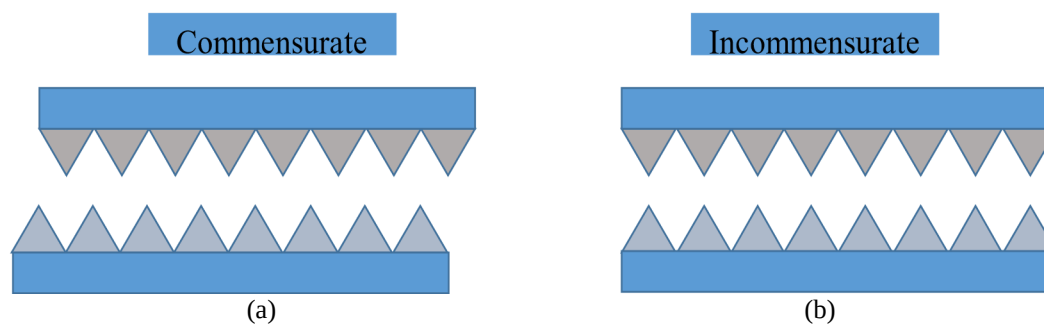


FIGURE 7. Commensurate and incommensurate with the frictional mechanism at the interfaces of two adjacent layers.

This paper examines the structural and crystallographic orientations of pure MoS₂ that lead to structural lubricity, contributing to its tribological performance under atmospheric conditions.

EXPERIMENTAL DETAILS

An RF magnetron-sputtered MoS₂ coating was deposited in a vacuum chamber on a silicon substrate using a 99.99% pure MoS₂ target purchased from Ultrananotech Pvt., India. The substrates were cleaned for 10 minutes in an acetone bath using ultrasonication and dried before deposition. The detailed parameters for the deposition process are given in **TABLE 1**. After deposition, the films are characterized by XRD (Rigaku, Smart Lab 9KW, Japan) and Raman spectroscopy (Renishaw, wavelength 514 nm) to determine the phase crystallinity and molecular bonding of the deposited films, respectively.

TABLE 2. Detailed parameters of the deposition process.

Substrate	RF Power	Gas flow	Duration
Silicon	120 Watts	30 sccm	150 min

RESULTS AND DISCUSSION

FIGURE 2(a) shows the XRD analysis of the sputtered MoS₂ as-deposited films, which revealed a strong peak corresponding to the (002) plane at approximately 14°, indicating a preferential orientation of the basal planes parallel to the substrate. This (002) plane is crucial for tribological applications, as sliding primarily occurs along these planes. The presence of sharp and intense (002) reflections confirms high crystallinity and ordered stacking, both of which are amenable to consistent lubrication performance.

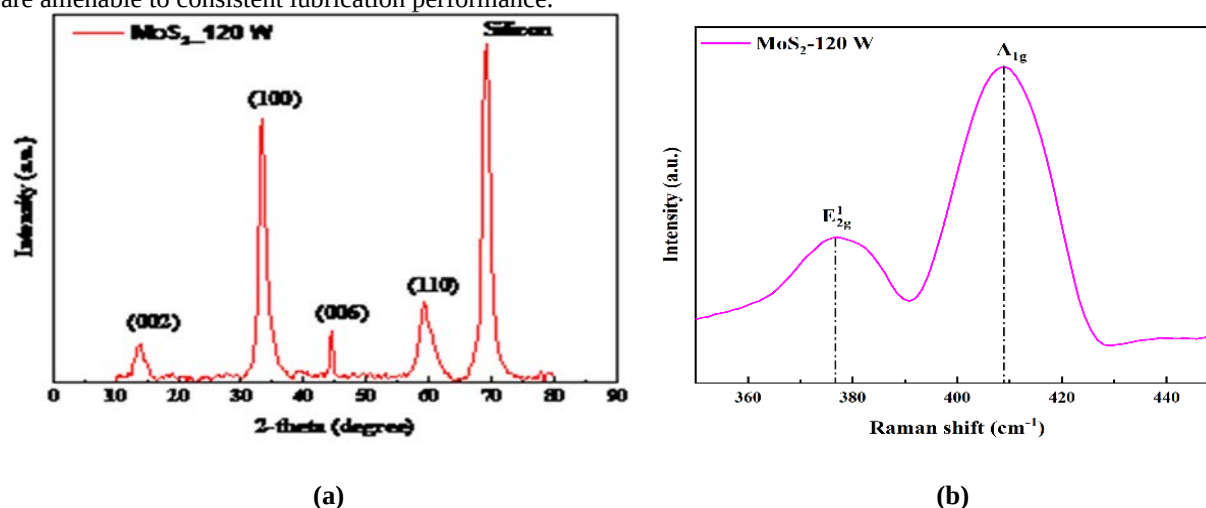


FIGURE 8.(a) X-ray diffraction pattern of the as-deposited film; and (b) Raman spectra of deposited film.

FIGURE 2 (b) shows that the Raman spectroscopy further confirmed the structural integrity of the deposited MoS₂. The characteristic E_{2g}^1 (in-plane) and A_{1g} (out-of-plane) modes were observed near 376 cm⁻¹ and 409 cm⁻¹, respectively. The defined peak positions indicate a well-ordered 2H phase. The separation between these modes also reflects the layer thickness and strain within the film, which influence interlayer interactions and affect the frictional behaviour.

The lubrication efficiency of MoS₂ is strongly governed by its structural orientation and crystallinity. A high degree of (002) alignment ensures that sliding occurs along the van der Waals gaps between layers, minimizing resistance and wear. Moreover, preserving the 2H phase and avoiding oxidation or phase transitions (e.g., to the 1T metallic phase) are essential for maintaining low-friction properties. Disruptions in the stacking order or the presence of defects can hinder interlayer sliding and degrade performance.

CONCLUSIONS

In this research, structural characterization through XRD confirmed a strong (002) orientation, indicating the alignment of basal planes parallel to the substrate, which is an efficient method in the sliding contact leading to the superlubricity. Raman spectroscopy verified the presence of MoS₂ in the form of the well-ordered 2H phase through two distinct vibrational modes, further supporting the material's structural suitability for lubrication.

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Quasiperiodic Ga Monolayer on *i*-Al-Pd-Mn Surface

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Abstract. In this study, we employ scanning tunneling microscopy to demonstrate the presence of quasiperiodicity in elemental Ga adlayer grown on a fivefold icosahedral Al-Pd-Mn quasicrystal at low temperature. STM topographies reveal the formation of distinct quasiperiodic motifs such as τ -GaWF and ring motifs, indicative of quasiperiodic ordering. Moreover, the Fourier transform of these real-space images displays sharp tenfold spots, confirming the presence of quasicrystalline order. Low-energy electron diffraction measurements also demonstrate the presence of fivefold symmetry in the Ga monolayer.

INTRODUCTION

Quasicrystals (QCs) [1] are materials that lack translational periodicity, yet they exhibit long-range order with forbidden rotational symmetries such as fivefold, tenfold, etc. These materials show the formation of a pseudogap, i.e., a dip in the electronic density of states (DOS) near the Fermi level (E_F), which is the reason for their stability [2,3]. QCs exhibit unusual physical properties such as a low frictional coefficient, reduced electrical and thermal conductivity. However, it remains an open question whether these unusual properties are primarily a consequence of these forbidden rotational symmetries or the specific chemical composition. To address this question, considerable efforts have been devoted to growing single elemental QCs. So far, only a few elements [4–7] have shown quasiperiodicity in adlayer form on quasicrystalline substrates. For instance, Bi and Sb have been shown to grow in quasiperiodic arrangement on *i*-Al-Pd-Mn and decagonal (*d*) Al-Ni-Co substrates up to one monolayer coverage, as evidenced from low-energy electron diffraction (LEED) and He atom scattering [4]. Later studies using LEED, photoemission, and density functional theory (DFT) revealed that Na can form a fivefold quasiperiodic structure up to 2 ML on *i*-Al-Pd-Mn [5]. Recently, using scanning tunneling microscopy (STM), LEED, and DFT, it was shown that thick Sn films up to 4 nm on *i*-Al-Pd-Mn exhibit a metastable long-range quasiperiodic order [6]. Similarly, Sn films grown on *d*-Al-Ni-Co also display decagonal clathrate-type quasiperiodic ordering up to 0.9 nm, with partial retention of these correlations observed up to 10 nm [7]. Ga is an interesting element due to its low melting point (303 K) and various solid-state structures reported in literature [8]. Moreover, its electronic DOS displays a notable dip at E_F , attributed to the partial covalent bonding [9,10]. Recently, using STM, LEED, and DFT, quasiperiodic growth of one monolayer of Ga on *i*-Al-Pd-Mn surface has been reported at room temperature [11]. Motivated by this work, here we investigate using STM and LEED whether it is possible to grow quasiperiodic Ga at low temperatures where the diffusion rate is lower.

EXPERIMENTAL

Single-grain icosahedral (*i*) Al-Pd-Mn quasicrystal with a bulk composition of $\text{Al}_{69.4}\text{Pd}_{20.8}\text{Mn}_{9.8}$ was grown using the Bridgman method. It was cut and oriented to expose the fivefold surface, followed by mechanical polishing using 0.25-micron diamond paste to get a mirror finish. After that, the sample was inserted into the ultrahigh vacuum chamber with a base pressure of 2×10^{-11} mbar. The polished surface was treated in-situ using repeated cycles of Ar^+ ion sputtering (1-2 keV, 30-60 min) followed by annealing to 970 K for 2-2.5 hr, to obtain an atomically flat and contaminant-free surface with composition similar to the bulk [12]. Ga of 99.99% purity was evaporated using a water-cooled Knudsen cell [13] operated at 1050 ± 10 K with a chamber pressure $\leq 2 \times 10^{-10}$ mbar. The Ga adlayers were deposited with the substrate held at 140 ± 10 K, and the LEED measurement was performed at this temperature using a four-grid rear-view optics. STM measurements were performed in constant current mode at 80 K using VT-STM from Scienta Omicron GmbH. All STM images are recorded using an electrochemically etched W tip that was prepared using sputtering and voltage pulses. The tip was biased while the sample was kept at ground potential.

RESULTS AND DISCUSSION

In Fig. 1, we compare the LEED patterns for Ga/*i*-Al-Pd-Mn for a deposition time (t_d) of 4 min and 8 min with that of the pristine *i*-Al-Pd-Mn surface ($t_d = 0$ min) for two different beam energies (E_p) of 60 eV and 81 eV. In Figs. 1(a-b), a distinct fivefold symmetry of the LEED spots that is characteristic of the quasicrystallinity is observed. The LEED pattern shows two concentric rings of fivefold symmetry with a low background. For $t_d = 4$ min, the quasiperiodic LEED spots are visible [Figs. 1(c-d)]. These LEED spots persist up to 8 min [Figs. 1(e-f)] for both E_p , indicating the existence of quasiperiodic order in the Ga adlayer up to this coverage. The coverage corresponding to this deposition is quantified using STM, as discussed below.

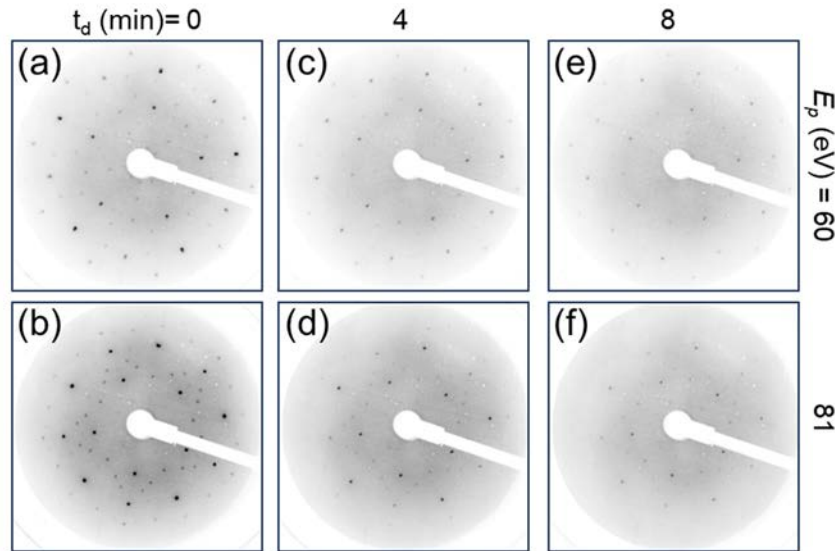


FIGURE 9. LEED patterns for Ga/*i*-Al-Pd-Mn with t_d (in min) of (a-b) 0, (c-d) 4, and (e-f) 8. E_p is indicated on the right side.

An atomic resolution STM topography image for an almost fully covered Ga adlayer, corresponding to $t_d = 8$ min, is presented in Fig. 2(a). Quasiperiodic motifs are highlighted by yellow and red circles, which we refer to as τ -GaWF (τ inflated GaWF, where $\tau = 1.618$ is the golden mean) and the ring motif, respectively. The τ -GaWF motif consists of a central 6-Ga cluster with pentagonal symmetry adsorbed at the vertices of a larger-sized τ -P1 pentagon, which has a Mn atom at its center. The ring motif consists of a nearly circular arrangement of outer pentagons. The center of the ring motif is bright and is surrounded by a relatively darker region. DFT calculation in Ref. 12 shows that these motifs arise because Ga adsorbs at particular sites on the Al-Pd-Mn surface. Note that these motifs are different from the well-known white flower and dark star motifs of the substrate. The sizes of quasiperiodic Ga motifs, estimated by measuring the diameters of circumscribed circles enclosing them, are 3.0 ± 0.03 nm and 5.12 ± 0.05 nm for τ -GaWF and ring motifs, respectively. Note that similar motifs are observed for the quasiperiodic Ga monolayer at RT [11], which shows that the growth mode at low temperature is similar despite a decrease in the diffusion rate. The height of the Ga layer, extracted from the height profiles taken along the green and orange dashed arrows in Fig. 2(a) and plotted in Fig. 2(b), turns out to be 0.18 nm. Here, additionally, the Fourier transform (FT) of the STM image, displayed in Fig. 2(c), shows sharp tenfold spots, numbered 1-10. The corresponding intensity profiles [Fig. 2(d)], display clear peaks for each of the spots, thereby confirming their presence. Thus, the observation of quasiperiodic motifs and sharp FT spots, as well as the fivefold symmetry in the LEED patterns, demonstrates the quasiperiodicity in the Ga monolayer at 140 K.

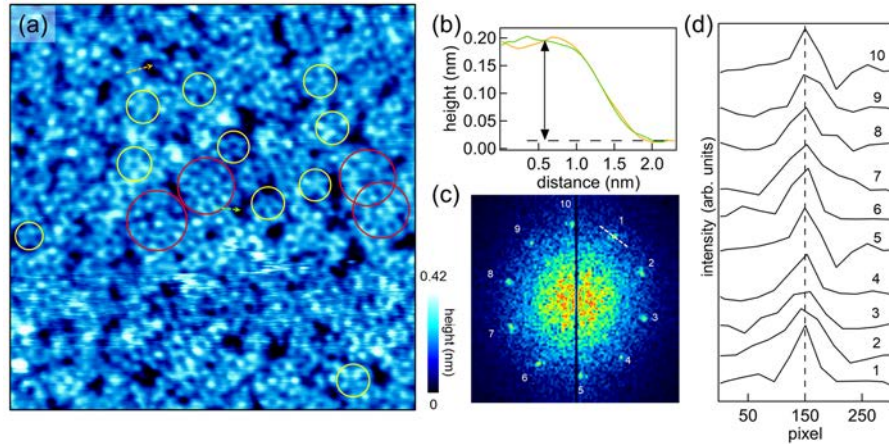


FIGURE 10. (a) STM topography image ($36.7 \text{ nm} \times 36.7 \text{ nm}$; $I_T = 0.5 \text{ nA}$, $U_T = 0.7 \text{ V}$) of 1 ML Ga/*i*-Al-Pd-Mn. The τ -GaWF and the ring motifs are highlighted by yellow and red circles. (b) Height profile along the orange and green dashed arrows in panel a. (c) FT of the STM image in panel (a). (d) Intensity profiles through the FT spots numbered 1-10 in panel (c).

CONCLUSION

In summary, the present study demonstrates that a Ga monolayer grown on *i*-Al-Pd-Mn exhibits quasiperiodic order. This is established by an atomic resolution STM image that reveals quasiperiodic motifs such as τ -GaWF and the ring motif. Furthermore, the Fourier transform of the STM image exhibits tenfold spots, confirming quasiperiodicity. LEED provides additional evidence from the presence of characteristic quasiperiodic spots nearly similar to the substrate.

ACKNOWLEDGEMENTS

We are grateful to Marian Krajčí for useful discussions. D. L. Schlager and T. A. Lograsso are thanked for providing us with the *i*-Al-Pd-Mn quasicrystalline substrate. S.R.B. is thankful to Council of Scientific and Industrial Research for grant under Emeritus Scientist Scheme (21/1170/24/EMR-II).

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Quasiperiodic Potassium Adlayer on Five-fold Al-Pd-Mn Surface

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Abstract. Quasiperiodicity of potassium (K) monolayer on the icosahedral Al-Pd-Mn (i-Al-Pd-Mn) five-fold surface is demonstrated using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Atomically resolved STM images reveal the formation of distinct quasiperiodic pentagonal motifs that resemble, but are larger than, the white flower motifs of *i*-Al-Pd-Mn. The quasiperiodic nature of the K monolayer is confirmed by the Fourier transform of the STM image and the LEED pattern.

INTRODUCTION

The interaction of alkali metal adlayers with various surfaces leads to a wide range of intriguing phenomena, including dispersed phase growth, surface reconstructions, work function reduction, and altered surface reactivity [1-5]. Adsorption of alkali metals on metal surfaces exhibits interesting phenomena such as an electric-field-induced redistribution of electronic charge at the edges of K islands on graphite [2], multipole and bulk-like plasmon modes whose frequency and intensity varied with alkali metal coverage [3,4], quantum well states without a confining barrier [5], to mention a few. While quasiperiodicity has been observed in different elemental films such as Bi, Sb [6], Pb [7, 8], Sn [9-12], Ga [13], scanning tunnelling microscopy (STM) studies of K adsorption on quasicrystalline surfaces are scarce. Very recently, K monolayer on decagonal Al-Ni-Co has been shown to exhibit quasiperiodic STM motifs [14]. Early low energy electron diffraction (LEED) and XPS studies showed that up to one monolayer (ML), K forms a dispersed phase [15,16], where the pseudogap [17] of the substrate was suppressed. DFT calculations mapped the potential energy surface of alkali metal adsorption and identified the energetically favorable sites on the quasiperiodic surface [18]. In this work, we present an STM investigation, supported by LEED, of K growth on the 5-fold surface of *i*-Al-Pd-Mn to demonstrate the formation of a quasiperiodic K monolayer with five-fold motifs.

EXPERIMENTAL

Polished and oriented monocrystalline icosahedral (*i*) Al-Pd-Mn quasicrystal with a bulk composition of Al_{69.4}Pd_{20.8}Mn_{9.8} was synthesized using the Bridgman technique [9]. The process for obtaining a contamination-free and stoichiometric surface has been discussed elsewhere [19]. The base chamber pressure was 5×10^{-11} mbar. K was deposited *in-situ* using a well-degassed SAES getter source at 6.2 A with the substrate cooled to 165 ± 10 K. Low temperature was used to avoid possible surface alloying [20]. STM imaging was performed in constant-current mode at 80 K using a variable-temperature STM, with tips cleaned by sputtering and voltage pulsing. Cleanliness of the surface after K deposition was verified by the absence of O KLL (510 eV) and C KLL (272 eV) signals in the Auger electron spectra, while the LMM Auger peak of K confirmed its presence on the surface [Fig. 1(a)].

RESULTS AND DISCUSSION

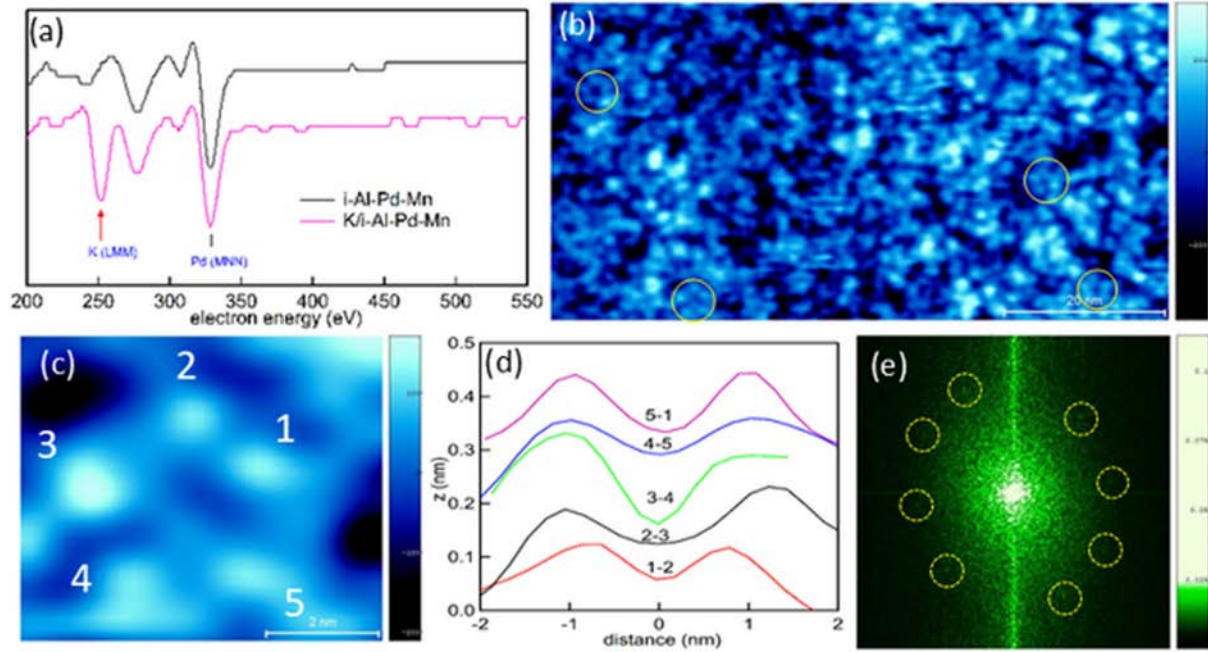


FIGURE 1. (a) Auger spectra after K deposition on *i*-Al-Pd-Mn, compared to the pristine substrate. The LMM (MNN) Auger peak of K (Pd) at 252 eV (330 eV) is highlighted by a red arrow (black tick). (b) STM topography image of the K monolayer on *i*-Al-Pd-Mn (tunneling current $I_T = 1.5$ nA, bias voltage $U_T = 1.5$ V) with the pentagonal motifs of K marked by yellow circles. (c) A zoomed pentagonal motif, the vertices are marked from 1 to 5. (d) Height profiles showing the distances $d_{n,m}$ ($1 \leq n, m \leq 5$) between the vertices, the horizontal scale's minima are aligned to zero. (e) Fourier transform of panel **b** with the spots shown within dashed yellow circles.

An atomically resolved STM topography of 1 ML K/*i*-Al-Pd-Mn in Fig. 1(b) shows the presence of pentagonal K motifs (highlighted by yellow circles, expanded image in Fig. 1(c) where the vertices are numbered). These resemble the white flower motifs of *i*-Al-Pd-Mn, although in this case the central region is dark and its size is substantially larger (average diameter being 4.4 ± 0.1 nm compared to 2 nm for the white flower). The lengths of its sides are determined from the height profiles [Fig. 1(d)] exhibit a nearly regular pentagon with an average side length of 2.1 ± 0.1 nm ($d_{23} \approx 2.3$ nm, $d_{34} \approx 2.1$ nm, $d_{45} \approx 2.0$ nm, $d_{51} \approx 2.0$ nm). This shows that K adatoms attach to favorable adsorption sites that are distributed in a quasiperiodic fashion on the substrate surface determined by DFT [15], indicating pseudomorphic growth driven by adsorbate-substrate interaction. The Fourier transform in Fig. 1(e) shows a set of ten-fold spots (8 spots are clearly visible as encircled by yellow circles) that is indicative of quasiperiodicity [9,13,10]. The tenfold symmetry of the Fourier transform spots is, however, somewhat distorted due to the thermal drift in the STM measurement. It may be noted that at small coverages such as 0.2 ML, motifs are not observed and the K atoms are uniformly dispersed, as shown earlier by XPS [15].

The LEED pattern of the K monolayer has a ratio of the radii between the inner and the outer rings of spots from (0, 0) spot equal to τ [Fig. 2(b)], where $\tau = 1.618$ i.e. golden mean. The pattern is similar to the five-fold patterns of the substrate pattern [Fig. 2(a)], further establishing the quasiperiodicity of the K adlayer. The intensity line profiles across the dashed white line in Fig. 2(a) are plotted in Fig. 2(c). The positions of the spots are similar between 1 ML and the substrate, and there is no splitting of the spots or appearance of extra spots. The plot of intensity versus voltage (I-V) for the (000 $\bar{1}\bar{1}0$) and (11000) spots (shown by red and blue circles in Fig. 2(a), respectively) are nearly similar to the substrate [Figs. 2(d,e)]. In agreement with STM, LEED reconfirms the quasiperiodic growth of the K monolayer on *i*-Al-Pd-Mn.

CONCLUSION

We establish quasiperiodicity of the potassium monolayer on the five-fold surface of *i*-Al-Pd-Mn using STM and

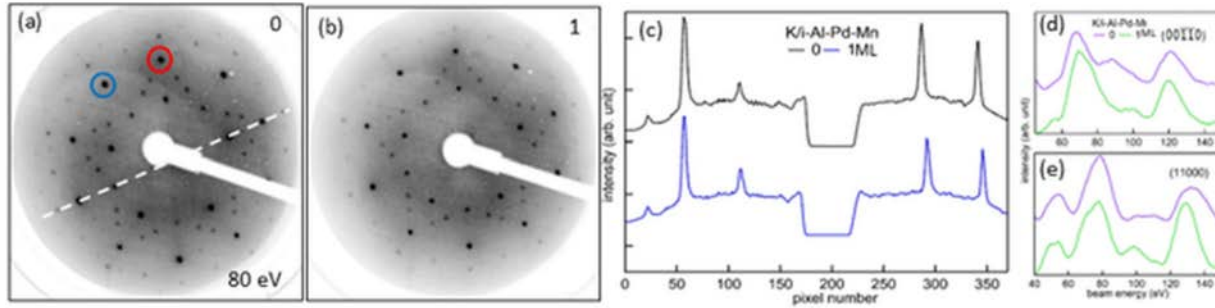


FIGURE 2. LEED patterns of (a) substrate *i*-Al-Pd-Mn [(000 $\bar{1}$ 10), and (11000) LEED spots are marked by red and blue circles, respectively, compared with (b) 1 ML K/*i*-Al-Pd-Mn. (c) Intensity line profiles along the dashed white line in panel **a**. Comparison of the *I*-*V* curves of 1 ML K/*i*-Al-Pd-Mn with *i*-Al-Pd-Mn for (d) (000 $\bar{1}$ 10) and (e) (11000) LEED spots.

LEED. STM reveals pentagonal K motifs of a size larger than the substrate. This indicates that K atoms prefer to adsorb at the DFT-predicted [15] adsorption sites. Quasiperiodicity of the K monolayer is confirmed by the presence of ten-fold spots in the Fourier transform of the STM image and similarity of the LEED patterns of the adsorbate and the substrate.

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Effect of Annealing on the Properties of Electrodeposited InSb Thin Films

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Abstract: Indium antimonide (InSb) thin films were successfully grown on stainless-steel substrates by DC electrodeposition. Elemental analysis showed the deposited films consisted of 51.9% indium and 48.1% antimony. X-ray diffraction (XRD) studies revealed the films to be polycrystalline with a predominant (111) orientation. Key structural parameters, including crystallite size (D), dislocation density (δ), and strain (ϵ), were evaluated. The crystallite size increased with annealing temperature, ranging from 61.64 nm to 66.27 nm. Raman spectroscopy confirmed the presence of the transverse optical (TO) phonon mode, indicating the crystalline nature of the electrodeposited films.

INTRODUCTION

Indium antimonide (InSb) is a promising semiconductor material for the development of a wide range of electronic and optoelectronic devices, possessing a melting point of 525 °C. It is a direct band gap semiconductor with an energy band gap of 0.17 eV at 300 K and 0.23 eV at 80 K [1]. Owing to its superior electronic properties, InSb has been widely employed in the fabrication of Hall sensors and magnetoresistors [2], speed-sensitive sensors [3], magnetosensors [4], and high-speed transistors [5]. Among the available thin-film growth methods, electrodeposition stands out as a simple, cost-effective, and scalable technique suitable for large-area deposition. In the present study, the effect of annealing on the structural, morphological, and optical properties of electrodeposited InSb thin films is investigated.

EXPERIMENTAL DETAILS

InSb thin films were potentiostatically deposited using a conventional three-electrode cell system. A stainless-steel sheet served as the working electrode, a carbon electrode was used as the counter electrode, and an Ag/AgCl electrode was employed as the reference electrode. Prior to electrodeposition, the substrate was ultrasonically cleaned in acetone and subsequently rinsed with distilled water. The chemical bath consisted of an aqueous solution containing 0.05 M indium trichloride (InCl_3), 0.04 M antimony trichloride (SbCl_3), and 0.20 M citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$). Tri-sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) was used as a complexing agent to bring the reduction potentials of In and Sb closer, enabling co-deposition. The deposition was carried out at a potential of -1.3 V for approximately 15 minutes at room temperature. Uniform, silver-grey, and well-adherent films were obtained using an EG&G PARC (VERSASTAT-II) computer-controlled potentiostat.

To investigate the influence of annealing temperature on the properties of the electrodeposited InSb thin films, the samples were annealed at 250 °C, 300 °C, and 350 °C, respectively. The crystal structure of the films was analyzed by X-ray diffraction (XRD) using $\text{Cu-K}\alpha$ radiation. The surface morphology and elemental composition were examined using a Philips FE-SEM/EDAX Quanta 200 FEG microscope equipped with an energy-dispersive X-ray analysis (EDAX) system. Raman spectroscopy measurements were performed using a confocal Raman spectrometer to further characterize the films.

RESULTS AND DISCUSSIONS

Figs. 1(a) – (d) show the X-ray diffraction (XRD) profiles of as-grown InSb films and those vacuum-annealed at 250 °C, 300 °C, and 350 °C, respectively. The diffraction patterns reveal the InSb phase with characteristic peaks corresponding to the (111), (220), (311), (400), (331), (422), and (511) planes, along with an additional indium (In) peak at (112). Upon annealing, the (111) peak becomes significantly sharper, while the intensity of the In (112) peak gradually decreases with increasing annealing temperature. Notably, the In (112) peak completely disappears for films

annealed at 350 °C. Annealing at 300 °C enhances the crystallinity of the InSb intermetallic compound, whereas annealing at 350 °C yields high-quality material free from extraneous In and Sb peaks. Further annealing at 350 °C for 2 h in vacuum results in additional sharpening of the diffraction peaks, indicating grain growth at this elevated temperature. However, weaker InSb and Sb peaks also emerge. The diffraction pattern for the sample annealed at 350 °C matches well with the standard JCPDS-ICDD data for InSb (Card No. 6-2008). XRD analysis reveals that the InSb films adopt the zinc blende structure, with a predominant (111) orientation. The crystallite size for the (111) plane was determined using Bragg's equation [6]. The measured particle size, strain [7], dislocation density [8], and lattice spacing [9] for the as-grown and annealed films are summarized in Table 1. An increase in annealing temperature leads to larger crystallite sizes, likely due to a reduction in strain. This grain growth is attributed to the coalescence of smaller grains. The dislocation density decreases with annealing temperature, suggesting enhanced migration and annihilation of dislocations, which results in improved film quality [10].

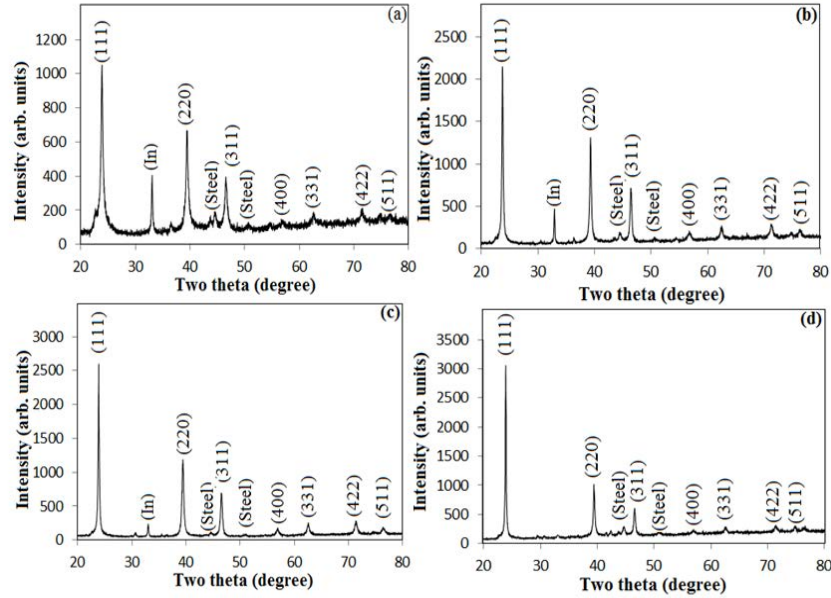


Figure. 1 XRD spectra for (a) as grown film and vacuum annealed at (b) 250 °C, (c) 300 °C, and (d) 350 °C respectively.

The surface morphology was examined using scanning electron microscopy (SEM). Fig. 2(a) shows the SEM image of an InSb film annealed at 350 °C, revealing a uniform, crack-free surface covered with well-adherent spherical particles. Atomic force microscopy (AFM) images [Fig. 2(b)] confirm that the surface is uniformly covered with micron-sized particles. The average surface roughness, as measured by AFM, is approximately 35 nm.

Table 1 Structural parameters of InSb thin films for (111) plane

Annealing T_s (°C)	Crystallite size (D) nm	Strain (ϵ) $\times 10^{-3}$ line $^{-2}$ m $^{-4}$	Dislocation Density $\delta \times 10^{14}$ line m $^{-2}$	$d_{(111)}$ (Å)	Lattice Parameter ($a \times 10^{-10}$ m)
As grown	61.64	0.0337	2.6319	3.74240	6.47
250	63.77	0.0325	2.4590	3.74240	6.47
300	65.25	0.0318	2.3487	3.74240	6.47
350	66.27	0.0313	2.2770	3.74240	6.47

The chemical composition, determined by energy-dispersive X-ray analysis (EDAX), was found to be 52.9% In and 48.1% Sb. The EDAX results indicate that the chemical composition of the electrodeposited films is independent of annealing temperature. Raman spectroscopy of the film annealed at 350 °C [Fig. 3] shows a single peak at 178 cm $^{-1}$, corresponding to the transverse optical (TO) phonon mode of InSb. The presence of the TO mode confirms that the electrodeposited films are crystalline in nature.

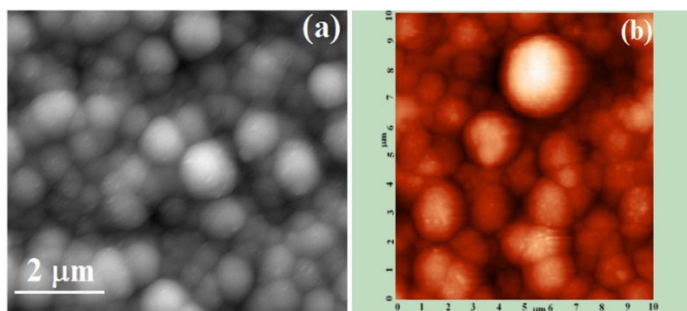


Figure. 2 (a) SEM image and (b) AFM image of thin films at annealed 350 °C

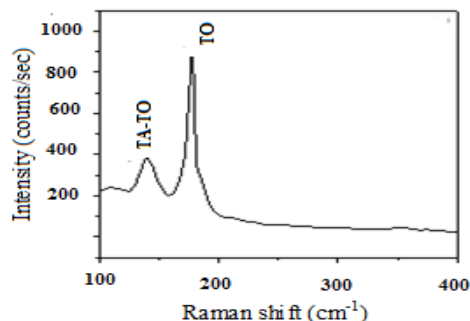


Figure. 3 Raman image of sample annealed at 350 °C.

CONCLUSION

InSb thin films were successfully electrodeposited on stainless-steel substrates using the DC electrodeposition technique. EDAX analysis confirmed a near-stoichiometric composition of 52.9% In and 48.1% Sb. XRD results indicated that the films were polycrystalline with a predominant (111) orientation. An increase in the (111) peak intensity with annealing temperature was observed, indicating improved crystallinity. The presence of the transverse optical (TO) phonon mode in Raman spectra further confirmed the crystalline nature of the electrodeposited films.

ACKNOWLEDGEMENTS

The author gratefully acknowledge Mr. S. D. Sharma and Mr. Shiv Kumar, IIC, IIT Roorkee, India, for providing access to the XRD and SEM/EDAX facilities. He also thanks Head, SAIF, School of Environmental Sciences, Mahatma Gandhi University, Kottayam, Kerala, India, for providing the Raman spectroscopy facilities.

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Annealing Driven Modulation of Nonlinear Optical Characteristics in TiO₂ Thin Films

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Abstract. In the present article, nonlinear optical characteristics of TiO₂ thin films have been investigated. The DC magnetron sputtering technique were used to deposit the films in an argon and oxygen environment. The grown films were post-annealed at two distinct temperatures. The crystalline properties of the films were investigated using X-ray diffraction (XRD) analysis, which confirmed the crystalline nature of the films upon annealing. From the UV–Vis spectra, it was observed that the band gap value decreases for the film annealed at a higher temperature. The intensity-dependent nonlinear optical behavior of the films was investigated using the Z-scan method in both open- and closed-aperture configurations. From this analysis, the nonlinear absorption and nonlinear refraction coefficients were determined, along with the impact of annealing temperature on these properties.

INTRODUCTION

Semiconducting materials such as TiO₂ have gained significant attention because of their strong nonlinear optical (NLO) response to incident light. These characteristics make them promising candidates for use in photonic devices, sensors, and solar energy systems. As a result, researchers continue to investigate methods to improve their performance and uncover additional functionalities. Among wide bandgap semiconductors, titanium dioxide (TiO₂) stands out due to its well-established applications in areas such as solar cells, self-cleaning surfaces, and photocatalysis. Considering its importance in optical technologies, extensive research has been carried out to understand its nonlinear optical behavior [1–3]. For example, Long et al. [1] employed the Z-scan technique to study nonlinear refraction and absorption in TiO₂ thin films fabricated by pulsed laser deposition, using an 800 nm femtosecond laser source. Their results indicated that the anatase phase exhibits a stronger nonlinear optical response compared to the rutile phase. In our earlier work [4], we also reported the presence of notable dispersive and absorptive nonlinearities in TiO₂ thin films. Building on this, the present study focuses on examining the nonlinear optical properties of annealed films. To achieve this, the Z-scan method is utilized with a CW He–Ne laser source operating at wavelength 632.8 nm.

EXPERIMENTAL DETAILS

Thin films of TiO₂ were deposited on quartz substrates using the direct current magnetron sputtering (DCMS) technique. A high-purity titanium target (99.999%, 2-inch diameter) was used as the source material. The sputtering procedure was conducted in a mixture of argon and oxygen gases, both of which were 99.999% pure. The proportion of oxygen in the gas mixture was controlled through the relative oxygen flow ratio ($R_{O_2} = (P_{O_2}/P_{O_2} + P_{Ar}) \times 100\%$, where P_{O_2} and P_{Ar} are partial pressures of O₂ and Ar, respectively) which was maintained at 5%. The gas flow rate during deposition was fixed at 50 sccm, and the distance between the target and the substrate was fixed at 13 cm. Before deposition, the chamber was evacuated to a base pressure of 5×10^{-7} Torr, while the working pressure during sputtering was maintained at 2.7×10^{-3} Torr. A portion of the films annealed in a vacuum furnace at 350°C and 450°C, which were designated as S1 and S2, respectively. The structural characteristics of the annealed films were analysed using XRD with a Bruker D8 Advance diffractometer, where Cu-K α radiation served as the X-ray source. To evaluate the optical behaviour, ultraviolet–visible (UV–Vis) spectroscopy was carried out using a Cary 60 spectrophotometer (Agilent Technologies), from which the optical band gap and linear absorption coefficients were determined.

Additionally, the Z-scan method was used to analyze the nonlinear optical characteristics using a continuous-wave He–Ne laser at a wavelength of 632.8 nm.

FIGURE 1: X-ray diffraction patterns of

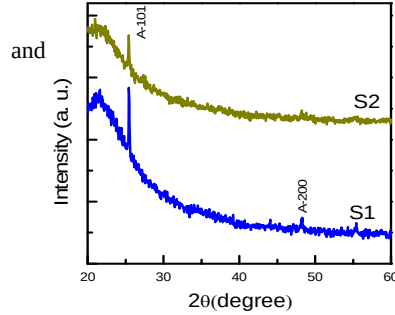
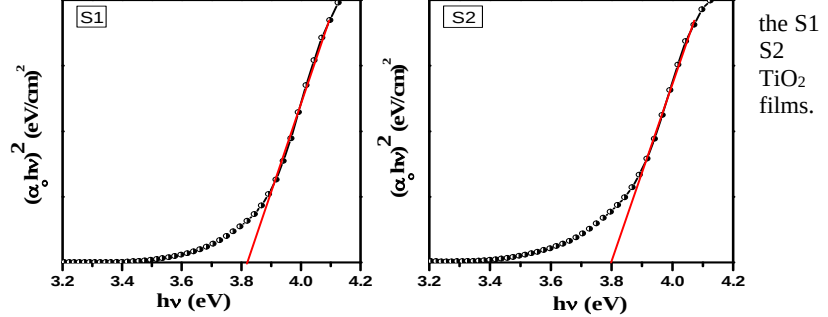


FIGURE 2: $(\alpha h\nu)^2$ vs $h\nu$ plot of the grown S1 and S2 TiO₂ films.



RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the annealed TiO₂ films, confirming their crystalline nature. All observed diffraction peaks are consistent with the anatase phase. Peak intensity decreases, and the peaks slightly shift toward lower angles as the annealing temperature is raised above 350°C. The standard Scherrer equation was used to determine the crystallite size. The findings show that there is no discernible change in grain size when the annealing temperature increases from 350°C to 450°C. Despite this, the S2 sample shows lower peak intensity, which may be caused by defect states such as partial surface amorphization or oxygen vacancies. These factors can disrupt the long-range crystalline order, leading to broader and less intense diffraction peaks. The optical band gap value is obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$ using the standard Tauc formula $(\alpha h\nu)^2 = A(h\nu - E_g)$, where α corresponds to linear absorption coefficient, A is the constant and $h\nu$ represents the incident photon energy. The energy band gap (E_g) is determined by linear extrapolation of $(\alpha h\nu = 0)^2$ to energy $h\nu$ (Fig. 2) and was found to be 3.82 and 3.79 eV for S1 and S2, respectively. Both the band gap values are in line with the earlier reported value. To investigate the intensity-dependent nonlinear optical behaviour of the films, Z-scan measurements were carried out in both open and closed aperture configurations. The analysis was first focused on the nonlinear refraction properties. Since the film thickness (100 nm) is much smaller than the Rayleigh length Z_R , the thin film approximation can be safely applied. Figure 3(a) presents the normalized transmittance as a function of the sample position relative to the focal point ($z=0$) under closed aperture conditions. The characteristic pattern of a pre-focal valley followed by a post-focal peak is clearly observed, indicating a self-focusing effect. This behaviour is a typical signature of positive nonlinear refraction. In the figure, the symbols denote the experimental observations, while the solid line represents the best theoretical fit based on the model developed by Sheik-Bahae et al. [5].

$$T[a, \Delta\phi_0] = \left(1 + \frac{4\Delta\phi_0 a}{(a^2 + 1)(a^2 + 9)}\right) \dots \dots \dots (1)$$

where $a (=z/z_R)$ is the dimensionless distance parameter and $\Delta\phi_0$ is the fitting parameter representing the on-axis phase shift given by $\Delta\phi_0 = n_2 I_0 k L_{eff}$, here k denotes the propagation constant and I_0 is the maximum intensity at the focal point, respectively. The effective length (L_{eff}) is given by $(= (1 - e^{-\alpha L})/\alpha)$. Based on the values obtained from UV-Vis analysis and L_{eff} , the values of nonlinear refractive index coefficients are $1.56 \times 10^{-8} \text{ m}^2/\text{W}$ and $3.06 \times 10^{-8} \text{ m}^2/\text{W}$ for S1 and S2, respectively. From the value we can clearly see that the enhancement in nonlinearity is observed for the S2 film. It was reported that the high-temperature annealing process causes a reduction in band gap value and can introduce mid-gap states, making it easier for nonlinear processes to occur under incident light due to increased electronic polarizability. Nonlinear refraction can arise from different mechanisms, including molecular, electronic, and thermal effects. Since a continuous-wave (CW) He–Ne laser was employed in the present research, thermal effects are primarily responsible for the observed third-order nonlinearity.

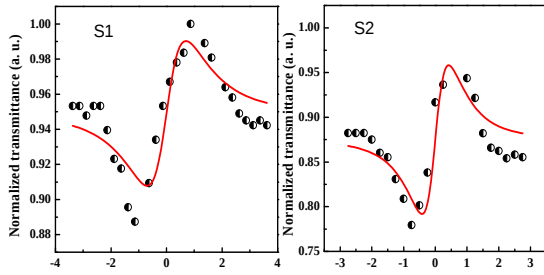


Figure 3(a): Closed-aperture Z-scan curves for the S1 and S2 films. The symbols represent the experimental data points, while the solid lines correspond to the best theoretical fits obtained using Eq. (1).

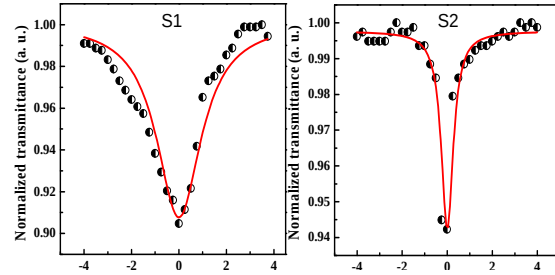


Figure 3(b): Open-aperture Z-scan curves for the S1 and S2 films. The symbols represent the experimental data points, while the solid lines correspond to the best theoretical fits obtained using Eq. (1).

sample experiences localized heating and excitation to higher energy levels when it is subjected to the incident CW laser beam, as it absorbs some of the optical energy. Figure 3(b) illustrates the variation of normalized transmittance with respect to sample position under open-aperture conditions. There is a noticeable decrease in transmittance close to the focal point ($z = 0$). This reduction in transmission at the focus indicates the presence of reverse saturable absorption (RSA), which corresponds to a positive nonlinear absorption coefficient. For the open-aperture arrangement, the normalized transmittance can be described by the standard expression reported in [5].

$$T[a] = \sum_{m=0}^{\infty} \frac{[-q_0(a)]^m}{[m+1]^{3/2}} q_0 < 1 \dots \dots \dots (2)$$

where m is an integer and q_0 is the fitting parameter given as $q_0(a) = \beta I_0 L_{eff} / 1 + (Z^2 / Z_R^2)$, from the knowledge of $q_0(a)$, the calculated values are 1.43×10^{-2} m/W and 2.4×10^{-2} m/W for S1 and S2 film, respectively. In semiconducting materials, Two photon can typically occurs when the photon energy of the incident light is lower than the band gap energy (E_g) but greater than half of it ($E_g/2$)[5]. In the present case, the incident photon energy is 1.95 eV, which is lower than the band gap energy of 3.8 eV but still exceeds half of that value. This satisfies the necessary condition for TPA to take place. Therefore, the observed third-order nonlinear absorption is primarily attributed to the two-photon absorption process. For the S2 film, a larger value of β is observed, which is due to the smaller band gap value as compared to S1 film. It was mentioned earlier that the drop in bandgap increases light absorption, allowing more photon-induced electronic transitions, which are foundational for nonlinear optical phenomena.

CONCLUSION

The sign and magnitude of the third-order nonlinear refractive index and absorption coefficients were obtained from the Z-scan measurements. The closed aperture results indicate a self-focusing mechanism, which can be caused by thermal lensing effect. On the other hand, the open aperture measurements demonstrate reverse saturable absorption behavior.

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Room temperature XPS studies of Non evaporable getter thin films

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Abstract: Non-evaporable getter (NEG) materials have emerged as a powerful solution for achieving extreme high vacuum (XHV) environments. These materials are typically deposited using sputtering techniques and are characterized using X-ray Photoelectron Spectroscopy (XPS). A variety of elemental combinations can be employed for NEG films, each offering distinct gettering properties. In this study, we have investigated a ternary combination of titanium (Ti), vanadium (V), and zirconium (Zr) as a potential NEG material. The chemical composition and surface characteristics of the films were analyzed using XPS. Atomic percentage of different elements on the surface of thin film at different temperatures were calculated.

INTRODUCTION

Non-evaporable getter (NEG) materials have been an area of active research for the past two decades. Several experiments have been done to find the optimum ratio which gives lowest activation temperature. Among various compositions, alloys of titanium (Ti), vanadium (V), and zirconium (Zr) in different proportions have shown promising performance. The chemical interaction between these elements significantly influences the activation behavior of the NEG films.

NEG materials are now crucial in achieving extreme high vacuum (XHV), which is essential for applications such as particle accelerators. While ultra-high vacuum (UHV) levels can be attained using mechanical pumps like rotary pumps, turbomolecular pumps, and sputter ion pumps, NEG films offer a passive and power-free solution to maintain pressures below 10^{-12} mbar. These films, typically composed of group IV and V elements, are deposited using DC magnetron sputtering, with a fabrication duration of approximately three hours.

A key challenge in vacuum systems is outgassing from chamber walls, which continuously releases gases such as O₂, H₂, N₂, CO₂, CO, H₂O, CH₄, and noble gases. NEG films function by chemically reacting with some of these gases and physically adsorbing others. In recent years, NEG coatings have gained popularity as efficient, compact vacuum pumps due to their low cost and zero power consumption. This paper focuses on studying the behaviour of Ti-V-Zr NEG films prior to activation.

SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The deposition of the Ti-Zr-V non-evaporable getter thin film was carried out in a custom-built cylindrical DC magnetron sputtering system [1]. A cylindrical substrate was fabricated by rolling a Stainless Steel (SS304L) sheet into tubular form, serving as the anode. The cathode consisted of twisted metal wires comprising Titanium (Ti), Zirconium (Zr), and Vanadium (V). The cathode-anode assembly was connected to a high-voltage DC power supply, and voltage control was achieved via an external rheostat. Argon gas, used as the sputtering medium, was introduced into the vacuum chamber via a calibrated leak valve, with flow rate monitored by an inline mass flow meter. Discharge can be seen in figure 1.

RESULTS

The XPS studies were conducted in an ultra-high vacuum (UHV) chamber (base pressure $<10^{-9}$ mbar) using hemispherical analyzer with Mg X-ray source. Samples were mounted on sample manipulator with the help of sample transfer mechanism samples are loaded inside the chamber. Pressure of the range of 10^{-9} mbar range is acquired with

the help of rotary pump, turbo molecular pump and sputter ion pump. Data is then acquired using XPS detector and subsequently analysed.

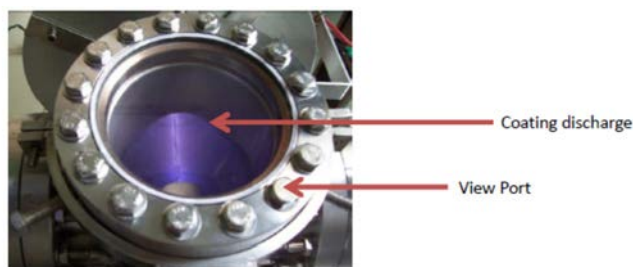


FIGURE.1 Discharge while coating

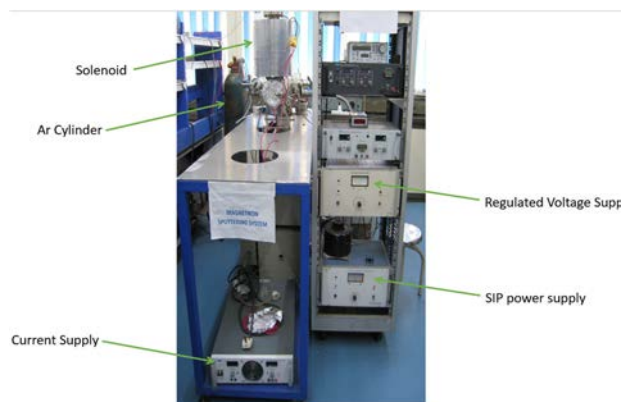


FIGURE 2: DC magnetron setup

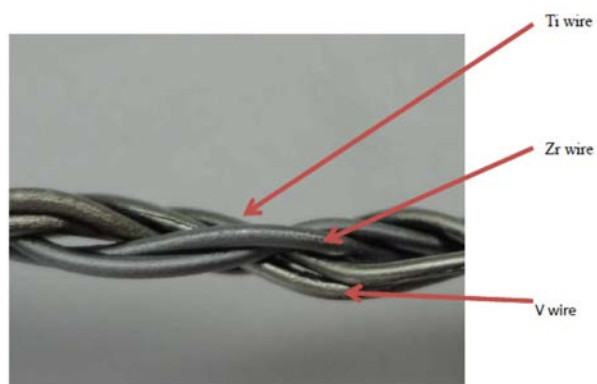
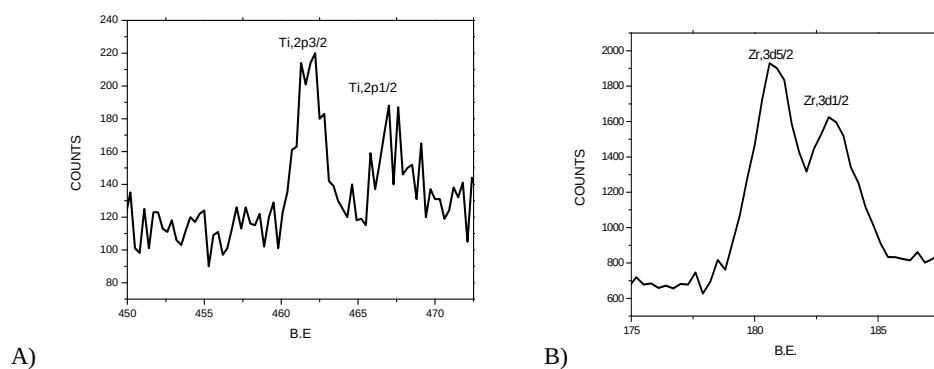


FIGURE.3. twisted wires of Ti, Zr, and V to form cathode

The XPS spectra obtained from the as-deposited NEG film exhibit clear and well-resolved peaks. Quantitative analysis confirms the presence of all major elements—Ti, V, Zr, O, and C—with peak positions corresponding to their oxidized states. This suggests that the NEG film, in its as-deposited form, exists primarily in an oxide state. Upon thermal activation, these oxides are expected to reduce to their metallic forms, thereby initiating the gettering action. The results also demonstrate that DC magnetron sputtering is an effective technique for producing high-quality, uniform NEG coatings. The clarity and consistency of the spectra support the suitability of this method for reliable NEG film fabrication and subsequent use in ultra-high and extreme-high vacuum applications.

XPS results are shown in figure 4.. Zr peak at 182.3eV has a peak broadening at room temperature showing formation of different compounds. Oxygen peak at room temperature showing presence of water molecule at 534.2eV energy. The presence of all NEG element Ti, V, Zr along with C and O was found. The detailed scans for each element were taken. The clear peaks of XPS for Ti 3p_{3/2}, Zr 3d, and C1s are shown in a), b) and c) of Fig 4. Peak positions for Ti and V are observed around 461.2 eV and 521.3eV, which belong to oxide state of these element.



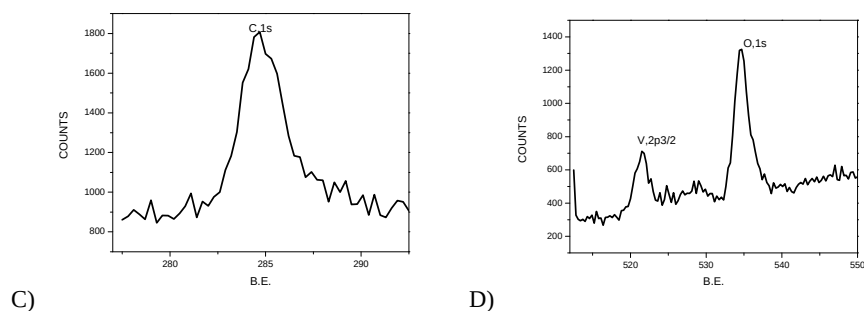


FIGURE 4-A)Ti peak B) Zr peak C) V peak D)O and V peak

Peak name	Area of the peak	Sensitivity factor	Area/Sensitivity factor	Element%
Zr 3d5/2	3204	4.33	740	16.1%
Ti 2p3/2	296.5	5.2	57	1.24%
V 2p3/2	849.7	6.3	135	2.93%
O 1s	2309.1	2.85	810	17.6%
C 1s	2865.6	1	2865.6	62.2%

Table1. quantitative analysis of the coated film

$$(V\%) = (I_{V2p3/2}/S_{V2p3/2}) / [I_{V2p3/2}/S_{V2p3/2} + I_{Zr3d5/2}/S_{Zr3d5/2} + I_{Ti2p3/2}/S_{Ti2p3/2} + I_{O,1s}/S_{O,1s} + I_{C,1s}/S_{C,1s}] = 2.93\%$$

$$(Zr\%) = (I_{Zr3d5/2}/S_{Zr3d5/2}) / [I_{V2p3/2}/S_{V2p3/2} + I_{Zr3d5/2}/S_{Zr3d5/2} + I_{Ti2p3/2}/S_{Ti2p3/2} + I_{O,1s}/S_{O,1s} + I_{C,1s}/S_{C,1s}] = 16.1\%$$

$$(Ti\%) = (I_{Ti2p3/2}/S_{Ti2p3/2}) / [I_{V2p3/2}/S_{V2p3/2} + I_{Zr3d5/2}/S_{Zr3d5/2} + I_{Ti2p3/2}/S_{Ti2p3/2} + I_{O,1s}/S_{O,1s} + I_{C,1s}/S_{C,1s}] = 1.24\%$$

$$(O\%) = (I_{O,1s}/S_{O,1s}) / [I_{V2p3/2}/S_{V2p3/2} + I_{Zr3d5/2}/S_{Zr3d5/2} + I_{Ti2p3/2}/S_{Ti2p3/2} + I_{O,1s}/S_{O,1s} + I_{C,1s}/S_{C,1s}] = 17.6\%$$

$$(C\%) = (I_{C,1s}/S_{C,1s}) / [I_{V2p3/2}/S_{V2p3/2} + I_{Zr3d5/2}/S_{Zr3d5/2} + I_{Ti2p3/2}/S_{Ti2p3/2} + I_{O,1s}/S_{O,1s} + I_{C,1s}/S_{C,1s}] = 62.2\%$$

(where S is sensitivity factor of the peak and I is intensity of the peak)

CONCLUSION

XPS analysis confirmed the presence of all key NEG elements—titanium (Ti), vanadium (V), and zirconium (Zr)—along with carbon (C) and oxygen (O) in the deposited film. The Zr 3d peak at 182.3 eV exhibited noticeable broadening at room temperature, indicating the formation of multiple zirconium-based compounds. The O 1s peak at 534.2 eV further confirmed the presence of adsorbed water molecules on the film surface. Detailed scans of individual elements revealed clear and well-defined peaks, specifically for Ti 3p_{3/2}, Zr 3d, and C 1s. Additionally, the Ti and V peaks observed around 461.2 eV and 521.3 eV, respectively, suggest the presence of their oxidized states. These results indicate that the as-deposited NEG film undergoes surface oxidation and compound formation even before activation, emphasizing the importance of pre-activation surface characterization for optimizing NEG film performance.

Thus, the fabricated Ti-Zr-V film behaves as an effective NEG coating capable of chemisorbing active gases upon moderate thermal activation. The study not only verifies the feasibility of cylindrical magnetron-based NEG coating deposition but also provides valuable insight into the thermal behaviour and activation window for practical vacuum applications.

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Bipolar Resistive Switching in Spin Coated ZrO₂ thin film

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Abstract. In this work, we report the resistive switching (RS) behavior of Zirconium dioxide (ZrO₂) thin-film-based resistive random-access memory (RRAM) device deposited on Si (p++) substrate using spin coating technique with the configuration Al/ZrO₂/Si. The tetragonal structure has been confirmed with X-ray diffraction (XRD) as prepared thin film. Current-Voltage (I-V) measurement shows the impressive bipolar resistive switching characteristics, including stable operation up to 250 cycles. The device exhibits low set voltage (V_{Set}) and reset voltage (V_{Reset}), enabling reduced operating power consumption and improved energy efficiency.

INTRODUCTION

The development of modern information technology relies primarily on the advancement of nonvolatile memory (NVM) with higher density, faster speed, and lower power consumption. Conventional memories, which utilize the technology of floating gate FLASH devices, causes performance degradation as size scaling limits are approached. Therefore, the development of RRAM devices with improved performance is necessary. The RS mechanism is based on the transition between a high resistance state (HRS) and a low resistance state (LRS) when a voltage is applied across the top and bottom electrodes. The underlying mechanism of resistive switching is likely electrochemical oxidation, which includes the migration of metal ions within the active layer and the transport of oxygen vacancies [1]. RRAM devices are generally formed by sandwiching an active layer between two conducting electrodes. Till date several metal oxides such as ZnO, NiO, ZrO₂, HfO₂, TiO₂ etc. have been investigated for RRAM devices. Among them, with its high dielectric strength, chemical durability, improved operational efficiency, and superior thermal stability relative to silicon, ZrO₂ emerges as an ideal material for active layers in upcoming RRAM applications. Many studies highlight that ZrO₂ based memory devices offer good switching performance. Ha et al. have studied the effect of annealing conditions and reported that vacuum annealed film exhibits the larger crystallinity, improved non-volatile nature and good endurance [2,3]. The resistive switching behavior of ZrO₂ can be effectively tailored by optimizing key fabrication parameters such as the deposition process, annealing temperature, oxygen environment, film thickness, and the materials used for the electrodes.

The present work focuses on the structural and resistive switching behavior of the low-cost solution processed ZrO₂ thin film. From I-V characteristics, the device shows a bipolar resistive switching behavior without any initial forming voltage.

EXPERIMENTAL

ZrO₂ thin film was prepared on the Si p++ (100) substrate through spin coating method, utilizing Zirconyl Chloride octahydrate (ZrOCl₂ • 8H₂O) from Sigma Aldrich and 2-Methoxy ethanol (2-ME) from Himedia. Prior to deposition, the substrate was cleaned through ultrasonication in deionized water (DIW), acetone and Isopropyl Alcohol (IPA). To prepare the precursor solution of ZrO₂, ZrOCl₂ • 8H₂O (0.1972 g) was mixed in 2ml of 2-ME with stirring for 1 h at 80 °C and subsequently kept overnight for aging. Then, the prepared solution was spin-coated on Si substrate (1×1cm) at 3000 rpm for 50 s and then dried at 150 °C for up to 2-3 min on hot plate. The coating was repeated twice to control the film thickness the coating was repeated twice. The prepared film was annealed at 400 °C for 1 h. Finally, Al was fabricated as a top electrode by thermal evaporation technique using a metal shadow mask of diameter 0.5 mm. Structural and phase analysis of ZrO₂ thin film was carried out by using Rigaku mini flex 600 benchtop XRD Cu K α

radiation ($\lambda=1.54 \text{ \AA}$). I-V characteristics were measured by Kethley source meter semiconductor parameter analyzer (B1500A).

RESULTS AND DISCUSSION

Fig.1 illustrates the X-ray diffraction pattern of the ZrO_2 layer formed on the Si p++ substrate. The intensity of diffraction peaks suggest that the film has good crystallinity. Diffraction peaks match with previously reported tetragonal structure (t- ZrO_2 JCPDS card no. 17-0923). The absence of impurity peaks denotes the existence of pure phase of ZrO_2 . The diffraction peak at 25° corresponds to the presence of Si p++ substrate.

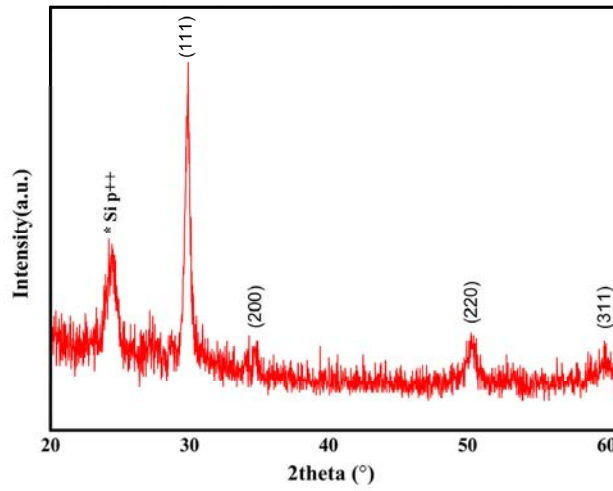


FIGURE 1. XRD result obtained through spin coated ZrO_2 thin film.

Further, to study the RS behavior of the fabricate device, I-V characteristics have been performed, as depicted in Fig. 2 To perform the measurements, the bias voltage was varied in a stepwise manner following a particular sequence $-2.2 \text{ V} \rightarrow 0 \text{ V} \rightarrow 2.67 \text{ V} \rightarrow 0 \text{ V} \rightarrow -2.2 \text{ V}$ for 150 cycles and $-2.061 \text{ V} \rightarrow 0 \text{ V} \rightarrow 1.86 \text{ V} \rightarrow 0 \text{ V} \rightarrow -2.061 \text{ V}$ for 250 cycles under typical ambient conditions, the Al/ ZrO_2 /Si p++ device has been tested with a compliance current limit of 100 mA to prevent damage during the forward bias sweep. The voltage is swept from -2.2 V to 2.67 V and -2.061 to 1.86 in cyclic manner. I-V characteristics show the bipolar resistive switching behavior of the Al/ ZrO_2 /Si device, which exhibits reversible switching behavior between HRS and LRS upon applied voltage of different polarities. A sudden increment of current in forward bias scan voltage around 2.67 V and 1.65 V can be observed indicating the formation of a conductive filament between bottom and top electrodes and the corresponding voltage is denoted as V_{Set} , as shown in fig.2. When negative bias voltage is applied, the device transitions from LRS back to HRS once the scan voltage reaches specific value. -2.2 V and -1.67 , corresponding to the transition back to HRS, known as V_{Reset} . The set and reset voltage of the device corresponding to 250 and 150 RS $V_{\text{Set}} = 1.7 \text{ V}$, $V_{\text{Reset}} = 1.6 \text{ V}$ and $V_{\text{Set}} = 2.32 \text{ V}$, $V_{\text{Reset}} = 1.86 \text{ V}$ respectively. As compared to previously reported HfO_2 films fabricated using the ion beam sputtering technique, which is costly and typically exhibits high V_{Set} and V_{Reset} voltages with limited switching cycles [4-6], our work employs a cost-effective spin coating technique. This approach demonstrates improved performance, achieving 150 and 250 stable switching cycles with lower V_{Set} and V_{Reset} voltages. The RRAM device exhibits stable performance over multiple cycles, indicating reliable switching behavior and good endurance.

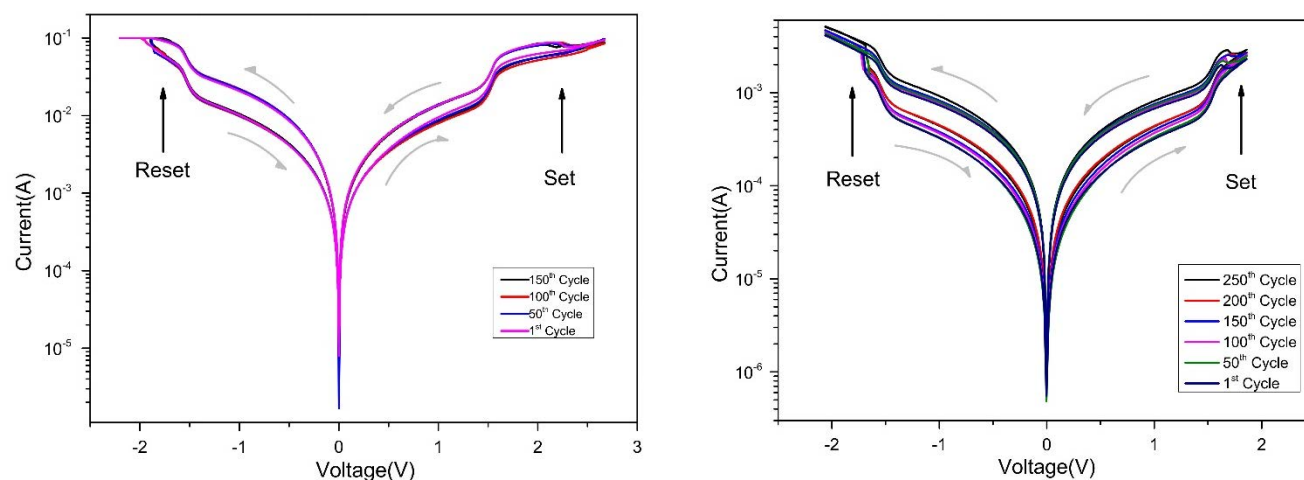


FIGURE 2. Current-voltage (I–V) characteristics in semilogarithmic scale for RRAM devices with 150 and 250 stable bipolar switching cycle.

CONCLUSION

In this work, we fabricated ZrO_2 thin film using spin coating method on Si-p++ substrate and annealed at 400 °C, exhibiting enhanced resistive switching behavior. Electrical characterization demonstrated stable switching up to 150 and 250 cycles, with HRS and LRS ratio of ~ 2.26 and ~ 2.11 respectively, confirming the suitability of the optimized ZrO_2 based structure for non-volatile memory applications.

ACKNOWLEDGEMENT

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SCA For Searching Suitable Cutting-Edge Optoelectronic Applications in Se-Sb-Ag ACMs on Account Of LID

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Abstract. A well-known Space charge analysis (SCA) is employed for the analysis of defect density for different illumination time, and quantitatively found Light induced defects (LID) on the thin films ($\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$) of Amorphous Chalcogenide Materials (ACMs) for different atomic proportions (x), which varies from 0 to 8. The outcomes show that density of defect states (DOS) raises with illumination time. The fractional increase has, however, been found to depend on the concentration of Ag in Se-Sb-Ag system. An appropriate explanation is given for LID creation in these novel ACMs and also discussed suitability for cutting-edge optoelectronic applications.

INTRODUCTION

Space Charge analysis refers to the trapped charges within the materials or at interfaces, influencing device performance. Space Charge Limited Conduction (SCLC) in Amorphous Chalcogenide Materials (ACMs) is a super interesting and active area, especially in the context of non-volatile memories, neuromorphic computing photonics, thermoelectric and phase change devices and these materials can be utilized to fabricate technologically important devices like IR detectors, optical recordings, IR lenses, optical fibers, solar cells, optical switches, and electronic switches [1-3]. The ACMs found to be suitable candidates for high field conduction studies due to low conductivity and negligible small joule heating. Last few decades various research groups motivated towards the electrical properties of ACMs and interpreted their experimental results by heating effects, Poole-Frankel effect, and Space Charge Limited Conduction (SCLC). For optoelectronic applications there is requirement of materials of less DOS because these defects can capture charge carriers' electrons & holes, causing non-radiative recombination. It has been researched that for quantitative estimation of DOS, SCA is one of most important analysis due to inadequate knowledge of electronic structures of ACMs and have more experimental freedom. The study of addition of third impurity in Se-Sb binary system is very interesting in research point of view. Ag doped ACMs have numerous potential applications [4] in optoelectronic, basic science point of views, cell-based device applications, optical components, optical memories, microlenses, waveguides, electrochemical and natural sensors, solid electrolytes, and batteries etc. As of late it has been observed that assortment of photoinduced phenomena happens in ACMs [5]. Numerous past studies have demonstrated that Ag-based ACMs indicate most prominent applications in optoelectronic and assortment of photo induced impacts are seen in these technological important materials [6]. To quantify DOS in ACMs, several techniques have been pre-owned which have completely precedence and their respective confinements. Due to difficulties in forming a p-n junction, spectroscopic techniques couldn't be used to estimate the density of states (DOS) in ACMs. The SCLC technique [7] has commonly been employed for quantitative experimental estimation of the density of states (DOS) in ACMs. In perspective of above mentioned, this study announces the quantitative assessment of light-induced defects (LID) in thin films of ACMs $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ ($x=0,2,4,6,8$) by using SCLC analysis and their correlation with device applications. Thus, for this, white light of intensity 1500 lux exposed to the above-mentioned thin films of ACMs from 0 to 6 hours. The DOS increment with exposure time demonstrates that additional DOS are made as increment of light illumination time.

EXPERIMENTAL METHODS

The whole process of $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ ($x = 0, 2, 4, 6, 8$) ACMs thin film preparation is given by process flow: weighing, sealing, quenching, crushing and vacuum evaporation thin film preparation technique [3-7]. The amorphous character of prepared ACMs is affirmed by the absence of diffraction peak in XRD. For the measurements of SCA the thin films of ACMs of $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ ($x = 0, 2, 4, 6, 8$) are arranged in a uniquely composed high temperature metallic sample holder containing vacuum of 10^{-3} Torr. First annealing for one hour then I-V characteristics under d. c. voltage (0-440V) at various fixed temperatures (300K - 450K) have been done for all thin films of ACMs. For exposure of white light, sample holder containing transparent window is used. For avoiding thermal impacts of light source, proper care is already taken.

RESULTS AND RELATED DISCUSSIONS

I-V properties are investigated with respect to temperatures in ACMs thin films of $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ ($x = 0, 2, 4, 6, 8$) prior and after prolonged illumination of white light. An Ohmic and super-ohmic conduction phenomenon is seen at electric fields below 10^3 V/cm and approximately 10^4 V/cm, respectively. $\ln(I/V)$ versus V curves have been plotted in the high-field conduction region, and observed to be linear both, before and after prolonged illumination with white light. Figure 4 (a-d) illustrates that the slopes (S) of $\ln(I/V)$ versus V curves exhibit temperature-dependent characteristics. At low voltages, the number of infused charge carriers is lower than the number of charge carriers generated thermally, thereby enabling ohmic conduction. At very high voltages, the dominance of the infused charge carrier thickness may lead to conduction being predominantly governed by a trap-limited space-charge-limited current (SCLC) mechanism in this particular region. Lampert et.al. [8] worked the SCA, on account of a uniform distribution of localized states of density g_0 , the current (I) at specific voltage (V) is written by:

$$I = (2 e A \mu n_0 V / d) [\exp (SV)] \quad (1)$$

$$S = 2 \epsilon_r \epsilon_0 / e g_0 k T d^2 \quad (2)$$

In above equations, symbols have their usual meanings [8].

According to Eqs. (1) and (2), the $\ln(I/V)$ versus V curves are straight lines. As temperature increases, the slope S of these curves decreases. It is intelligible that the slope (S) of $\ln I/V$ versus V curves is reversed relative to the temperature for every present sample of ACMs. The particular outcomes show the existence of SCLC in all samples of ACMs. The density of states (DOS) is quantitatively determined from the slope of S vs $1/T$ plots. For the calculations, the relative dielectric constant (ϵ_r) is assumed to be 70 for all the ACM samples. The calculated values of DOS for various illumination times are presented in Tables 1 and shown in Fig. 1'. It is intelligible from the present figures that the DOS (g_0) raises with the rise of time white light illumination. Results shows that an increase in the density of states (DOS) upon light illumination at 300K indicates that these defects can act as traps, thereby affecting the space charge current. According to the recommendations by Shimakawa and colleagues, the LIDs of the current ACMs of Se-Sb-Ag can be chosen as random pairs [9,10]. The fractional increase in DOS caused by light illumination have been evaluated for every white light illumination time in all these thin films of ACMs and also with Ag atomic % (see Fig.1a, 1b and Table1). A differentiation of the present experimental outcomes demonstrates that partial rise in DOS reduces as concentration of Ag rises with the exception at 4 at. % of Ag. This kind of interruption is seen by various researchers in numerous ACMS [11] at a doping of chemical element of specific concentration by which average co- ordination number attains a specific value just for example of 2.4 in Ge-Se ACMs. Model given by Phillips and Thorpe [12], Fabric with an average coordination number below a certain threshold is considered floppy, while fabric with an average coordination number above this threshold is considered mechanically optimized. The study of light-induced defects in the current samples of ACMs presents intriguing opportunities in science and technology, particularly in the search for materials suitable for optoelectronic applications due to the presence of light-induced metastable defects. The reduction in value of partial rise in DOS at larger concentration of silver demonstrates that alloys made with silver doped, might be utilized for materials to design optoelectronic devices application such as photoconductive and photovoltaic. The sensitivity of Se-Sb-Ag ACMs to LID makes them highly suitable for advanced optoelectronic applications. Here for cutting edge optoelectronic good device performance DOS should be less by prolonged exposure of light because more defects introduce more recombination centres causes reduction in carrier life time and non-radiative recombination. The average co-ordination number $\langle z \rangle$ of the present chalcogenide materials has been found by utilizing the conventional methodology of researcher Tanaka [13].

It has been found that $\langle z \rangle$ varies from 2.10 to 2.18 for our glassy system. A maxima for 4 atomic % of silver and calculated value of this composition is 2.14 However model given by Phillips and Thorpe threshold have been found at $\langle z \rangle = 2.4$.

TABLE 1. g_0 in thin films of $\text{Se}_{90}\text{Sb}_2\text{Ag}_8$ ACMs before and after prolonged illumination of white light:

Illumination Time (hrs)	Slope of S vs. $1/T$ curves	g_0 ($\text{eV}^{-1} \text{cm}^{-3}$)	Fractional increase in g_0 on light illumination
0	4.150	1.10	0
2	3.444	1.35	0.23
4	3.053	1.52	0.38
6	2.735	1.70	0.55

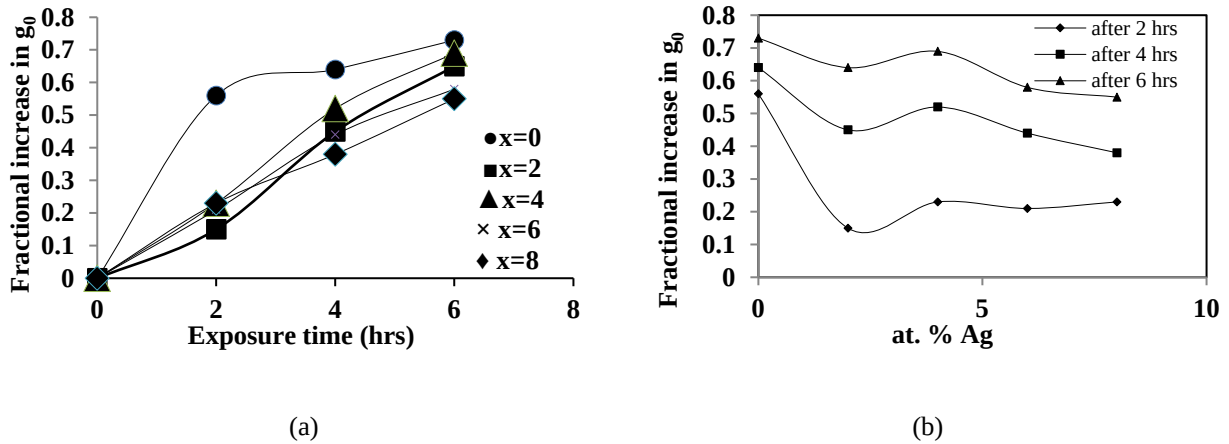


FIGURE 1. (a) Plots of fractional increase in g_0 vs. light exposure time in amorphous thin films of $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ ($x = 0, 2, 4, 6, 8$), (b) Fractional increase in g_0 vs. at. % Ag concentration in thin films of $\text{Se}_{90}\text{Sb}_{10-x}\text{Ag}_x$ ($x=0,2,4,6,8$) ACMs.

CONCLUSIONS

Thus, one hand on the basis of fractional increase in DOS for cutting edge optoelectronic device applications up to light exposure operational 2 hours $\text{Se}_{90}\text{Sb}_8\text{Ag}_2$ ACMs can be processed and on other hand light exposure operational 4 or more hours $\text{Se}_{90}\text{Sb}_2\text{Ag}_8$ ACMs can be processed for better output.

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Pulsed laser deposited electron-rich micro-crystallites of MAX phases on silicon as Schottky junctions

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Abstract. Exploring MAX and MXene materials in bulk and thin film forms has been an area of high interest, especially for miniaturised unconventional device structures, storage applications and as sensors. The synthesis of high-quality MAX phase thin films is inherently challenging due to their complex nano-laminated structure and strict stoichiometric requirements. Among the available deposition techniques, Pulsed Laser Deposition (PLD) stands out as a versatile and effective approach for achieving near-stoichiometric transfer, particularly when combined with appropriate substrate selection. In this work, Ti_3AlC_2 MAX phase thin films were deposited on Si (100) substrates using PLD, with a focus on their structural characteristics and potential device-oriented applications. The films were grown from a MAX phase target using a KrF excimer laser (248 nm, 20 ns pulse duration) under optimised conditions of 700 °C substrate temperature, $\sim 2.5 \text{ J/cm}^2$ laser fluence, 5 Hz repetition rate, and a base pressure of $\sim 1 \times 10^{-4}$ Torr. These parameters enabled the formation of uniform thin films with a thickness of approximately 2000 Å on silicon substrates. Uniform, pin-hole-free smooth films were seen through Electrostatic Force Microscopy (EFM). X-ray diffraction data and Raman spectroscopy data indicated stoichiometric transfer of MAX phase ((101) oriented) on the silicon substrates; however, the films were strained due to lattice mismatch (MAX phase, $a = 0.307 \text{ nm}$ and silicon $a = 0.543 \text{ nm}$). There were no indications of fragmented growth. The films showed good conductivity as compared to their bulk counterparts. I-V characteristics showed excellent Schottky junction behaviour with the pick-up voltage to be 0.2 V. Conductive-Atomic Force Microscopy (C-AFM) reveals the presence of mobile charge carriers at the film surface, confirming the metallic behaviour of the film on a semiconducting substrate. It is envisaged that stoichiometry-maintained micro-crystallites are ablated from the MAX target with laser pulses, terminating at the weakest Al-bonds; thereby generating dangling bond surfaces with a large number of free electrons. The intrinsic strain facilitates this growth, which offers highly conducting film surfaces, yielding semiconductor-metal junctions. This could be explored in silicon-technology-friendly non-conventional device electronics.

INTRODUCTION

MAX phases are a group of layered materials made from a combination of transition metals, Carbon or Nitrogen, and an A-group element like Aluminium. These materials are special because they combine the useful properties of both metals and ceramics. For example, they are strong and heat-resistant like ceramics, but also conduct electricity and are easy to machine like metals. Titanium Aluminium Carbide (Ti_3AlC_2) is one of the most studied MAX phases and has potential for use in electronics, sensors, and high-temperature applications. Growing thin films of MAX phases on silicon can help integrate them into electronic devices, but it is often challenging due to differences in structure and thermal behaviour between the film and the silicon substrate.

Pulsed Laser Deposition (PLD) is a powerful method used to create thin films with high control over their structure and composition. In PLD, a high-energy laser hits a target material, turning it into a vapour that deposits onto a substrate like silicon. This technique is especially useful for making complex materials such as MAX phases. In this study, we use PLD to grow Ti_3AlC_2 films on silicon and analyse how well the film grows, its structure, and how it behaves electrically. Understanding these properties is important for developing future electronic devices that require strong, conductive, and thermally stable thin films [1,2].

EXPERIMENTAL

High-purity Ti_3AlC_2 powder (>99%, 40 μm) was used to prepare the PLD target. One gram of the powder was pre-annealed at 650 $^{\circ}\text{C}$ for 3 hours, then mixed with 2 wt% polyvinyl alcohol (PVA) as a binder. The mixture was pressed into a pellet using a 15-ton hydraulic press and post-annealed at 900 $^{\circ}\text{C}$ for 3 hours under a nitrogen atmosphere, with a ramp rate of 3 $^{\circ}\text{C}/\text{min}$ and slow cooling to reduce brittleness and prevent TiC formation from carbon residues. After deposition, the thin films were annealed at 500 $^{\circ}\text{C}$ for 1 hour with a slow ramp rate to improve the film-substrate interface and enhance structural quality.

RESULTS AND DISCUSSION

Structural Characterisation: The crystallographic features of Ti_3AlC_2 films were probed through X-ray Diffraction using Cu $K\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$) on a Bruker AXS D8 Diffractometer. As shown in FIGURE 11. (a), the XRD pattern confirms the formation of the MAX phase with preferred orientation along the (101) plane. The MAX lattice parameters were found to be $a = 3.07 \text{ \AA}$ and $c = 18.5 \text{ \AA}$, while the Silicon (100) substrate has a face-centred cubic (FCC) diamond structure with a lattice constant of 5.43 $\text{\AA}$. This mismatch leads to a strained MAX structure along the X–Y plane at the film–substrate interface.

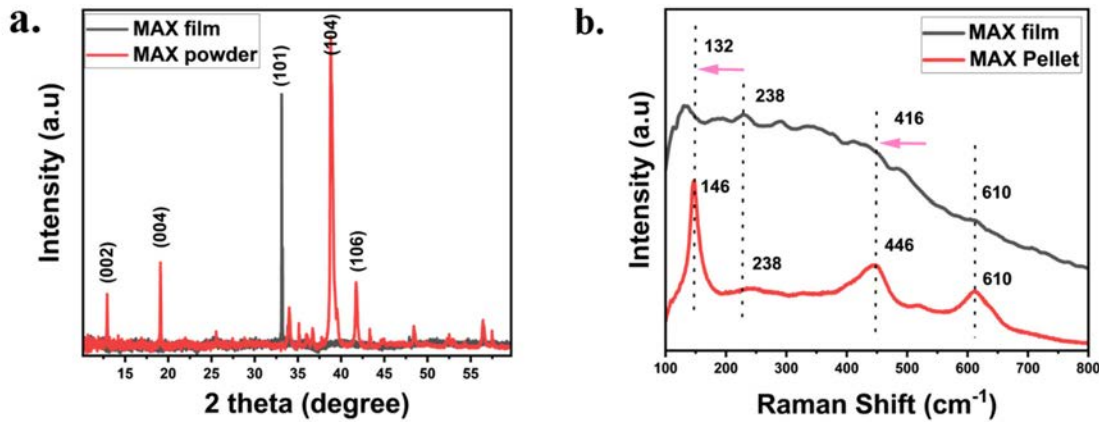


FIGURE 11. (a) XRD data of Ti_3AlC_2 MAX phase powder and PLD-deposited thin film on silicon substrate. (b) shows the Raman spectra confirming the MAX phase in the MAX pellet and on film.

To further verify the chemical composition of the MAX phase, Raman spectroscopy (Horiba Labram HR, Wavelength 532nm) was performed on both the sintered pellet and the deposited film. The Raman spectra, also presented in FIGURE 11. (b), display characteristic peaks corresponding to Ti_3AlC_2 , confirming the chemical composition and phase integrity of the material in both forms [3]. The Ti_3AlC_2 phase displays Raman peaks at 146 (ω_1), 238 (ω_2), 446 (ω_{13}) and 610 (ω_4) cm^{-1} . These correspond to in-plane Al-Ti vibrations ($E_{g(1)}$), Carbon bonds (A_{1g}) and Oxygen bonds (A_{1g}) respectively, with ω_4 attributed to Ti-C vibrations ($E_{g(2)}$). Comparative analysis of PLD film with pristine MAX phase pellet indicates that ω_2 and ω_4 remain invariant signifying the retention of specific vibrational characteristics post-deposition. In contrast, the red shifts observed for ω_1 and ω_3 are indicative of strained effects induced during pulsed laser deposition. This interpretation is consistent with the XRD analysis, supporting the presence of a strained MAX-phase structure.

Electrostatic force microscopy EFM and Conductive-AFM Studies were performed using an Asylum Research MFP-3D-BIO AFM. FIGURE 12.a.(i) shows EFM data, indicating a uniform surface charge distribution with no visible pinholes. FIGURE 12.a.(ii) shows the topography of the film from AFM with RMS roughness $\sim 7 \text{ nm}$. FIGURE 12.a.(iii) reveals a significant increase in current after applying a higher voltage. Similarly, FIGURE 12.a.(iv) demonstrates a strong current response under high negative bias. These non-linear behaviours hinted at further device-like characteristics and hence further investigation through I–V characterization [2] was undertaken.

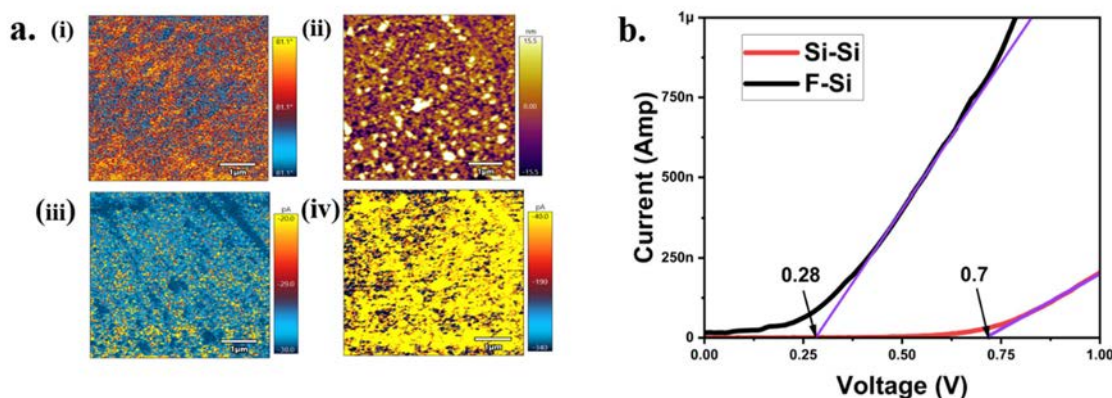


FIGURE 12.a) (i) EFM image showing a uniform surface potential distribution. (ii) depicts the topography of the film. (iii) & (iv) Current maps obtained from C-AFM at applied biases of +5 V, and -5 V, respectively, between the sample surface and the conductive AFM tip. (b) Current-Voltage (I-V) Characteristics of the MAX film.

I-V Characterisation: FIGURE 12. (b) depicts the I-V plot of film–substrate (silver contacts were made on the substrate and film surfaces, and two-probe measurements were performed) and substrate-substrate interfaces. The pick-up potential was seen to be dramatically decreased from 0.7V to 0.27 V for the film, indicating a metal-semiconductor junction, following a Schottky diode. On similar lines of conductive AFM data, the Schottky barrier height was estimated to be approximately 1.12 eV, supporting the observed rectifying behaviour. This confirms the potential of the MAX thin film for electronic and diode-based device applications. It is envisaged that the pulsed laser deposition ablates micro-crystallites of MAX phases, which terminate at the weakest linkages of Al-Al bonds, creating a uniform layer of MAX on the silicon surfaces. Since the lattice matching of MAX matches fairly well with Si (100), the phase and stoichiometry are maintained; however, the films are strained. These films, therefore, have a large number of free electrons on the surface, which is also due to multiple dangling bonds created during micro-crystallite formations. When potential is applied, these electron-rich surfaces exhibit metallic behaviour and a Si-MAX junction, hence showing Schottky characteristics. The same is also seen through C-AFM studies, wherein there is a huge change in conductivity when substantial voltages are applied between the tip and the surface as compared to lower applied bias. If the film is applied with positive voltage, the conductivity is higher, whereas for negative voltage, the conductivity is highest. Non-linear characteristics can be studied further for better understanding, which can be further fine-tuned with deposition parameters; this work is underway.

CONCLUSION

Ti₃AlC₂ MAX thin films on silicon showed semiconducting behaviour with Schottky junction characteristics and enhanced current response after voltage treatment. The observed diode-like I–V behaviour and uniform surface conduction suggest suitability for applications in IR detectors, high-frequency electronics, and sensor devices. This work demonstrates the potential of MAX films as active components in next-generation electronic interfaces.

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Microstructural and Mechanical Properties of Nickel Nitride Coated NAB Prepared by Magnetron Sputtering

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Abstract. Nickel nitride thin films, i.e., Ni₃N, were deposited on nickel-aluminum bronze substrates by utilizing a DC magnetron sputtering technique. This was done to improve the mechanical properties. The results were verified by XRD, which confirmed the presence of nickel nitride films. FE-SEM images revealed a dense, uniform, and defect-free surface morphology of the films. EDX and XPS results verified the composition of the films. Also, optimal conditions were used to achieve good adhesion of the films to the substrate. Nanoindentation results revealed a hardness of ~9.01 GPa, which was much higher compared to bare nickel-aluminum bronze. This proves the excellent mechanical properties of nickel nitride films. Thus, it can be concluded that nickel nitride films deposited by a sputtering technique can be a good solution to increase the lifespan of nickel-aluminum bronze materials in harsh environmental conditions.

INTRODUCTION

Nickel-aluminum bronze (NAB) alloys are extensively used in marine, aerospace, and heavy engineering applications due to their exceptional corrosion resistance and mechanical strength. However, under severe wear conditions, the surface hardness of NAB may be insufficient to prevent degradation. [1] Surface modification through hard nitride coating has emerged as a reliable approach to enhance the mechanical performance of copper-based alloys. Nickel nitride (Ni₃N) is a popular coating material owing to its high hardness, excellent wear resistance, and chemical stability. The use of DC magnetron sputtering allows precise control over film thickness, uniformity, and adhesion. Although nickel-based coatings have been extensively studied, the deposition of Ni₃N films on NAB substrates remains relatively unexplored in certain areas of application. [1, 2]

The objective of this study is to obtain the Ni₃N thin film coatings on NAB alloy by utilizing DC magnetron sputtering technique, characterize their microstructure and chemical composition through sophisticated surface analysis methods and determine the enhancement in hardness by employing nanoindentation test.

EXPERIMENTAL SECTION

NAB alloy samples (1 cm × 1 cm × 0.8 cm) were mechanically polished to a mirror finish using successive grades of SiC papers and alumina suspensions. The samples were ultrasonically cleaned in acetone for 15 minutes each, followed by drying in nitrogen gas, which ensures that even the smallest dirt particles are removed from the surface of the substrate.

Ni₃N thin films were deposited using DC reactive magnetron sputtering with a high-purity nickel target (99.99%). The sputtering chamber was evacuated to a base pressure of 2.0×10^{-6} Torr using a turbomolecular and rotary pump. Argon (20 sccm) and nitrogen (4 sccm) were introduced as the working gases, with total working pressure maintained at 5 mTorr. Deposition was carried out at 50 W DC power for 10 minutes at 350 °C, ensuring uniform film growth. The crystallographic structure was determined using XRD (Cu K α radiation, $\lambda = 1.5406$ Å). Surface morphology was analysed via FE-SEM, and elemental composition was examined using EDX attached to the SEM. XPS measurements were executed to identify the chemical states of nickel and nitrogen. Hardness measurements were conducted using a nanoindenter with a Berkovich diamond tip, applying a maximum load sufficient to avoid substrate effects.

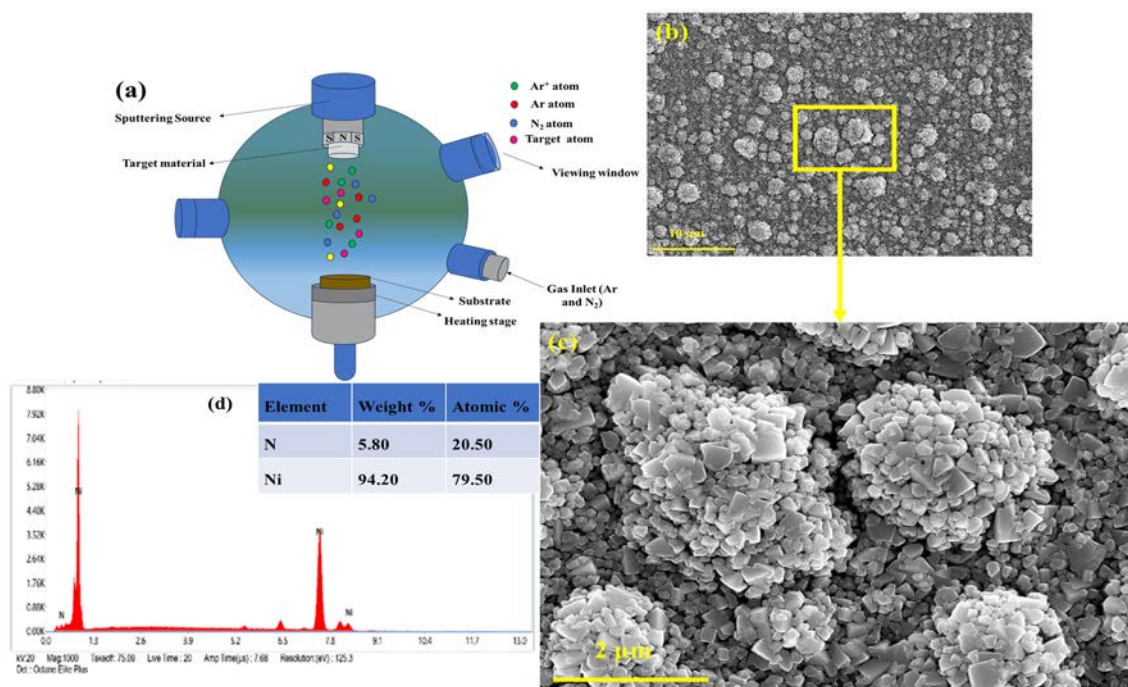


FIGURE 1. (a) Schematic diagram of the magnetron sputtering chamber used for sputtering, (b) FE-SEM image of Ni_3N coating on NAB substrate, (c) FE-SEM images showing the nano cauliflowers of Ni_3N coatings, and (d) EDX plot and the table for atomic and weight percentage of the Ni_3N coated sample.

RESULTS AND DISCUSSION

The diffraction patterns of the bare NAB and the Ni_3N coated NAB samples are depicted in Fig. 2(a). The bare NAB sample displays clear peaks attributable to the α -Cu phase as well as secondary intermetallic found in the NAB alloys. After depositing Ni_3N on the NAB sample, additional peaks attributed to the planes of hexagonal Ni_3N (JCPDS No. 10-0280) with indices of (002), (110), (111), and (112) can be observed. Absence of peaks attributable to oxides confirms that the nitride film was deposited without oxidation. [3]

FE-SEM photographs revealed Fig. 1(b-d) that there was no cracking or delamination in the fine-grained and dense structure of the film. The evenly distributed grains suggested the control of grain growth during optimized sputtering. The even distribution of the nickel and nitrogen elements was proved by the EDX map. [4-5]

The XPS survey spectrum (Fig. 2(d)) confirms the presence of Ni, N, C, and O on the coated surface. Oxygen and carbon signals arise from minor surface contamination due to atmospheric exposure. [5-6]

The high-resolution N 1s spectrum (Fig. 2(c)) shows a dominant peak at ~ 397.5 eV, corresponding to nitrogen bonded with nickel in Ni-N, and a smaller peak at ~ 399.6 eV attributed to oxidised nitrogen species. The high-resolution Ni 2p spectrum (Fig. 2(b)) reveals two main spin-orbit doublets. The Ni 2p_{3/2} peak at ~ 852.6 eV and Ni 2p_{1/2} peak at ~ 869.9 eV correspond to metallic Ni^0 states, while peaks at ~ 855.8 eV (Ni 2p_{3/2}) and ~ 873.6 eV (Ni 2p_{1/2}) indicate Ni^{2+} species. A well-defined satellite peak further supports the mixed oxidation state. The dominance of Ni-N related peaks in both N 1s and Ni 2p spectra confirms the successful formation of Ni_3N with minimal oxidation. [7-8].

TABLE 1. Nanoindentation Results for the Deposited Coating.

Coating	Hardness (GPa)	Elasticity (GPa)	Young's modulus (GPa)	Maximum Depth h_{max} (nm)	H^3/E^2 (GPa)
Ni_3N	~ 9.01	161.07	~ 170.5	101.17	0.028

The nanoindentation results demonstrated a significant improvement in hardness for the Ni_3N -coated NAB substrate, with a hardness of ~ 9.01 GPa, as shown in a Fig. 2(e) compared to the typical 2-5 GPa of uncoated NAB,

as shown in the Table 1. [9-10] This enhancement is attributed to the inherent hardness of Ni_3N and the strong coating-substrate adhesion provided by magnetron sputtering. [11-12]

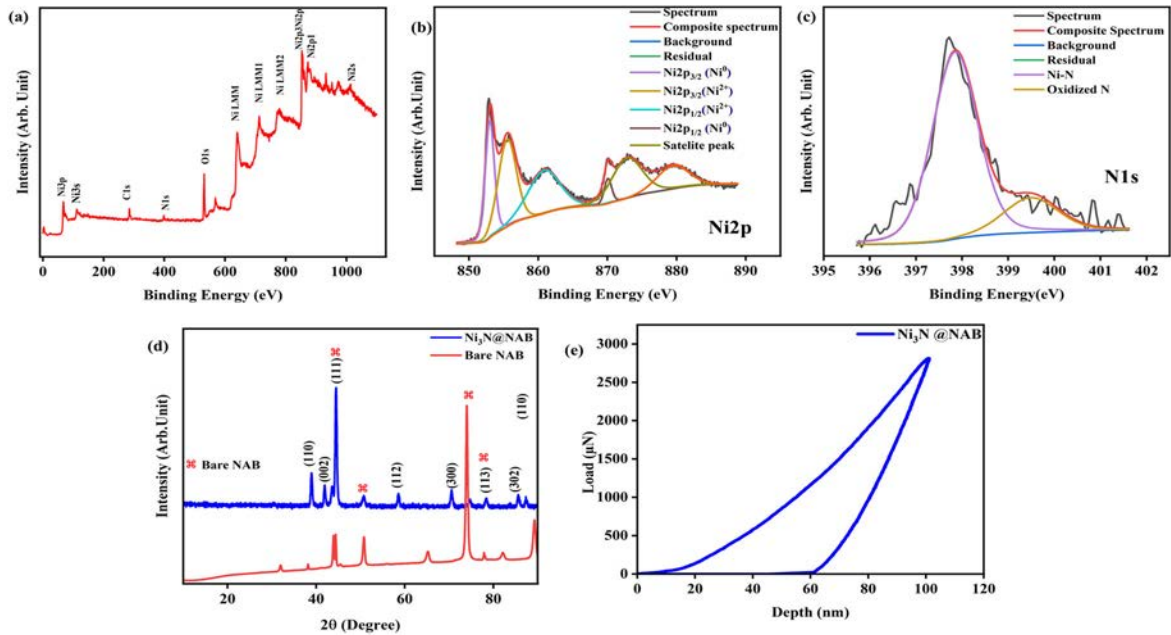


FIGURE 2. XPS (a) survey spectra, (b) Ni 2p (3/2 and 1/2) spectra and (c) N1 spectra, (d) XRD patterns of bare NAB and $\text{Ni}_3\text{N}@$ NAB coating, and (e) Nanoindentation curve of Ni_3N coated NAB substrate.

CONCLUSION

Ni_3N coatings have been successfully deposited onto the NAB alloy substrate using the DC magnetron sputtering technique. The characterisation tests have shown that stoichiometric, crystalline, and dense coatings are formed. The coatings have shown good adhesion and improved hardness, reaching ~ 9.01 GPa. Thus, it is believed that the sputtering method for depositing the Ni_3N coatings is effective in improving the wear resistance of the NAB alloy, allowing for its usage in marine and industrial environments.

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Structural and Electronic Properties of Nb₃Li

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Abstract. Using the *ab-initio* FP-LAPW technique, the structural and electronic characteristics of Nb₃Li are investigated. The value of vacancy migration enthalpy indicates strong interatomic bonds in the crystal. The electronic band structure reveals that similar to other A15 compounds, Niobium *d*-states contribute largely in the partial density of states. Similar to the other A15 compounds studied, the Dirac points are noted at M and R points. In addition, such symmetry driven features is also noted at the X point. It turns out to be a topological phase.

INTRODUCTION

The discovery of superconductivity in V₃Si with $T_c \sim 17$ K by Hardy and Hulm [1] has attracted considerable attention in the family of compounds with A15 structure because of their appealing physical characteristics. In addition to superconductivity, these intermetallics find several uses in the chemical, aerospace, biomedical, and hydrogen storage industries [2].

Niobium constitutes a number of superconductors with a wide range of T_c [3-10]. A number of Nb₃X compounds are studied by several authors where X belongs to the *p*-block elements. Tuleushev et al. [3] synthesized the A15 type Nb₃Be using thermal treatment of the amorphous film system and found the T_c 10 K. Later the electronic properties are studied by several authors [2,4]. Since lithium belongs to the same group, following the analogy, it is suggested that Nb₃Li may also possess A15 structure.

In this study, we apply the full potential linearised augmented plane wave (FP-LAPW) method to see stability of the Nb₃Li in the A15 structure. The *ab-initio* calculations are applied to determine the lattice constant and bulk modulus. Diffusion is one of the important property, recognized quite later in A15 compounds. Thus diffusion coefficient affects the vacancy migration enthalpy H^M . Hence the vacancy migration enthalpy of Nb₃Li is also evaluated. After achieving the ground state, the electronic properties such as electronic band structure and density of states (DOS) are calculated.

COMPUTATIONAL DETAILS

The crystal structure of Nb₃Li belongs to the space group $Pm\bar{3}n$ (SG#223). The calculations are carried out using the FP-LAPW method [11]. The PBE exchange–correlation function formulated under the generalized gradient approximation is considered [12]. The plane wave cut-off parameter rgk_{max} was set to 8.5 and the Brillouin zone sampling was carried out using the 24×24×24 size of Monkhorst-Pack mesh [13]. The Broyden mixing [14] was applied to compute the equilibrium lattice parameter.

RESULTS AND DISCUSSION

Structural Parameters and Vacancy Migration Enthalpy

The equilibrium lattice constant and bulk modulus are obtained by fitting the Murnaghan equation of state to the computed data set of total energies. We find the lattice constant $a = 5.15$ Å and bulk modulus $B_0 = 126.67$ GPa. Vacancy migration enthalpy H^M is the energy barrier that must be overcome for a vacancy to move within the crystal. Low vacancy migration enthalpy implies less energy is needed for a vacancy to move in the crystal while high value signifies more energy required to move the vacancy within the crystal. Angesten and co-workers [15] suggested that the vacancy migration enthalpy H^M for a cubic system is given by the following relation:

$$H^M = 0.016 B_0 a^3$$

where B_0 is the bulk modulus and a is the lattice constant. This gives H^M to be 17.28 eV. The low value of H^M implies faster diffusion, increased atomic mobility and enhanced recovery of the material. The materials with low H^M can be used in solid state electrolytes due to fast ion transport. Stronger interatomic bonds lead to higher H^M values. Essentially, the material is more resistant to atomic diffusion through vacancy movement. It can lead to slower diffusion rates of atoms within the material, as the movement of vacancies is a key mechanism for atomic transport. Materials with high H^M might be more resistant to certain types of damage or degradation, as the movement of defects is hindered. This point out no possibility of usage of Nb_3Li in hydrogen storage and in electrolytes but the materials with high H^M find applications in areas where structural stability and resistance to atomic movement are crucial, such as in high-temperature alloys, nuclear materials, and certain types of catalysts.

Electronic Properties

The electronic band structure of Nb_3Li is shown in Fig. 1. The shell wise contributions from Nb and Li atoms in the partial DOS is shown in Fig. 2. For the sake of discussion, the band structure can be divided in four regions, i.e. from -6 eV to -4 eV, -4 eV to -2 eV, -2 eV to E_F and up to 2 eV above E_F . The A15 compounds are found to show Dirac cone on weyl metal characteristics. Such features are noted in similar A15 compounds at M and R points of the band structure [16]. In Nb_3Li also accumulation of bands at and near E_F at the M and R points signify such features. Unlike other A15 compound the X symmetry point is also a Dirac point in Nb_3Li to recognize the three points as symmetry protected Dirac points more work is under progress.

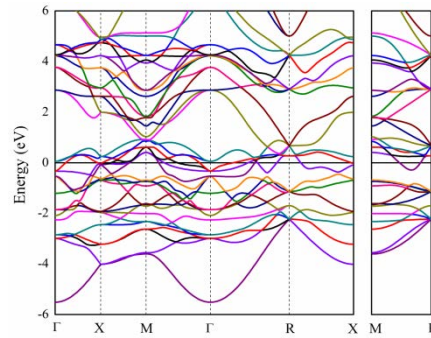


FIGURE 1. The band structure of Nb_3Li .

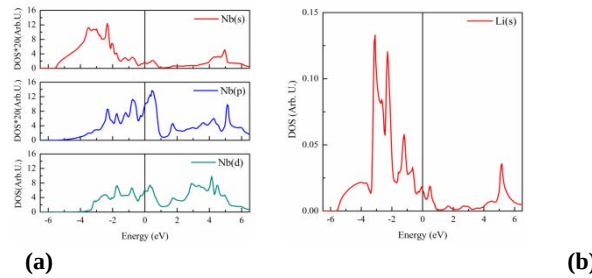


FIGURE 2. Partial DOS of (a) s, p and d state of Niobium and (b) s state of Lithium atoms in Nb_3Li . To improve visibility the scale of DOS in case of Nb(s) and Nb(p) is multiplied by 20.

In -6 eV to -4 eV region, the bands are parabolic in nature hence resulting no peak in the DOS. In -4 eV to -2 eV region, the bands are albeit flat resulting into peaks in the DOS. In the formation of bands in this region the major contribution comes from Nb (p,d) states and partial contribution from Nb (s) and Li(s) states. In -2 eV to E_F region, the bands dispersion results high value of DOS. These bands arise mainly due to the Nb(d) states. The bands above 2 eV constitute the DOS with some peaks dominated by Nb(d) and Nb(p) states. Similar to other Nb_3X compounds, the d-states of transition metal shows major contribution in the DOS [3-10]. Overall the band structure indicates metallic nature of the compound. It is known that the DOS in the neighborhood of E_F , $N(E_F)$ signify salient features of the

electronic, optical, transport and magnetic properties of crystals. The $N(E_F)$ for Nb_3Li is found to be $288.31 \frac{\text{States}}{\text{Hartree.Unitcell}}$. In metallic systems, $N(E_F)$ can be used to find the contribution of the electronic part of the specific heat. The factor $\gamma_{elec.}$ quantifying the linear dependence of the electronic contribution is evaluated using $\gamma_{elec.} = \frac{\pi^2 K_B^2 N(E_F)}{3} \frac{\text{Joule}}{\text{mole.K}^2}$ [17]. The calculated value of $\gamma_{elec.}$ for Nb_3Li is $24.9 \frac{\text{m.Joule}}{\text{mole.K}^2}$. This value is comparable and well within the 2 to $24 \frac{\text{m.Joule}}{\text{mole.K}^2}$ range reported for other A15 compounds [18].

CONCLUSIONS

After achieving the ground state, the lattice constant and bulk modulus of Nb_3Li are reported. The value of H^M indicates stronger interatomic bonds suggests possible usages in high-temperature alloys. Signatures of Dirac cones are clearly visible in the band structure very similar to the other A15 compounds. Distinctively, however, in addition to M and R, X is also found to be Dirac point. The study clearly points that Nb_3Li shows the topological phase. In the DOS, the peaks are originated mainly from Nb(d) states with partial contribution from Nb(s,p) and Li(s) states. The value of specific heat constant is comparable and well within the range reported for other A15 compounds.

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THERMAL PROPERTIES OF V₃BE

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Abstract. Using the *ab-initio* FP-LAPW method, the thermal characteristics of V₃Be are investigated. The internal energy, Helmholtz free energy, entropy, specific heat at constant volume and pressure, Grüneisen parameter, thermal expansion coefficient and Debye temperature of V₃Be are determined by linking the *ab-initio* total energy calculations with the second-generation code Gibbs2. The calculations are performed using the Debye Slater and Debye Grüneisen models.

INTRODUCTION

Intermetallics are distinctive materials characterised by elevated melting point, substantial strength, ordered structure, and brittleness at ambient temperature. These are well-known for the technological uses in plasmonics, water splitting, catalysis, thermal spray coating, and hydrogen storage [1].

The low density metal, beryllium, has the ability to form a variety of numerous compounds with different stoichiometries and forms intermetallic compounds with a number of different metals [2]. XBe_n (n=1,2,3,5,12,13,22) and the X₂Be₁₇ are the known binary beryllides. The metallic element X from groups VB and VIB is typically used to create the XBe₂, XBe₃, and XBe₁₂ beryllides. It appears that very few intermetallics of a transition metal and a low density metal, like beryllium, are investigated. For example, the initial synthesis of Nb₃Be involved thermal treating amorphous film coatings [3]. It's interesting to note that the valence electron states and chemical behavior of the elemental transition metals vanadium and niobium are known to be similar [4-6].

In this study, we apply the full potential linearised augmented plane wave (FP-LAPW) method to model and determine the lattice constant, bulk modulus, and vacancy migration enthalpy of V₃Be. To study the thermal properties, the calculations are combined with Gibbs2, a second-generation package that uses the Debye Slater (DS) and Debye Grüneisen (DG) models. We discuss the thermal characteristics of V₃Be, including its Debye temperature (Θ_D), Grüneisen parameter (γ_{th}), specific heat at constant volume (C_V), and thermal expansion coefficient (α) [7-9].

COMPUTATIONAL DETAILS

The details of the total energy calculations are described in the extensive study of electronic properties of Nb₃Be and V₃Be carried out by us [10]. The thermal characteristics namely Debye temperature, heat capacity at constant volume and pressure, Grüneisen parameter, thermal expansion coefficient, internal energy (U), Helmholtz free energy (F) and entropy (S) of V₃Be have been determined in the temperature range 0 to 2000K using the DS and DG models using Gibbs2 [11]. The DS and DG models are the correct approaches to know the broad features of the thermal behavior of solids. The mathematical formulations of these models can be found elsewhere [12].

RESULTS AND DISCUSSION

THERMAL PROPERTIES

The equilibrium lattice constant and bulk modulus are obtained by fitting the Murnaghan equation of state to the computed data of the total energies. The obtained lattice constant $a = 4.61\text{\AA}$ and bulk modulus $B_0 = 169.88\text{ GPa}$. These results are accurately replicated using Gibbs2 also. The prescription of Fine et al [13] gives the melting point of V₃Be=1600K. The variation of specific heat at constant volume (C_V) in the temperature range 0-1500K, following the DS and DG models is shown in Fig. 1(a). The $C_V(T)$ shows rapid increase up to 750 K. Thereafter, the heat capacity becomes constant. Both the DS and DG models give identical variation.

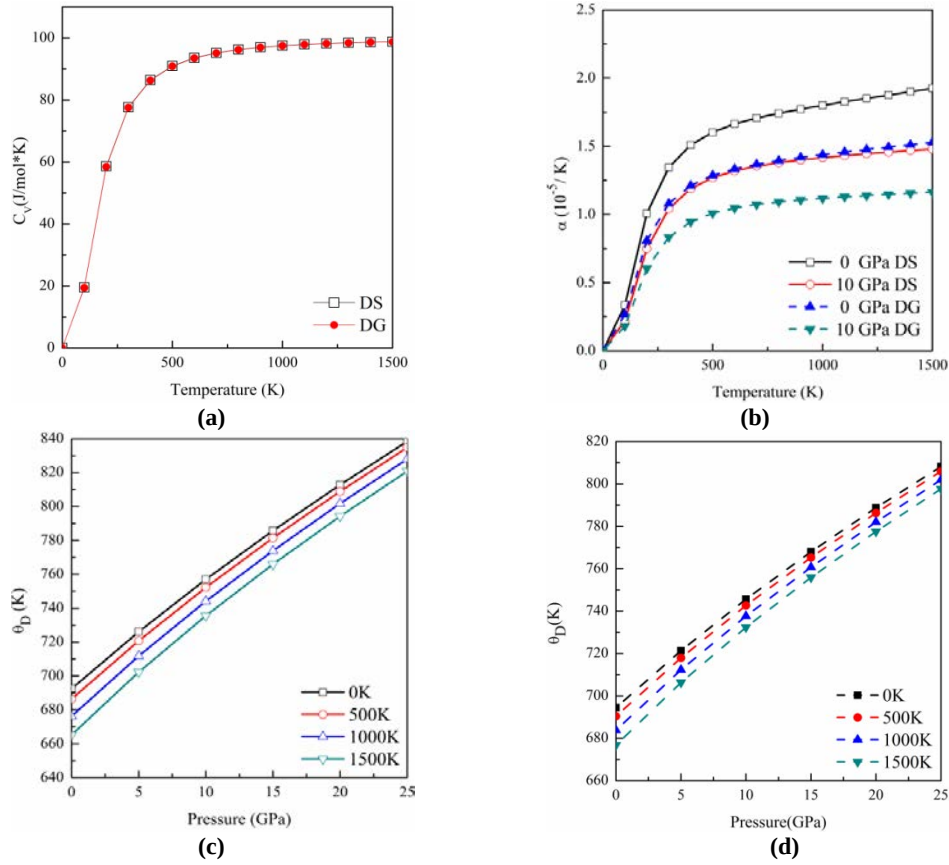


FIGURE 1. (a) Variation of C_v with temperature using the DS and DG models. (b) Thermal expansion coefficient α using DS and DG models (c) Debye Temperature Θ_D (K) with pressure using the DS) model and (d) using the DG model.

The temperature and pressure dependence of the thermal expansion coefficient (α) is plotted in Fig. 1(b). It is obvious that there is a negligible difference between the values calculated by the DS and DG models. In both models, α increases up to $T = 500$ K and thereafter it becomes nearly constant. At 500 K the value of α is $1.6 \times 10^{-5}/K$. This is comparable to the most of the A15 metals [14].

The Debye temperature Θ_D is related to the vibration properties and it correlates the elastic properties with the thermodynamic properties such as phonons, thermal expansion, thermal conductivity and specific heat. The variation of the Θ_D (K) as a function of pressure and temperature using the DS and DG models is presented in Figs 1(c,d). The pressure dependence is not perfectly linear. This behavior remains the same over the temperature range of 0-2000K. Beyond $P = 10$ GPa, the DG model shows less variation of the Θ_D on temperature in comparison to the DS model. This is a consequence of the lower value of α ($10^{-5}/K$).

The dependence of Grüneisen parameter on temperature and pressure is shown in Fig. 2. It reveals that both the DS and DG models exhibit negligible dependence on temperature. Despite changes in pressure, this trend prevails. The DS model gives a slightly higher value for the γ_{th} . In both curves, there is a slight increase in γ_{th} with temperature. A low value of γ_{th} can be seen with increasing pressure.

A few thermodynamic functions like internal energy (U), Helmholtz free energy (F) and entropy (S) are also determined using these two models. In Table 1, the values of these functions are given at certain values of pressure. We notice some difference in the values of S and F from the DS and DG models beyond 5 GPa. This can be attributed to the quasi harmonicity not considered by the DG model, which becomes prominent at higher pressure.

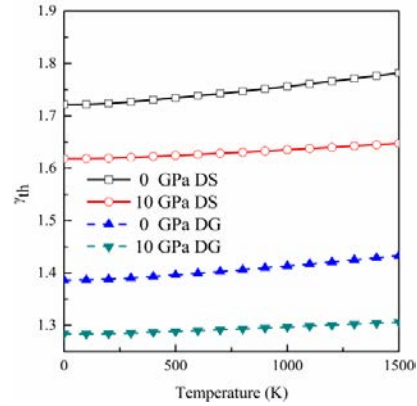


FIGURE 2. Grüneisen parameter γ_{th} using DS and DG model.

TABLE 1. The calculated U ($J/mol \cdot K$), F ($J/mol \cdot K$), and S ($J/mol \cdot K$), for V_3Be in the pressure (P) range 0-25 GPa using DS and DG models.

P	DS			DG		
	U	F	S	U	F	S
0	37.39	18.41	62.00	37.45	18.94	61.68
5	38.10	20.60	58.31	38.01	20.39	58.73
15	39.41	23.69	52.39	39.03	22.83	54.00
25	40.63	26.31	47.74	39.94	24.85	50.29

CONCLUSIONS

For the first time, after achieving the ground state of V_3Be the lattice constant and bulk modulus of V_3Be are reported. A number of thermal characteristics are determined using the DS and DG models. The temperature dependence of C_V , α and γ_{th} follow the general trend of metals. The obtained value of α is $1.6 \times 10^{-5}/K$ which is close to the value of α for another A15 compound V_3Si and having the same order as that of other similar compounds.

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First-Principles Investigations of Structural And Electronic Properties Of Lead-Free Double-Perovskite Halide $\text{Cs}_2\text{AgBiBr}_6$ Using WIEN2K

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Abstract. In recent years, double perovskite materials have been considered potential candidates for different applications. Therefore, in this study, we investigated the structural and electronic properties of $\text{Cs}_2\text{AgBiBr}_6$ – a lead free double perovskite halide based on first-principles calculations using the WIEN2K computational package within the framework of DFT. The material was structurally optimized and the lattice constant was determined. The electronic band gap and DOS reveal that $\text{Cs}_2\text{AgBiBr}_6$ is an indirect band gap semiconductor. Our analysis demonstrates that $\text{Cs}_2\text{AgBiBr}_6$ is a suitable material for photovoltaic and optoelectronics applications.

INTRODUCTION

Metal halide perovskites have rapidly advanced the field of optoelectronics due to their excellent light absorption and charge transport properties. In general, hybrid perovskite materials ($\text{CH}_3\text{NH}_3\text{PbX}_3$; $\text{X} = \text{I}, \text{Br}, \text{Cl}$) have shown exceptional efficiency in solar cells and other devices [1], because of their outstanding electrical and optical properties. Despite their success, the presence of lead and their susceptibility to environmental hazards remain critical drawbacks. In present scenario, perovskite increasing the global demands for clean and stable energy alternative. To overcome these drawbacks, attention has shifted toward lead-free systems. Double perovskites, described by the general composition $\text{A}_2\text{BB}'\text{X}_6$, offer a structurally stable and less toxic alternative. In these materials, cesium typically occupies the A site, while B and B' correspond to mono- and trivalent cations. Among the proposed candidates, $\text{Cs}_2\text{AgBiBr}_6$ has emerged as a promising system due to its chemical stability and reduced toxicity. Its potential use spans photovoltaic devices as well as photo-detection systems [2].

COMPUTATIONAL METHODOLOGY

Investigations was carried out by using Density functional theory within the full-potential linearised augmented plane wave approach, which is excellently mentioned in WIEN2K computational package [3,4]. Investigated ground state structural and electronic properties of the double perovskite halide $\text{Cs}_2\text{AgBiBr}_6$. The generalized gradient approximation in the PBE formulation counted Exchange-correlation effects. Structural optimization calculations were performed to locate the minimum energy configuration. A plane-wave cutoff corresponding to $\text{RMT} \times K_{\text{max}} = 7$ and an energy threshold of -6.0 Ry were selected. The Brillouin zone was sampled using a $5 \times 5 \times 5$ k-point grid to ensure convergence of the self-consistent calculations.

RESULT AND DISCUSSION

Structural properties

$\text{Cs}_2\text{AgBiBr}_6$ is a double-perovskite halide, it is reported that based on X-ray diffraction measurements $\text{Cs}_2\text{AgBiBr}_6$ has a cubic structure with lattice parameter $11.2711 \text{ \AA}$ Which is belonging to $\text{Fm}\bar{3}\text{m}$ (No. 225) space group [5]. Space group defined the specific sets of equivalent points within unit cell. The atomic arrangement places Cs, Ag, Bi, and

Br at well-defined fractional coordinates within the unit cell. The optimized structure of $\text{Cs}_2\text{AgBiBr}_6$ is shown in Fig.1 below. Computed the optimized value of lattice constant is 11.06 Å which is highly matches with experimental results. The structure consists of corner-sharing octahedra, contains cesium, bismuth and silver in ratio 2:1:1 and six bromine where bismuth atoms are surrounded by six bromine atoms, forming a stable framework characteristic of double perovskites.

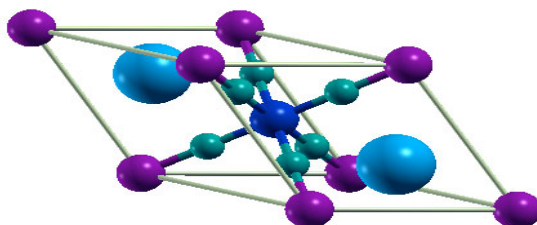


FIGURE 13. The primitive cell of $\text{Cs}_2\text{AgBiBr}_6$. The Cs, Ag, Bi, and Br are represented by light blue, purple, dark blue and green balls respectively.

Electronic properties

After analysing the structural stability of $\text{Cs}_2\text{AgBiBr}_6$, understand the nature of band gap by computing electronic band structure. Analysed electronic band structure for $\text{Cs}_2\text{AgBiBr}_6$ using GGA–PBE exchange-correlation potential without SOC is shown by figure 2(a). Mentioned band structure show that highest occupied and lowest unoccupied states occur at different k-points which confirming an indirect band gap of approximately 1.1 eV. By Analysis the density of states is shown by figure 2(b) provides further insight. Density of states reveals that bromine p-states and silver d-states largely influenced the valance band, whereas bismuth orbitals have largely contributions to the conduction band. In DOS spectrum the interaction among these orbitals leads to noticeable features which are reflected by the compound's electronic configuration.

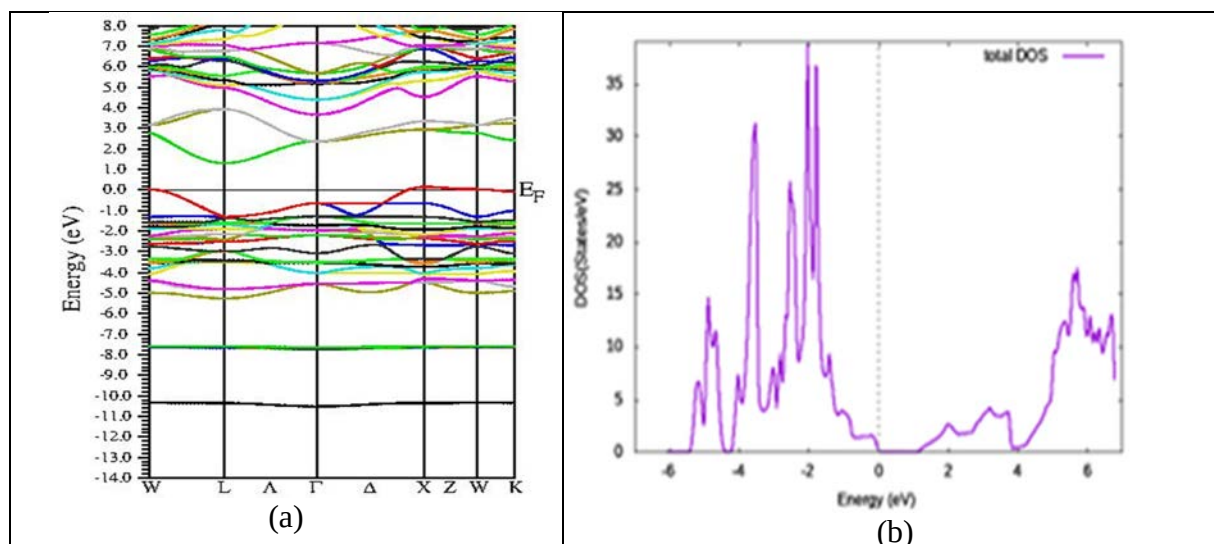


FIGURE 2. (a) The energy band structure of $\text{Cs}_2\text{AgBiBr}_6$, (b) Total density of states using GGA-PBE Calculation.

CONCLUSION

By using first-principles methods, a detailed theoretical investigation of $\text{Cs}_2\text{AgBiBr}_6$ has been performed. With the help of computational approach, the optimized structural parameters agree well with available experimental data. Electronic structure calculations reveal that the material exhibits an indirect band gap semiconductor. Owing to its lead-free character and excellent electronic properties, $\text{Cs}_2\text{AgBiBr}_6$ stands out as a promising material for future optoelectronic and photovoltaic applications.

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Development and Experimental Validation of a FLUKA-Based Monte Carlo Model for a Portable HPGe Detector

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Abstract. This study presents the development and experimental validation of a detailed FLUKA-based Monte Carlo model of the Canberra GC2018 portable high-purity germanium (HPGe) detector. The detector was modeled using manufacturer supplied dimensions. Energy calibration and full width at half maximum (*FWHM*) measurements were performed using standard gamma-emitting radionuclides including ¹³³Ba, ¹³⁷Cs, and ⁶⁰Co. The experimentally obtained *FWHM* values were fitted as a function of energy and used to apply Gaussian broadening to the simulated spectra. The simulated ⁶⁰Co spectrum generated with a source-to-detector distance of 25 cm was compared with the measured spectrum. Relative efficiency values from both experiment and simulation were also compared, and were in good agreement. The validated FLUKA detector model enables reliable efficiency calibration for practical geometries and supports virtual calibration in field applications where experimental calibration is not feasible.

INTRODUCTION

Portable high-purity germanium (HPGe) detectors have become indispensable in scenarios that demand high-resolution gamma-ray spectroscopy outside the controlled environment of a laboratory. Their ability to accurately identify and quantify radionuclides in situ makes them essential tools for applications such as environmental radiation monitoring, nuclear facility inspection, waste characterization, and emergency response to radiological incidents. By combining portability with superior energy resolution, these detectors bridge the gap between field usability and laboratory-grade spectral performance.

The Canberra GC2018 portable HPGe detector features a coaxial p-type Ge crystal with a nominal relative efficiency of $\geq 20\%$ and an *FWHM* of ≤ 1.8 keV at ~ 1332 keV. Designed for field applications, its compact and rugged design allows reliable operation in a variety of environmental conditions.

Accurate efficiency calibration is critical for quantitative gamma spectrometry, especially in complex or non-standard geometries where experimental calibration is impractical. In such cases, Monte Carlo simulations provide a powerful tool for modeling detector response. However, simulation-based efficiency estimates are only as reliable as the models they are based on, necessitating thorough validation against experimental data. A well-validated model improves confidence in simulation results and extends the detector's applicability to diverse field conditions.

Several studies have employed Monte Carlo simulations using codes such as PHITS, MCNPX, FLUKA and GEANT4 to model HPGe detectors, reproduce their experimental pulse height spectra by simulation, and predict their efficiencies [1-3]. While these efforts have demonstrated the general capability of Monte Carlo methods for detector modeling, limited work has focused specifically on portable HPGe systems, particularly with detailed experimental validation. This study addresses that gap by developing a comprehensive FLUKA model of the detector and validating it through measurements of energy spectra and relative efficiency.

MATERIALS AND METHODS

Detector Description

The detector used in this study is the Canberra GC2018—a portable coaxial p-type HPGe with a nominal active volume of ~ 93 cm³. The crystal has a nominal active diameter of 60.5 mm and an active length of 31.8 mm, housed

in a 3" diameter aluminum endcap, with a thin (1.5 mm) entrance window to facilitate low-energy gamma detection. The detector is cooled by liquid nitrogen (LN2) stored in a compact (~7 L) Dewar, enabling portable operation.

Experimental Measurements

Certified disc sources of ^{133}Ba , ^{137}Cs , and ^{60}Co were used to carry out energy calibration. Each source was placed at 25 cm from the detector face along its central axis. Spectra were recorded using an 8k multichannel analyzer. *FWHM* values were determined across energies from 276 to 1332 keV. The relative efficiency (η , %) was measured using the ^{60}Co source. Full-energy peak area (counts) at ~1332 keV was extracted via Gaussian fitting with linear background correction. Subsequently, η was calculated by using source activity (A , Bq), emission probability (I_γ , %), and measurement time (t , s):

$$\eta(\%) = \frac{\frac{\text{Peak Area (counts)}}{t(s) \times A(\text{Bq}) \times I_\gamma(\%)} \times 100 \times 100}{0.12(\%)} \times 100 \quad (1)$$

Here, 0.12% is the absolute full-energy peak efficiency (*FEPE*) of a 3"×3" NaI(Tl) detector at 1332 keV for a source-to-detector distance of 25 cm.

FLUKA Simulation Setup

A detailed model of the detector was developed using the FLUKA Monte Carlo simulation code (Fig. 1).

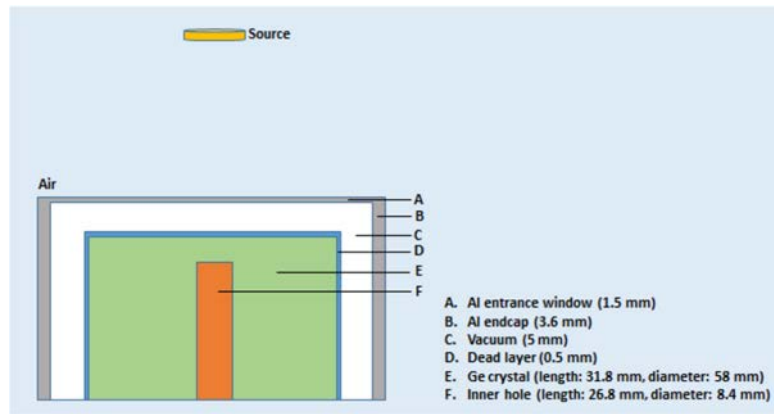


FIGURE 1. The optimized geometric model of the portable coaxial HPGe detector, as incorporated in FLUKA (not to scale).

The geometry included all critical components such as the cooling finger (inner hole), Ge crystal, dead layer, vacuum cavity, and aluminum endcap and entrance window. Dimensions and materials were taken from manufacturer specifications. A thin ^{60}Co disc source (1" diameter, 1 mm thick) was modeled and positioned 25 cm from the detector face along the central axis. The source was defined using the HI-PROPE card, and its decays were simulated using the RADDECAY card. The DETECT and USRBIN cards of FLUKA were employed to obtain energy deposition spectra and total energy deposition in the Ge crystal, respectively. The DETGEB card was used in association with the DETECT card in order to apply Gaussian broadening onto the simulated spectra, with an *FWHM* given as a function of energy (E) by,

$$FWHM = a + b\sqrt{E + cE^2} \quad (2)$$

Parameters (a , b , c) were obtained by fitting the experimentally obtained *FWHM* values at different energies with Eq. (2). Simulations were run with 10^8 histories to ensure relative errors in the energy deposition values were below 0.05%.

RESULTS AND DISCUSSION

The simulated ^{60}Co spectrum was compared with the background-subtracted experimental spectrum, as shown in Figure 2. Insets provide a closer view of the 1173 keV and 1332 keV peaks. The peak shapes and intensities showed

good agreement, indicating that the simulated detector geometry and material compositions were accurate. The accurate modeling and its experimental validation enables optimization of the detector parameters based on observing the effects of their variation on the simulated spectra.

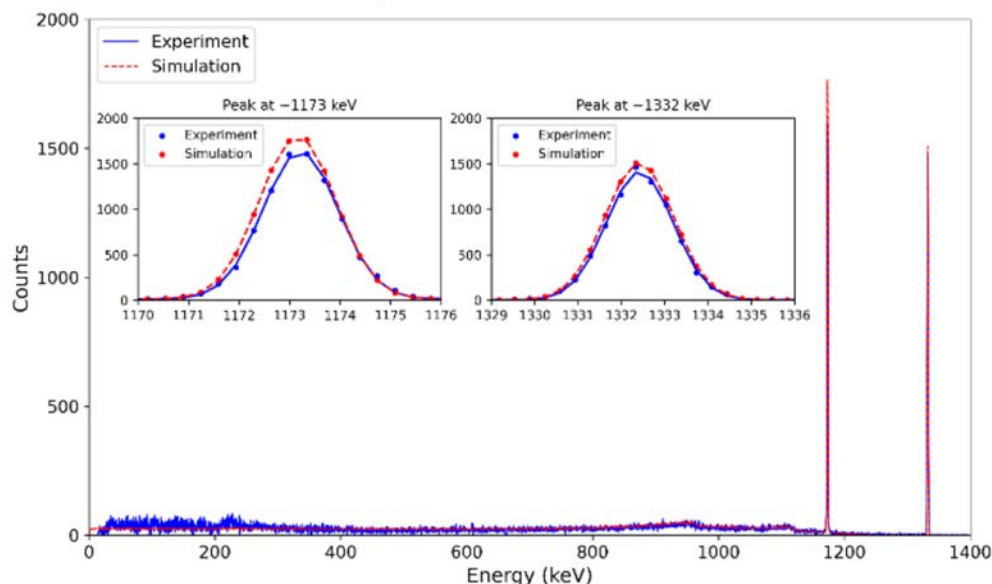


FIGURE 2. Comparison of the experimental and the simulated spectra for ^{60}Co source.

The experimentally measured relative efficiency was 22.06%. To match this, the simulated crystal diameter was iteratively optimized. With the optimized diameter, the estimated simulated relative efficiency was 22.18%, yielding a deviation of less than 0.5%. This result confirms the accuracy of the FLUKA model in reproducing the detector's full-energy peak efficiency at high energies.

Validated Monte Carlo models such as the one developed here can be used to generate efficiency curves for complex geometries and source configurations without requiring physical standards. This enhances the utility of portable HPGe detectors in field conditions, where experimental calibration is not feasible.

CONCLUSION

A detailed FLUKA model of the Canberra GC2018 portable HPGe detector was developed and validated through comparison with experimental energy spectra and relative efficiency measurements. The model reproduced the experimental relative efficiency within $\pm 0.5\%$, demonstrating its accuracy and robustness. This validated simulation approach can be used for efficiency calibration in a wide energy range for field measurement scenarios, thereby extending the applicability of portable HPGe spectrometry for environmental, emergency, and nuclear facility applications.

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Characterization of Organic Co-Crystal by Powder X-ray Diffraction and Vibrational Spectroscopy with DFT Computation

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Abstract. This work mainly focused on the crystal structure, vibrational spectral studies of the grown cocrystal between 2,3-dimethylquinoxaline (DMQ) and 3,5-dinitrobenzoic acid (DNB) molecules. The combined powder X-ray diffraction (PXRD) and Rietveld refinement analysis have been utilized to investigate the nature of crystal structures and affirm phase purity of the co-crystal. The cell parameters suggest that the co-crystal belongs to an orthorhombic structure. The vibrational spectral properties of the complex molecule have been studied using FTIR and simulated spectral analysis. The anharmonic corrections in vibrational wavenumbers are carried out using the GVPT2 method at B3LYP/6-311G(d,p) level of theory. Furthermore, the density functional theory (DFT) method is successfully applied to calculate natural atomic charges.

INTRODUCTION

Crystal Engineering has become a significant field of interest for two decades by organic and physical chemists, physicists, crystallographers and material scientists [1]. This field has been playing a crucial role in the design and development of new organic single crystals such as organic salt, co-crystal and hydrate organic salt along with desirable physical-chemical properties [2]. The organic single-crystal generally has specific properties such as high charge mobility, high nonlinear response and photochemical stability because of the delocalization of π -electron system and the presence of intermolecular hydrogen bond interactions [3]. Due to these properties, they have a large number of potential applications in various fields such as pharmaceutical industries, nonlinear optics, electronic devices, luminescent substances and biosensors [4].

EXPERIMENTAL AND COMPUTATIONAL DETAILS

The synthesis and crystal growth method has been used as described in the earlier reported paper [5]. PXRD pattern of cocrystal was measured by Shimadzu X-ray diffractometer (Cu-K α , λ = 1.5406 Å). The theoretical calculations were performed by the DFT method using Gaussian 09 software package [6]. The vibrational frequency calculations and the natural atomic charges analysis at an optimized geometry of complex molecules were carried out using B3LYP/6-311G(d,p) level of theory.

RESULT AND DISCUSSIONS

Powder XRD Analysis

The PXRD measurement of the crushed crystal was recorded in the range of the diffraction angle (2θ) from 5° to 60° at room temperature. The obtained X-diffraction pattern is compared with the simulated XRD pattern generated from the crystallographic information file using Mercury software and is shown in Fig. 1.

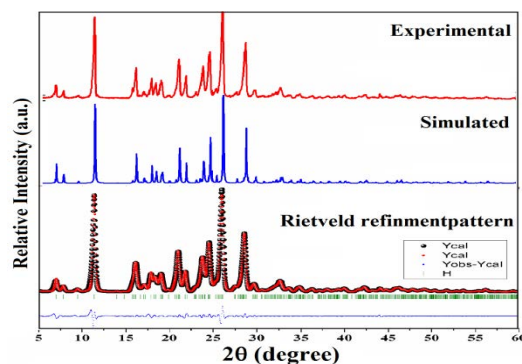


FIGURE. 1. The observed, simulated PXRD along with Rietveld refinement patterns

It is clear from figure 1; the observed PXRD is in good agreement with the simulated patterns from their single-crystal data which confirm their highly crystalline structure. The main diffraction peaks for monoclinic structure at 6.98° , 11.57° , 16.14° , 19.23° , 21.80° , 24.64° , 25.97° and 28.85° are assigned corresponding to (-101) , (102) , (110) , (112) , (-204) , (-114) , (-313) and (006) diffraction planes, respectively. Among the most intense peaks are associated with (102) , (-313) and (006) planes. The final Rietveld refinement pattern for co-crystal is also given in Fig. 1. Moreover, the low value of χ^2 confirm that the appropriate fitting between the experimental and calculated XRD data. In the current investigation, the obtained important structure parameters using the combined PXRD and Rietveld refinement and the important structure parameters are compared with acquired from the SCXRD study [5] which are shown in Table 1.

Table 1 Comparison of the Refined PXRD and SCXRD data.

Parameters	PXRD	SCXRD
Space group	P2 ₁ /n	P2 ₁ /n
Crystal system	Monoclinic	Monoclinic
Cell parameters (Å)	a= 15.6913Å, b= 5.8654 Å, c= 18.6966 Å, $\alpha=90^\circ$, $\beta= 96.53^\circ$, $\gamma=90^\circ$	a=15.5561(5) Å, b=5.8285(2) Å, c=18.6494 Å, $\alpha=90^\circ$, $\beta=96.7538(19)^\circ$, $\gamma=90^\circ$
Volume (Å ³)	1720.55 Å ³	1679.18 Å ³
Good of fit (χ)	1.20	1.01

Anharmonic Vibrational Studies

The vibrational frequency calculation of the complex molecule at an anharmonic approximation was done by GVPT2 method at B3LYP/6-311G(d,p) method and further compared with the observed one and it is depicted in Fig. 2.

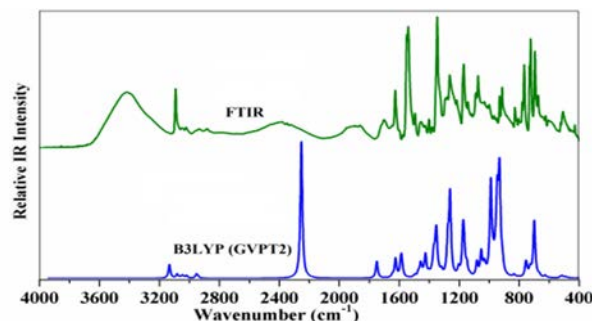


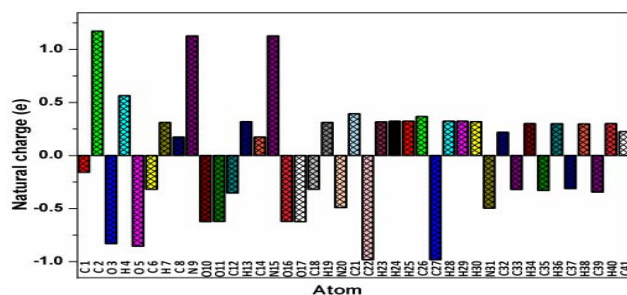
FIGURE 2. Comparison of the simulated anharmonic and IR spectra of the complex molecule

It was noticed that the calculated frequencies using an anharmonic approximation are in good agreement with the observed data. FTIR analysis revealed that the C=O stretching bands at 1701cm^{-1} . The corresponding anharmonic

wavenumber are simulated at 1750 cm^{-1} . The simulated anharmonic wavenumbers of NO_2 asymmetric and symmetric stretching are predicted at 1588 and 1370 cm^{-1} which are good correlated with 1549 and 1347 cm^{-1} , respectively. In the observed IR spectrum, the bands are assigned at 3021 , 2934 and 1379 cm^{-1} due to CH_3 asymmetric, symmetric stretching and CH_3 umbrella motion. The analogous anharmonic wavenumbers are calculated at 3036 , 2943 and 1384 cm^{-1} .

Natural atomic charges study

The computed NBO charges of the DMQNB molecular complex are presented by the histogram (Fig.3). All oxygen atoms (O3 , O5 , O10 , O11 , O16 and O17) in the molecular complex have high negative charges. The highly electronegative oxygen atoms among them are $\text{O3}(-0.831e)$ and $\text{O5}(-0.851e)$ of the carboxylic acid(COOH) group of DNB fragment. It shows that O3 and O5 oxygen atoms are participated in forming $\text{C-H}\cdots\text{O}$ hydrogen bonds. The nitrogen atoms (N9 , N15 , N20 and N31) have both positive and negative charges. The nitrogens (N9 and N15) of the nitro group in DNB moiety are acquired a high positive charge whereas the ring nitrogens (N20 and N31) in DMQ moiety are procured a negative charge. The C2 atom has the highest positive charge ($1.172e$) among all atoms in the molecular complex because this carbon form bond with two oxygen atoms of the carboxylic group in DNB. Moreover, all hydrogen atoms have a positive charge in the molecular complex.



SCAPS Simulation of Lead-Free $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ Based Solar Cell

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Abstract. We investigate the solar cell $\text{TiO}_2/\text{MoS}_2/\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}/\text{Cu}_2\text{O}$ structure using SCAPS simulation. The reported Cu-based perovskite is far more stable than Sn-based variants and non-toxic perovskites. The key performance parameters, i.e. short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE), have been evaluated using various experimentally reported parameters. Also, the impact of the absorber layer thickness, energy band gap and acceptor doping density, and the effect of the thickness of the electron transport layer on the solar cell performance has been evaluated. The simulated device parameters, V_{oc} , J_{sc} , FF, and PCE of 0.94 V, 35.71 mA/cm^2 , 83.24%, and 28.85%, respectively, have been obtained for the optimized solar cell.

INTRODUCTION

The rapid pace of global development is driving a significant surge in energy demand, in response to which the search for renewable sources has made solar power an increasingly popular option due to its availability and lack of hazards. Recently, in perovskite-based solar cell technology, significant efforts have been directed toward enhancing overall performance owing to their exceptional optoelectronic properties [1]. Most perovskites are based on lead and tin, where lead is a toxic material, and tin-based perovskite solar cells (PSCs) face stability issues [2]. Copper-based perovskite $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ has been selected for solar cell construction due to its non-toxic nature and improved stability. It remains stable for up to 500 h under high humidity conditions [3]. For this research, we are using the SCAPS-1D (3.3.10) software, which was developed by Marc Burgelman and Alex Niemegeers at Ghent University [4]. Under various illumination conditions, the majority of semiconductor devices are studied through the continuity and Poisson equations for electrons and holes.

DEVICE STRUCTURE AND SIMULATION PARAMETERS

The solar cell is composed of TiO_2 (Transparent Conductive Layer)/ MoS_2 (Electron Transport Layer (ETL))/ $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ (Absorber)/ Cu_2O (Hole Transport Layer (HTL))/Au (metal back contact). Table 1 presents the parameters of the ETL, HTL, and FTO, which are adapted from previously reported studies. Defects of all layers are modelled using a single distribution with characteristic energy 0.1 eV. Gold metal with a work function of 5.1 eV is used as the front and back contact. Our study focuses on the effects of absorber layer thickness, doping concentration, and defect density, as well as the temperature, series resistance, and shunt resistance of the overall setup. The simulation results obtained by using the initial parameters give the following parameters: J_{sc} is 25.30 mA/cm^2 , V_{oc} is 1.00 V, FF is 83.60%, and PCE is 21.21%.

TABLE 1. Basic parameters of each layer

Parameters	TiO_2 [5]	MoS_2 [6]	$\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ [7]	Cu_2O [8]
Thickness (nm)	50	50	500	95
Band Gap (eV)	3.2	1.23	1.60	2.17
Electron Affinity (eV)	4	4.2	3.74	3.2
Dielectric Permittivity	9	4	10	7.1
C_B effective density of states (cm^{-3})	2.2×10^{18}	2.2×10^{18}	4.5×10^{18}	2.1×10^{17}
V_B effective density of states (cm^{-3})	1.0×10^{19}	1.9×10^{19}	1.6×10^{18}	1.1×10^{19}

Electron Mobility (cm^2/Vs)	20	100	2.5	200
Hole Mobility (cm^2/Vs)	10	150	2.5	80
Shallow Donor Density (cm^{-3})	1.0×10^{18}	1.0×10^{17}	1.0×10^{13}	0
Shallow Acceptor Density (cm^{-3})	0	0	1.0×10^{13}	1×10^{18}
Defect Density (N_T)	1.0×10^{15}	1.0×10^{14}	1.0×10^{15}	1×10^{14}

RESULT AND DISCUSSIONS

In this section, analyses are performed to inspect the influence of the device key factors on cell performance.

Effect of changing the thickness of the absorber

In PSCs, the absorber layer plays a major role in enhancing the device efficiency. The optimization of device efficiency was achieved by adjusting the absorber layer thickness across a range of 100 nm to 1000 nm, which positively influenced the PSC's performance. More thickness improves the generation of electron-hole pairs due to the increased absorption rate; hence, PCE increases. We should keep in mind that a thicker absorber layer leads to the recombination of electrons and holes before reaching their respective electrodes [9].

Effect of changing the energy band gap (E_G) of the absorber

By altering the absorber layer thickness to 600 nm, the resulting changes in its energy band gap (from 1.4 eV to 1.8 eV) were assessed to understand their influence on device performance. As the band gap increases, the value of V_{OC} and PCE decreases from 31.25 to 21.38 mA/cm², 25.25 % to 14.94 %, respectively. As the band gap increases, the value of J_{SC} and FF increases with the band gap. The value of J_{SC} and PCE is maximum at 1.6 eV. This band gap is closest to the band gap of the ETL layer, due to which surface recombination minimized, the FF may be reduced to series resistance, and the V_{OC} may be because of less resistance. The PCE is maximum at a lower band gap, despite lower V_{OC} and FF, indicating that higher JSC outweighs them [9].

Effect of changing the acceptor doping concentration of the absorber

Variations in acceptor doping concentration within the absorber were found to significantly affect cell performance, highlighting its role in device optimization. The acceptor density is varied from 1.0×10^{13} to 1.0×10^{18} , V_{OC} and JSC decrease and increase, respectively, with acceptor concentration increases. $1.00 \times 10^{16} \text{ cm}^{-3}$ acceptor density gives the maximum value of efficiency. Increased doping reduces recombination losses [10].

Effect of ETL thickness on PCE

The MoS₂ thickness is varied from 100 nm to 500 nm in 100 nm increments to achieve maximum PCE. The ETL thickness critically affects solar cell performance, as an excessively thin layer leads to pinholes and increased recombination. In contrast, an overly thick layer raises series resistance and limits electron transport. Thus, an optimal thickness is essential to ensure efficient charge extraction, reduced recombination losses, and improved device efficiency. The optimum thickness of the electron transport layer can reduce the recombination rate and increase the rate of transmission. It attains maximum value at 500 nm.

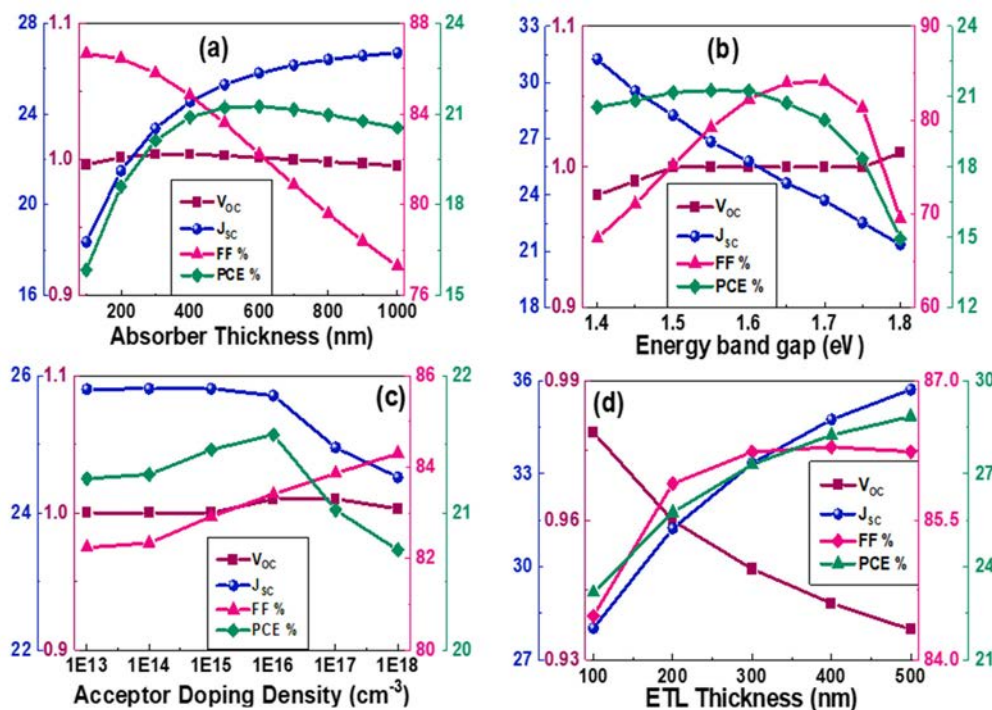


FIGURE 1. Variation of (a) absorber's thickness, (b) absorber's energy band gap, (c) absorber's acceptor doping density, and (d) electron transport layer's thickness as a function of photovoltaic response of solar cell.

CONCLUSION

Lead is a very toxic, various lead-free absorbers have been studied and recorded for use in PCE. $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ is a much better option, and it achieves remarkably good efficiency. The value of V_{OC} is decreased from 1.00 to 0.94 V. J_{SC} , FF and PCE increased from 25.30 to 35.72 mA/cm², 83.60 to 86.24% and 21.25 to 28.85%, respectively. The findings indicate that $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ has the potential to serve as a high-performance, lead-free inorganic perovskite absorber, paving the way for advanced solar cell technologies. These insights offer valuable direction for optimizing future experimental designs and improving overall device performance.

ACKNOWLEDGMENTS

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A Holistic Exploration of Structural, Elasto-Mechanical and Electronic Properties Cobalt Based Quaternary Heusler Alloy CoCrTiSb

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Abstract. Study of some physical properties like electronic and elastic phenomena of cobalt based alloy CoCrTiSb have been reported in this article. All the calculations have been performed using full-potential approach as employed in Wien2k. Structural parameters are obtained by performing structural optimization. Obtained elastic parameters shows that given compound is ductile and anisotropic in nature. Electronic band structure plot indicates that CoCrTiSb is semiconducting in nature which is also confirmed from density of states plot.

INTRODUCTION

Since few decades, quaternary Heusler alloys gained attention because of some interesting characteristics. These alloys are extensively studied because of promising applications in spintronics and other spin dependent devices. They produce high spin-polarized currents which enhance the efficiency of the devices. A numerous amount of these alloys are studied and observed half-metallicity behaviour observed by other researchers [1, 2]. The quaternary Heusler alloys (QHA) having general formula $XX'YZ$ having cubic symmetry crystalize within space group $F-43m$ (No. 216). These alloys having promising applications in spintronic devices. Various studies have been reported on different combinations of Cobalt based quaternary Heusler alloys. $CoX'MnSi$ and $CoXFeSi$ these two series of alloys were investigated by Kundu et al; [3]. $CoXMnAs$ ($X = Ru, Rh$) have been investigated theoretically [4]. Quaternary Heusler alloy CoCrTiSb not yet synthesized we are investigating CoCrTiSb alloy first time. The aim of this work is theoretical exploration of electronic and elastic phenomena of Cobalt based Heusler alloy CoCrTiSb.

COMPUTATIONAL DETAILS

All the calculations related to this work have been carried out within the framework of quantum mechanical approach density functional theory embedded in Wien2k [5]. A correlational functional used in this work is PBE-GGA for solids [6]. A cut-off value is set to $R_{MT} \cdot K_{max} = 7$. For brillouin zone integration 1000k-points has been used under Monkhorst Pack scheme [7]. The convergence criteria for energy and charge are 10^{-4} Ry and 10^{-3} e⁻, respectively.

RESULTS AND DISCUSSIONS

Structural and Elasto-Mechanical Properties

The unit cell structure of the quaternary Heusler alloy CoCrTiSb is face centred cubic, belonging to space group $F-43m$ (number 221). In CoCrTiSb, Co atom is reside at 4a (0, 0, 0), Cr atom at 4b (0.75, 0.75, 0.75), Ti is at 4c (0.25, 0.25, 0.25) and Sb atom located at 4d (0.5, 0.5, 0.5) site, respectively. The unit cell structure of CoCrTiSb is depicted in **Figure 1(a)**. The volume optimization curve is represented in **Figure 1(b)**. The obtained equilibrium lattice constant (a_0), unit cell volume (V_0) and total energy (E_0) are listed in **Table 1**.

In order to visualise elasto-mechanical properties, we have obtained elastic constants and derived elastic parameters which are tabulated in **Table 2**. Obtained elastic constants satisfied Born-Huang conditions which reveals that CoCrTiSb is mechanically stable. From the table, we found that Pugh's ratio (B/G) is more than 1.75 which reveals that CoCrTiSb is ductile which also confirms from positive value of Cauchy pressure ($C_{12} - C_{44}$). The value of Zener anisotropy parameter (A) deviates from 1 meaning thereby that CoCrTiSb is anisotropic.

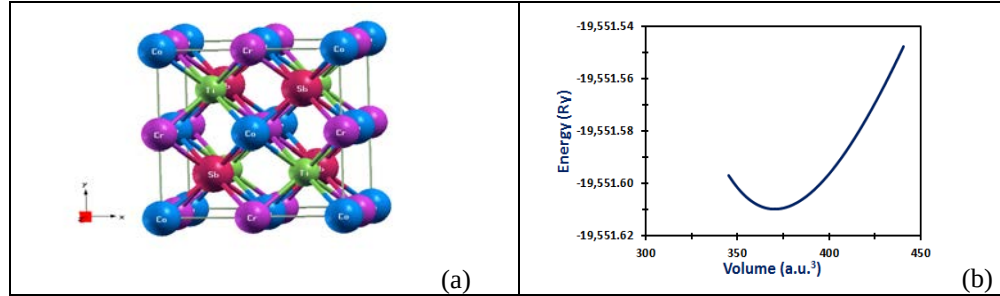


FIGURE 1. (a) The unit cell structure of CoCrTiSb, (b) The energy versus volume optimization curve for CoCrTiSb.

TABLE 1. Lattice constant a_0 (Å), equilibrium cell volume V_0 (Å³) and the equilibrium energy E_0 (Ry) for CoCrTiSb.

a_0 (Å)	V_0 (a.u. ³)	E_0 (Ry)
6.03	370.30	-19551.61

TABLE 2. Calculated values of C_{11} , C_{12} and C_{44} along with other parameters like shear modulus 'G', modulus of elasticity 'Y' (GPa), anisotropy parameter 'A' for CoCrTiSb.

C_{11}	C_{12}	C_{44}	B	G	Y	B/G	A
249.93	165.76	65.03	193.82	55.85	152.87	3.47	1.55

Electronic Properties

To visualise electronic properties of CoCrTiSb, band structure along with density of states calculation have been performed. Obtained plots in both spin up ($\uparrow$) as well as in spin down ($\downarrow$) channel in the highly symmetric directions are depicted in **Figure 2(a) and (b)**. In BS plot, the valence and conduction band having some energy gap and it is also observed that location of fermi level near valence band reveals that CoCrTiSb is *p*-type semiconductor. DOS plot shows similar characteristics and confirms the BS results.

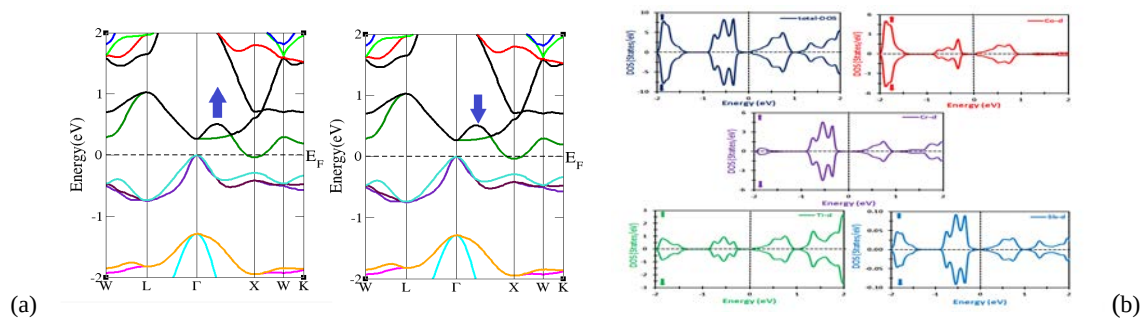


FIGURE 2. (a) Spin-polarized band structure of CoCrTiSb, (b) Total along with resolved partial density of states plots for CoCrTiSb.

CONCLUSIONS

We studied electronic and elastic behaviour of quaternary Heusler alloy CoCrTiSb using Wien2k. We obtained structural parameters by performing structural optimization. Obtained lattice constants was used to obtained elastic constants and derived elastic parameters. Elastic constants shows that CoCrTiSb is mechanically stable, having ductile and anisotropic behaviour. Electronic band structure and density of states plots reveals semiconducting nature in both spin channels. This study is done for the first time no other studies have been reported in literature till now.

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Inverse Design of 1D Photonic Crystal Reflectors Using a Physics-Informed Genetic Algorithm for Broadband Mid-IR Gas Sensing

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Abstract. This paper presents a physics-informed inverse design methodology for optimizing one-dimensional photonic crystal structures to achieve wideband reflectors tailored for mid-infrared gas sensing applications. A genetic algorithm, integrated with a Transfer Matrix Method-based spectral simulator, is employed to inversely determine the optimal layer thicknesses (d_1 , d_2) and number of bilayer periods (N) required to achieve user-defined stopbands with zero edge error and ultra-high reflectivity ($>99.9\%$). For a target stopband of 600 nm (2900–3500 nm), the proposed design achieves a total thickness of just 3.11 μm . Compared to conventional quarter-wavelength stack designs, which are constrained by their central wavelength and require significantly greater thickness to cover broadband ranges, our approach achieves user-specified performance with a $\sim 16\%$ reduction in total thickness. Furthermore, the algorithm generates reflectors with selectable bandwidths (500–2000 nm) across targeted mid-infrared windows (2900–9000 nm), corresponding to molecular fingerprint absorption bands. This compact and customizable reflector design facilitates the development of integrated and miniaturized gas sensing systems.

INTRODUCTION

Photonic crystals have garnered significant attraction due to their ability to manipulate light propagation via photonic bandgap engineering [1], [2], [3]. One-dimensional photonic crystals (1D PCs), composed of alternating layers of high- and low-refractive index materials, offer effective control over spectral reflectance, making them ideal candidates for optical filters, mirrors, and sensors [4].

In mid-infrared (MIR) gas sensing, wideband reflectors are often used for enhancing the signal-to-noise ratios by providing high reflectivity within absorption bands of target gases [5]. Conventional quarter-wave stack (QWT) designs, however, are limited by fixed central wavelengths and relatively large thicknesses. Inverse design techniques offer a promising alternative by employing optimization algorithms to explore the parameter space and tailor devices to meet desired spectral responses [6]. Among them, genetic algorithms (GAs) are especially effective for handling non-linear and multi-modal optimization problems [7]. However, conventional GAs often lack physical constraints, leading to impractical solutions. This work presents a physics-informed genetic algorithm framework for inverse design of one-dimensional photonic crystals, embedding Transfer Matrix Method (TMM) simulations into the optimization loop. The method enables compact reflectors with user-defined bandwidths and spectral positions across mid-infrared molecular fingerprint regions, while minimizing edge error and transmission leakage. Compared to conventional quarter-wavelength designs, the optimized structures achieve target performance with reduced thickness, enabling compact and integrated gas sensing platforms.

THEORETICAL MODELLING AND DESIGN

The proposed 1D PC structure consists of alternating layers of germanium (Ge) and zinc sulfide (ZnS), arranged periodically as $[\text{Ge/ZnS}]^N$ in an air environment ($n_0 = 1.0$), as shown in Fig. 1(a). Transmission spectra are computed using the Transfer Matrix Method [8], where the total transfer matrix is given by, $M = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = D_0^{-1} [M_A M_B]^N D_0$. Here, D_0 is the dynamical matrix of air, while M_A and M_B represent the transfer matrices for layers Ge and ZnS, respectively. The transmittance is then calculated as, $T = \left| \frac{1}{M_{11}} \right|^2$.

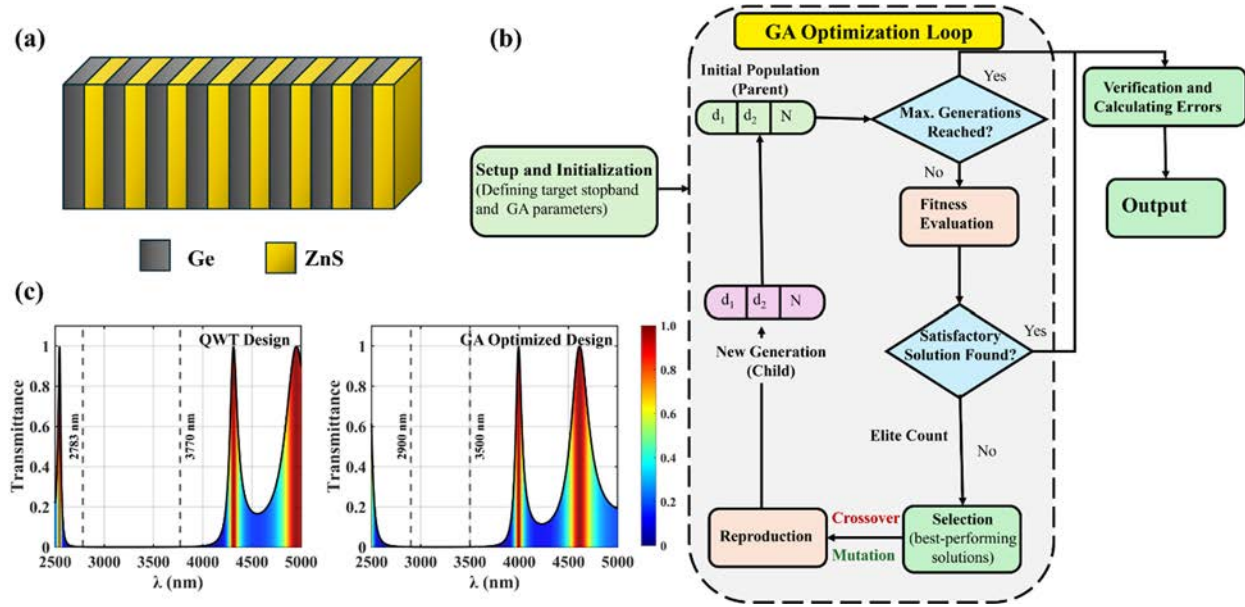


Figure 1. (a) Schematic diagram of a 1D photonic crystal, (b) Genetic algorithm flow for design optimization, and (c) Transmission spectrum of QWT structure and GA-optimized structure

The GA optimizes layer thicknesses (d_1 , d_2) and the number of bilayers (N) to achieve a >99.9% reflective band of user-defined width and positions. The parameter bounds over d_1 , d_2 , and N are $d_1 \in [50 \text{ nm}, 250 \text{ nm}]$, $d_2 \in [50 \text{ nm}, 400 \text{ nm}]$, and $N \in [6, 10]$. The fitness function minimizes errors in stopband edge mismatch, average transmission within the stopband, overshoot leakage, and sideband leakage. The GA operates with a population size of 150, up to 800 generations, a mutation rate of 0.15 (adaptive feasible), a crossover fraction of 0.8, and an elite count of 4 (Fig. 1(b)). For each solution, the spectrum is computed via a high-resolution TMM sweep from 2500 to 10000 nm, and the region with transmittance below 0.001 is identified as the stopband and compared with the target design.

NUMERICAL RESULTS AND DISCUSSION

To establish a baseline design, a conventional QWT structure is designed with a central wavelength of 3200 nm, producing a high-reflectivity stopband from 2783 to 3770 nm (Fig. 1(c)). The corresponding structure has a total thickness of approximately 3.7 μm . The physics-informed GA is then employed to inversely design the structure that achieves the same target stopband (2900–3500 nm). This optimization uses the parameters and methodology described in the previous section. The GA-predicted optimal structure consists of $d_1 = 220.72 \text{ nm}$, $d_2 = 224.22 \text{ nm}$, and $N = 7$ periods. The configuration achieved >99.9% reflectivity across the specified 2900–3500 nm range (Fig. 1(c)). Remarkably, the total physical thickness is significantly reduced by ~16% compared to the QWT design, demonstrating the effectiveness of the optimization. The GA-based optimization is completed in approximately 75 seconds using 8 parallel workers in MATLAB, demonstrating the practicality and computational efficiency of the method for real-world photonic device design. To further evaluate the robustness and generalization capability of the physics-informed GA, we extended the optimization to multiple target bandwidths, including 2900–3400 nm, 2900–3600 nm, 2900–3800 nm, and 2900–4200 nm (Fig. 2(a-d)). In all cases, the GA successfully generated high-reflectivity structures that satisfied the desired spectral constraints, demonstrating its adaptability to varying bandwidth requirements. Additionally, the method is tested across different spectral regions corresponding to characteristic molecular vibrational fingerprints relevant for sensing applications. These include the 4200–4500 nm range associated with C=O asymmetric stretching; 4500–5000 nm corresponding to N≡N and C≡O stretching modes; 5000–6000 nm covering C=O stretching and N–H bending vibrations; and the 7000–9000 nm region related to C–C and C–O stretching and C–H and N–H bending modes (Fig. 2(e-f)). The GA consistently produced optimized multilayer designs with high reflectivity across these diverse spectral windows, highlighting its potential for application-specific photonic structure designs in molecular sensing.

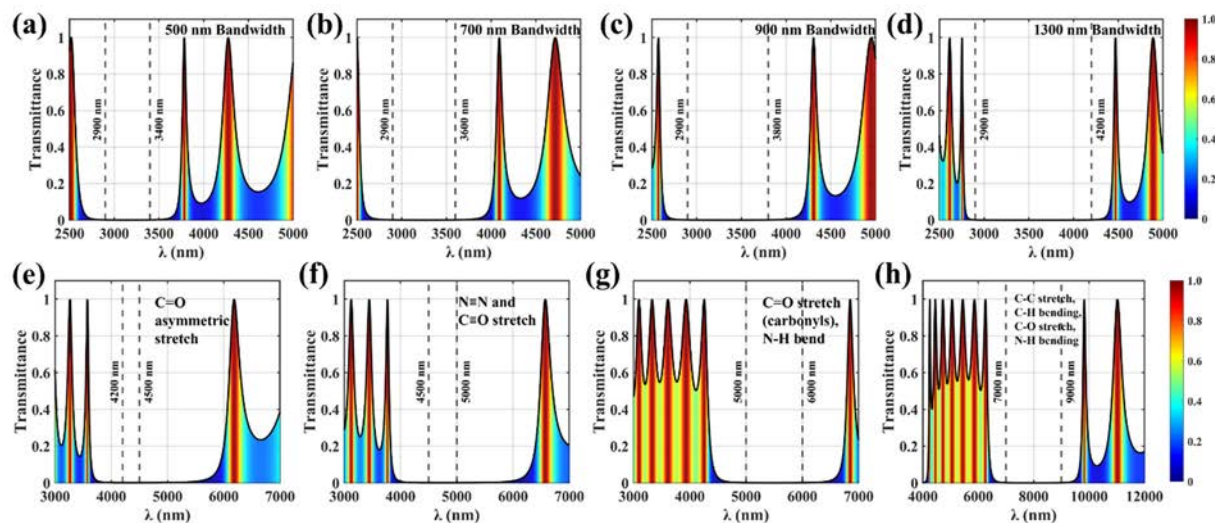


Figure 2. GA-optimized 1D photonic crystal reflectors showing (a–d) tunable stopbands with increasing bandwidths and (e–h) designs targeting specific mid-IR molecular fingerprint regions

CONCLUSION

In this work, a physics-informed inverse design approach is proposed to optimize 1D photonic crystal reflectors for mid-infrared gas sensing applications. By integrating a genetic algorithm with TMM simulations, the optimization framework effectively determined the optimal layer thicknesses and number of bilayer periods required to achieve high-reflectivity stopbands over user-defined wavelength ranges. The proposed method successfully achieves >99.9% reflectivity across target bands while reducing the overall device thickness compared to conventional quarter-wave designs, highlighting its effectiveness in producing compact photonic structures. The framework exhibits strong adaptability across varying bandwidths and spectral positions, including regions corresponding to key molecular vibrational fingerprints relevant to gas sensing. Moreover, the rapid optimization time enabled by parallel computation demonstrates the practical feasibility of integrating such inverse design strategies into real-world device development workflows.

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The Impact of Dual-Fluid Saturation on the Dispersion of SH-Waves in Geological Porous Medium

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Abstract. This paper investigates the SH-wave propagation in the porous layer saturated by two fluids and lying over an elastic half-space. The impacts of various fluid saturations in the porous layer are examined to understand how they collectively affect the dispersion characteristics of SH-waves. The dispersion relation of the SH-wave using suitable boundary conditions is derived. The numerical analysis shows that the different fluids in the porous layer significantly affect the phase speed of the SH-wave.

INTRODUCTION

SH-waves are horizontally polarized shear waves that propagate along the interface between an elastic half-space and a solid layer [1]. This study investigates SH-wave propagation in a porous layer saturated with two fluids over an elastic half-space and derives the dispersion relation using appropriate boundary conditions. Numerical analysis is performed to examine the influence of dual-fluid saturation on SH-wave behavior and its applications in seismic and geotechnical engineering.

DISPERSION RELATION

We examine the propagation of SH-waves at the interface between a porous layer and an isotropic half-space. The height of the porous layer is taken as H and is considered to be saturated by two viscous immiscible fluids. The SH-wave propagation is considered along the positive direction of the x -axis and the half space is along the positive direction of the z -axis. The upper surface of the layer is represented by $z = -H$ and the interface is defined by $z = 0$. Let $U_i(u_i, v_i, w_i)$ be represents the displacement vector of i^{th} phase within porous layer, where i takes the values of $s, 1, 2$, the subscripts $s, 1$, and 2 correspond to the solid phase, first fluid, and second fluid phases, respectively and $V(u, v, w)$ represents the displacement vector within half space. For SH-wave propagation in the x - direction, we have:

$$u_i = w_i = u = w = 0, v_j = v_j(x, z, t) \text{ and } v = v(x, z, t). \quad (1)$$

For elastic half-space, the equation of motion is given by

$$\nabla \cdot \tau = \rho D^2 V, \quad (2)$$

where $\tau = \lambda \nabla \cdot V + \mu (\nabla V + \nabla V^T)$ represents stress in the half-space, λ and μ are the elastic constants. The density of the elastic half-space is represented by ρ . Employing (1), equation (2) can be expressed as $\left[\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial z^2} \right] = \frac{1}{\Gamma_2^2} \frac{\partial^2 v}{\partial t^2}$, where $\Gamma_2^2 = \frac{\mu}{\rho}$ represents the velocity of shear wave in an elastic half-space. Considering the time-harmonic solution $v(x, z, t) = \psi(z) \exp \left\{ i \omega \left(t - \frac{x}{c} \right) \right\}$, and substituting in the above equation, we obtain the amplitude $\psi(z)$ as under:

$$\psi(z) = B_1 e^{\xi z} + B_2 e^{-\xi z}, \quad (3)$$

where B_1 and B_2 are arbitrary constants and $\xi = \frac{\omega}{c} \sqrt{1 - \frac{c^2}{\Gamma_2^2}}$. For the propagation of SH type surface wave the amplitude $\psi(z)$ must approach to zero as $z \rightarrow \infty$, hence B_1 must be zero. Making use of this condition, we get the displacement vector component in the half-space as:

$$v = B_2 e^{-\xi z} \exp \left\{ i\omega \left(t - \frac{x}{c} \right) \right\} \quad (4)$$

Following [2] and using (1), the equations of motion in the elastic porous layer with two viscous, immiscible fluids under isothermal conditions and neglecting body forces are as follows:

$$\left. \begin{aligned} \frac{\partial^2}{\partial t} [\rho_s \theta_s v_s + \sum_{i=1}^2 \sum_{j=1}^2 A_{ij} (v_j - v_s)] + \frac{\partial}{\partial t} [R_{11} (v_1 - v_s)] + \frac{\partial}{\partial t} [R_{22} (v_2 - v_s)] &= (G \nabla^2 v_s), \\ \frac{\partial^2}{\partial t} [\rho_1 \theta_1 v_1 - \sum_{j=1}^2 A_{1j} (v_j - v_s)] - \frac{\partial}{\partial t} [R_{11} (v_1 - v_s)] &= 0, \frac{\partial^2}{\partial t} [\rho_2 \theta_2 v_2 - \sum_{j=1}^2 A_{2j} (v_j - v_s)] - \frac{\partial}{\partial t} [R_{22} (v_2 - v_s)] = 0. \end{aligned} \right\} \quad (5)$$

The solid skeleton's shear modulus is G , the volume fraction of i^{th} phase is $\theta_i = \frac{V_i}{V_b}$, with V_b signifying the bulk volume of the Material, and its density is ρ_i . The expressions for inertial coefficients (A_{11} , A_{12} and A_{22}) and viscous coupling coefficients (R_{11} , R_{12} and R_{22}) are as follows:

$$A_{11} = \rho_1 \theta_1 (1 - \alpha_s), \quad A_{22} = \rho_2 \theta_2 (1 - \alpha_s), \quad A_{12} = A_{21} = -0.1 \sqrt{\alpha_s^2 \rho_1 \rho_2 \theta_1 \theta_2}, \quad R_{11} = -\frac{\theta_1^2 \eta_1}{k_s k_{r1}}, \quad R_{22} = -\frac{\theta_2^2 \eta_2}{k_s k_{r2}},$$

where $R_{12} = R_{21} = 0$, k_s is the intrinsic permeability of the solid phase, k_{ri} is the relative permeability, η_i the viscosity of the i^{th} phase and $\alpha_s = \frac{1}{2} \left(1 + \frac{1}{\phi} \right)$ the tortuosity factor. For SH-Wave propagation, we assume the

harmonic solution of the i^{th} phase as: $v_i = \psi_j(z) e^{i\omega(t - \frac{x}{c})}$, where c is the velocity of SH-Wave. Solving (5) for v_s , we get

$$\Psi_s''(z) - f^2 \Psi_s(z) = 0 \quad (6)$$

where $f = i \frac{\omega}{c} \sqrt{\frac{c^2}{\Gamma_1^2} - 1}$. The symbol $\Gamma_1^2 = \frac{G}{\rho_{ss} + \frac{2\rho_{s1}\rho_{s2}\rho_{12} - (\rho_{s1}^2\rho_{22} + \rho_{s2}^2\rho_{11})}{(\rho_{11}\rho_{22} - \rho_{12}^2)}}$ denotes the velocity of shear wave in the

porous layer, where $\rho_{ss} = \rho_s \theta_s - A_{11} - 2A_{12} - A_{22} + \frac{l}{\omega} (R_{11} + R_{22})$, $\rho_{s1} = A_{11} + A_{12} - \frac{l}{\omega} R_{11}$, $\rho_{s2} = A_{12} + A_{22} - \frac{l}{\omega} R_{22}$, $\rho_{11} = \rho_1 \theta_1 - A_{11} + \frac{l}{\omega} R_{11}$, $\rho_{12} = -A_{12}$, $\rho_{22} = \rho_2 \theta_2 - A_{22} + \frac{l}{\omega} R_{22}$.

Solving the second order differential equation (6), we get:

$$\Psi_s(z) = A_1 \cosh fz + A_2 \sinh fz \quad (7)$$

where A_1 and A_2 are arbitrary constants. So, we obtain the displacement vector component of the solid phase as:

$$v_s = (A_1 \cosh fz + A_2 \sinh fz) \exp \left\{ i\omega \left(t - \frac{x}{c} \right) \right\} \quad (8)$$

For any wave propagation problem, the appropriate selection of boundary conditions is essential to accurately model physical reality. When analyzing SH-wave propagation in a layered medium, two fundamental physical requirements must be satisfied along the interface between different elastic materials: (i) Continuity of displacement at the interface and (ii) Continuity of stress at the interface. Furthermore, we assume the upper surface of the layer as traction free. Using the boundary conditions and the equations (4) and (8) we obtain the following dispersion relation:

$$\tan \left(\frac{\omega H}{c} \sqrt{\frac{c^2}{\Gamma_1^2} - 1} \right) = \frac{\frac{\mu}{G} \sqrt{1 - \frac{c^2}{\Gamma_2^2}}}{\sqrt{\frac{c^2}{\Gamma_1^2} - 1}} \quad (9)$$

NUMERICAL ANALYSIS

To comprehensively investigate the influence of two fluids in the porous layer on SH-wave propagation, numerical analysis is centered on the complex transcendental implicit dispersion relation denoted as (9). As represented in Table1, the material parameters for the porous layer consisting of Columbia fine sandy loam that is saturated by an air-water mixture and oil-water mixture are taken from [2]. Figure 1 shows the variation of normalized phase speed with normalized frequency of SH-wave when the porous layer is saturated by air and water and Figure 2

depicts the variation of normalized phase speed with normalized frequency of SH-wave when the porous layer is saturated by water and oil. In both the cases, the phase speed is maximum when there is no fluid in the porous layer, that is, when the layer is an elastic solid. This shows that the solid structure supports SH-wave propagation. The air in the porous medium reduces the phase speed more because, unlike water and oil, air interacts less efficiently with the solid matrix and has a lower capacity to transmit shear stress. The stronger coupling effect of water enhances shear wave propagation, thereby increasing the phase speed. Oil also has a substantial impact on reducing phase speed than water due to its higher viscosity, leading to greater internal friction and wave attenuation.

TABLE 1. Material Parameters

Parameter	Density of air/oil (ρ_1)	Density of water (ρ_2)	Density of solid (ρ_s)	Viscosity of air/oil (η_1)	Viscosity of water (η_2)	Porosity (ϕ)	Shear modulus (G)	Rigidity (μ)	Density of half-space (ρ)
Value	1.1kg/m ³ /762kg/m ³	997 kg/m ³	2650 kg/m ³	18 X 10 ⁻⁶ Ns/m ² / 0.00144 Ns/m ²	0.001Ns/ m ²	0.4 5	3.85 MPa	8 MPa	2675 kg/m ³

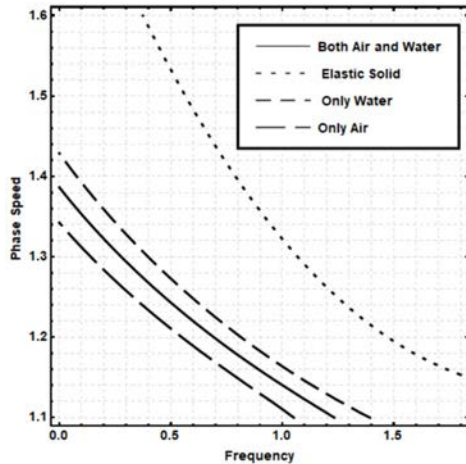


Figure 1: Variation of Phase speed with frequency of SH-wave when porous layer is saturated by air and water.

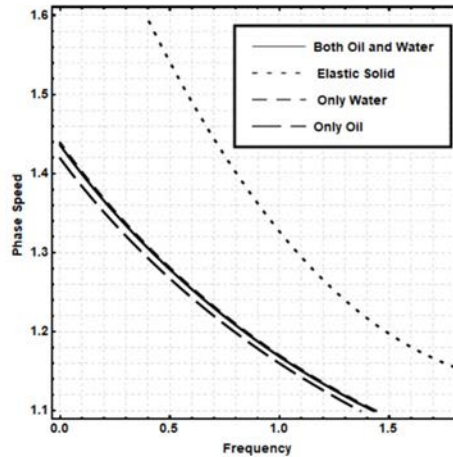


Figure 2: Variation of Phase speed with frequency of SH-wave when porous layer is saturated by oil and water.

CONCLUSION

Our comprehensive numerical study concludes that the fluids in the porous layer reduce the speed of SH-wave, and the reduction in phase speed depends on the type of fluid present in the media. Air causes the strongest reduction and water the least.

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Structural, Electronic And Magnetic Properties Of Ni Nanoalloy: A Combined First Principle And Experimental Study

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Abstract. The present work investigates a first-principle density functional theory (DFT) calculation on the structural, electronic, and magnetic properties of Ni nanoalloy. Using the generalized gradient approximation (GGA) within the Perdew-Burke-Ernzerhof (PBE) framework, we analyze band structure, density of states (DOS), and magnetic moment. By minimizing the total energy, structural optimization yields a lattice constant and unit cell volume that closely match experimental observations. Magnetic calculations illustrate a ferromagnetic ground state with the total magnetic moment per formula unit aligning well with previously reported moment. Further analysis with electronic band structure and DOS shows the metallic nature and overlapping of spin-split bands at E_F. The observed asymmetry between the spin-up and spin-down states, is ascribed to the strong hybridization of Ni 3d orbitals. Overall, these findings confirm that the PBE-GGA approach is indeed reliable for computational analysis of Ni and other transition metal nanoalloys in regard to their electronic and magnetic characteristics.

INTRODUCTION

Transition metal nanoalloys have fascinated the research world with their diverse electronic, magnetic, and catalytic properties which differ markedly from those observed in their bulk counterparts. Ni is a well-established ferromagnetic transition metal, widely employed in magnetic devices and catalysis [11]. As Ni approaches to nano dimensions, its electronic configuration and magnetic ordering exhibit significant deviations from bulk behavior due to quantum confinement and increased surface-to-volume ratio [1]. First-principle calculations based on DFT provide a powerful tool to probe such modifications in material properties [2–6]. In this work, we employ first-principle spin-polarized DFT calculations using the PBE-GGA approximation to illustrate the structural, electronic, and magnetic characteristics of Ni nanoalloy. The study focuses on determining optimized lattice parameter, analyzing band structure, along with evaluating spin polarization and magnetic moment. The results provide insights into the metallic nature and spin-dependent behavior of the nanoalloy.

COMPUTATIONAL DETAILS

The ground state structural parameters of the nanoalloys were approximated by relaxation and optimization of their unit cell structure. The first principle calculations were performed via the BURAI 1.3 graphical user interface (GUI), which operates on Quantum ESPRESSO as the backend. For doing the calculations, the GGA functional of the PBE exchange correlation function was implemented. The optimization of the structure was obtained by employing variable cell relaxation. Self-Consistent Field (SCF) calculations were carried out using ultrasoft pseudopotentials, with a plane-wave energy cutoff of 40 Ry and a charge density cutoff of 400 Ry. Brillouin zone integration was performed using an 8×8×8 Monkhorst–Pack k-point mesh. Structural relaxations were performed until forces were less than 0.01 eV/Å. For all calculations, the Fermi-Dirac function was regarded as smearing.

EXPERIMENTAL WORK

Ni nanoalloy was synthesized via a hydrothermal method following the same protocol reported in our recent study [1]. Briefly, Ni (NO₃)₂·6H₂O was dissolved in deionized water (DIW) to prepare an aqueous solution, which was then treated with NaOH to adjust the pH to approximately 11. Subsequently, 2 ml of NaBH₄ was added as a reducing agent.

The resulting mixture was stirred thoroughly and transferred into a 100 ml Teflon-lined stainless steel autoclave. After completion of the reaction, the obtained product was collected, washed, dried, and subsequently calcined at 550 °C in a reducing atmosphere to yield the final Ni nanoalloy. Powder X-ray Diffraction (XRD) equipped with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) was performed to identify the phase of nanoalloy. Magnetic property measuring system (MPMS-3, Quantum design) was employed to analyze the field dependent DC magnetization and to further obtain the experimental saturation magnetization.

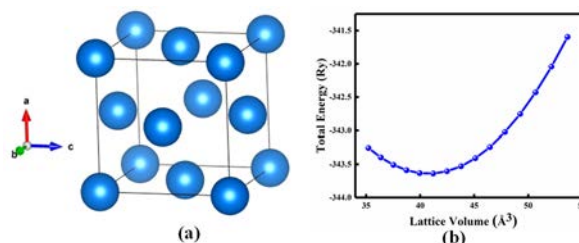


FIGURE 1. (a) Crystal structure of Ni nanoalloy as generated using VESTA software and (b) Total energy versus unit cell volume curve for Ni nanoalloy.

RESULTS AND DISCUSSION

Total energy as a function of unit cell volume is analyzed to determine the optimized lattice parameter of the Ni nanoalloy. Structural optimization is carried out using the total energy minimization approach [3,7]. It is well established that bulk Ni alloy crystallizes in a face-centered cubic (FCC) structure with $Fm\bar{3}m$ space group [12]. The unit cell structure (Fig. 1(a)) is initially generated using VESTA software, based on the Crystallographic Information File (CIF) obtained from Rietveld refinement of XRD patterns of Ni nanoalloys synthesized via the hydrothermal method, as reported in our recent study [1]. From the total energy versus unit cell volume plot, as shown in Fig. 1 (b), the optimized structural parameters are obtained as $a_0 = 3.5245 \text{ \AA}$ and $V_0 = 43.7816 \text{ \AA}^3$ for Ni nanoalloy, where a_0 is the equilibrium lattice constant and $V_0 = a_0^3$ is the equilibrium volume. These results show good agreement with previously reported experimental and theoretical values [8]. Table 1 presents the calculated structural parameters, total energy, and magnetization, in comparison with available experimental data. The discrepancy between the experimentally measured and DFT calculated lattice parameters can be attributed to the idealized assumptions in the simulations, which do not account for structural disorder or imperfections present in real samples [9].

Furthermore, the magnetic properties of the studied alloy systems are investigated using the PBE-GGA functional. Table 1 summarizes the total magnetic magnetization expressed in $\mu_B/\text{f.u.}$ along with the magnetic moments of Ni reported in bulk and related nanoalloy systems. These values are computed under the assumption of ferromagnetic spin ordering. The calculated total magnetic moment of the Ni alloy shows good agreement with experimental results, further validating the reliability of the PBE-GGA method for magnetic property prediction.

TABLE 1. Calculated structural and magnetic parameters. Experimental data from the present work is also included.

Parameters	This work (DFT)	This work (Experimental)	Other works
Lattice parameter ($\text{\AA}$)	3.5245	3.5223	3.51 [8]; 3.53 [4]
Volume ($\text{\AA}^3$)	43.7816	43.6997	----
Total energy (Ry)	-343.5818	----	----
Saturation Magnetization ($\mu_B/\text{f.u.}$)	0.45	0.33	0.62 [8]

After obtaining the optimized lattice parameter, the electronic properties of the Ni nanoalloy are investigated through calculations of the band structure and DOS to gain insight into the electronic configuration. As shown in Fig. 2 (a), the band structure for the majority spin channel reveals several bands crossing the E_F , particularly in the range of -5 eV to -2 eV. This indicates strong hybridization among Ni atoms and confirms the metallic character of the alloy, consistent with the total DOS. Such metallic behavior is comparable to that observed in Co-based half-Heusler alloys like CoNiSi and CoTiSi [10].

To gain deeper insight into the electronic structure, total DOS and PDOS of Ni are calculated using the Linearized Augmented Plane Wave (LAPW) method, as shown in Fig. 2 (b). The presence of finite DOS at E_F again confirms the

metallic nature of the alloy. Additionally, an evident asymmetry between spin-up and spin-down states in the energy window of -5 eV to 1 eV reflects spin polarization and supports the presence of magnetism in the system. The PDOS analysis shows the majority of the electronic states near E_F originate from Ni 3d orbitals, with minimal contribution from 4s orbitals. A more detailed orbital-resolved PDOS further reveals that the dominant contribution to the total DOS originates from the Ni 3d states, while the 4s states contribute minimally. Such an electronic distribution is typical signature of transition metal based conductive magnetic materials. These electronic features further substantiate the interpretation of Ni nanoalloys as spin-polarized metallic systems, in agreement with prior reports on Heusler-type alloys such as CoNiSi and CoTiSi [10].

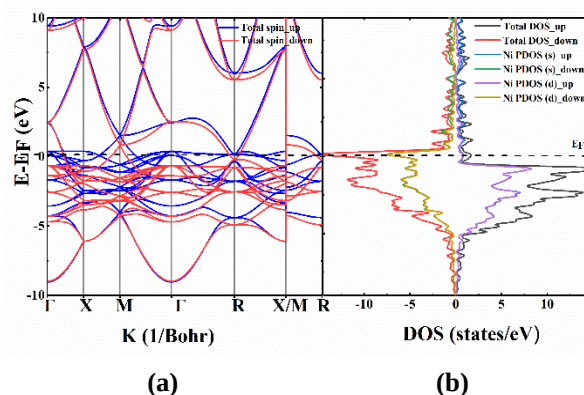


FIGURE 2. (a) Energy bands for spin-up ($\uparrow$) and spin-down ($\downarrow$) states and (b) Total and partial DOS for Ni nanoalloy.

CONCLUSION

The structural, electronic, and magnetic investigation of Ni nanoalloy were carried out by using first-principles computations within the PBE-GGA framework. The optimized lattice parameters and magnetic moments obtained from total energy minimization showed close agreement with both experimental and previously reported theoretical data, validating the accuracy of the computational approach. The calculated band structure and DOS confirmed the metallic character of the Ni nanoalloys, with noticeable spin polarization near the E_F . This spin-split behavior was primarily attributed to the Ni 3d states, which predominantly contributed to the total DOS. The observed enhancement in magnetic moment at the nanoscale was ascribed to surface-induced electronic redistribution and reduced atomic coordination. Overall, the study provided meaningful insights into the fundamental properties of Ni-based nanostructures and supported their prospective application in nanoscale magnetic and spintronic technologies.

ACKNOWLEDGEMENTS

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Tunable Electronic Properties of MXene/blueP Phosphorene Heterostructures under an External Electric Field

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Abstract. Van der Waals (vdW) heterostructures based on two-dimensional (2D) materials offer exciting opportunities by combining the strengths of individual layers. Of particular interest is the type-I to type-II band alignment transition, which enhances charge separation for photocatalytic and optoelectronic applications. Using *ab initio* calculations, we investigate the electronic properties of the MXene (Sc₂CO₂, Zr₂CO₂, and Hf₂CO₂) /blue phosphorene heterostructures. A perpendicular electric field is applied to tune its electronic properties, leading to notable changes in band gap and alignment without affecting structural integrity. These results highlight MXene/blueP heterostructures as promising candidates for tunable nanoelectronic and optoelectronic devices.

INTRODUCTION

Low-dimensional systems have attracted considerable attention due to their exceptional electronic, optical, and mechanical properties. Among 2D materials, MXenes, transition metal carbides, nitrides, or carbonitrides with the general formula $M_{n+1}X_nT_x$ ($T_x = O, OH, \text{ or } F$), have emerged as versatile candidates for diverse applications. While most functionalized MXenes are metallic, a few, such as Sc₂CO₂, Zr₂CO₂, and Hf₂CO₂, exhibit semiconducting behavior with tunable band gaps. In this work, we construct van der Waals heterostructures of these semiconducting MXenes with blue phosphorene (blueP), a stable 2D semiconductor with an indirect band gap, and investigate their electronic properties using first-principles calculations. An external perpendicular electric field induces indirect-to-direct band gap transitions and type-I to type-II band alignment transitions without affecting structural stability. In type-I alignment, the conduction band minimum (CBM) and valence band maximum (VBM) are confined within the same layer, favoring radiative recombination, whereas in type-II alignment they are distributed across different layers, enabling efficient separation of photoexcited carriers. These findings highlight the potential of MXene/blueP heterostructures for tunable nanoelectronic and optoelectronic applications.

COMPUTATIONAL DETAILS

All calculations were performed using DFT with the projector augmented-wave (PAW)¹ method, as implemented in VASP². The PBE-GGA³ functional was used for exchange-correlation, with van der Waals interactions treated via the optB88-vdW⁴ functional. A plane-wave cutoff of 500 eV, a 24 Å vacuum along the z-direction, and an 11×11×1 Monkhorst-Pack k-mesh were employed. Structural relaxations were performed until energy and force convergence of 10⁻⁴ eV and 0.01 eV/Å were achieved.

RESULTS AND DISCUSSION

Figure 1 shows the top and side views of (a) Hf₂CO₂/blueP, (c) Zr₂CO₂/blueP, and (e) Sc₂CO₂/blueP heterostructures, along with their corresponding projected band structures in (b), (d), and (f), respectively.

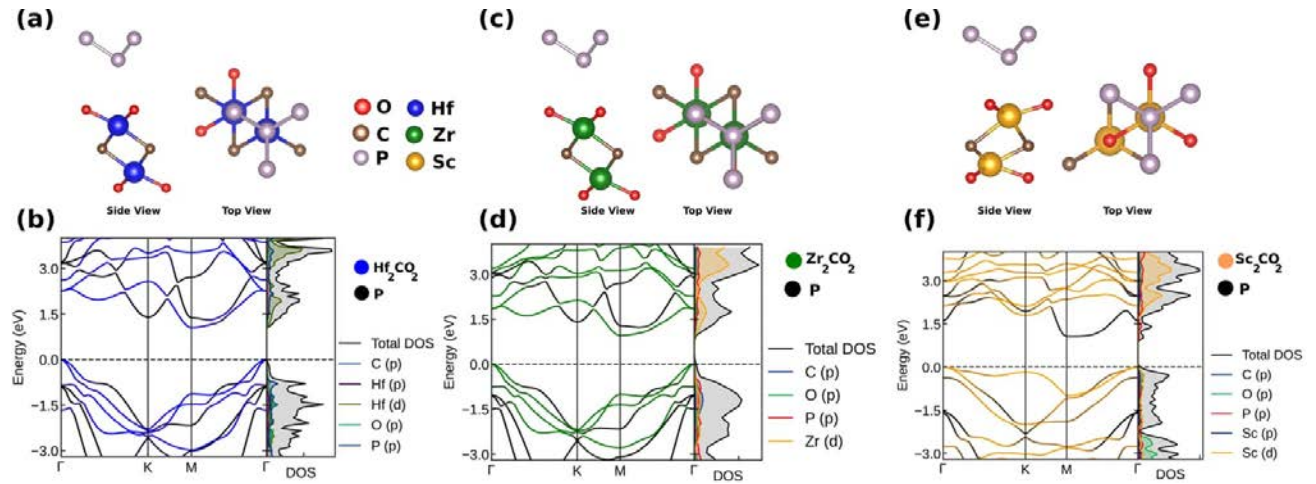


FIGURE 1. Crystal structures of (a) $\text{Hf}_2\text{CO}_2/\text{blueP}$, (c) $\text{Zr}_2\text{CO}_2/\text{blueP}$, and (e) $\text{Sc}_2\text{CO}_2/\text{blueP}$ heterostructures. Corresponding projected band structures and density of states (DOS) are shown in (b) $\text{Hf}_2\text{CO}_2/\text{blueP}$, (d) $\text{Zr}_2\text{CO}_2/\text{blueP}$, and (f) $\text{Sc}_2\text{CO}_2/\text{blueP}$, respectively.

In all cases, the VBM is located at the Γ point, and the CBM at the M point. Projected band structures show that in $\text{Hf}_2\text{CO}_2/\text{blueP}$ and $\text{Zr}_2\text{CO}_2/\text{blueP}$, both VBM and CBM are mainly influenced by the MXene layer, with the VBM originating from C-p and O-p states and the CBM from the d orbitals of Hf or Zr, indicating type-I band alignment. In $\text{Sc}_2\text{CO}_2/\text{blueP}$, the CBM is mainly contributed by blueP (P-p), while the VBM comes from Sc_2CO_2 (Sc-d and O-p), resulting in a type-II band alignment.

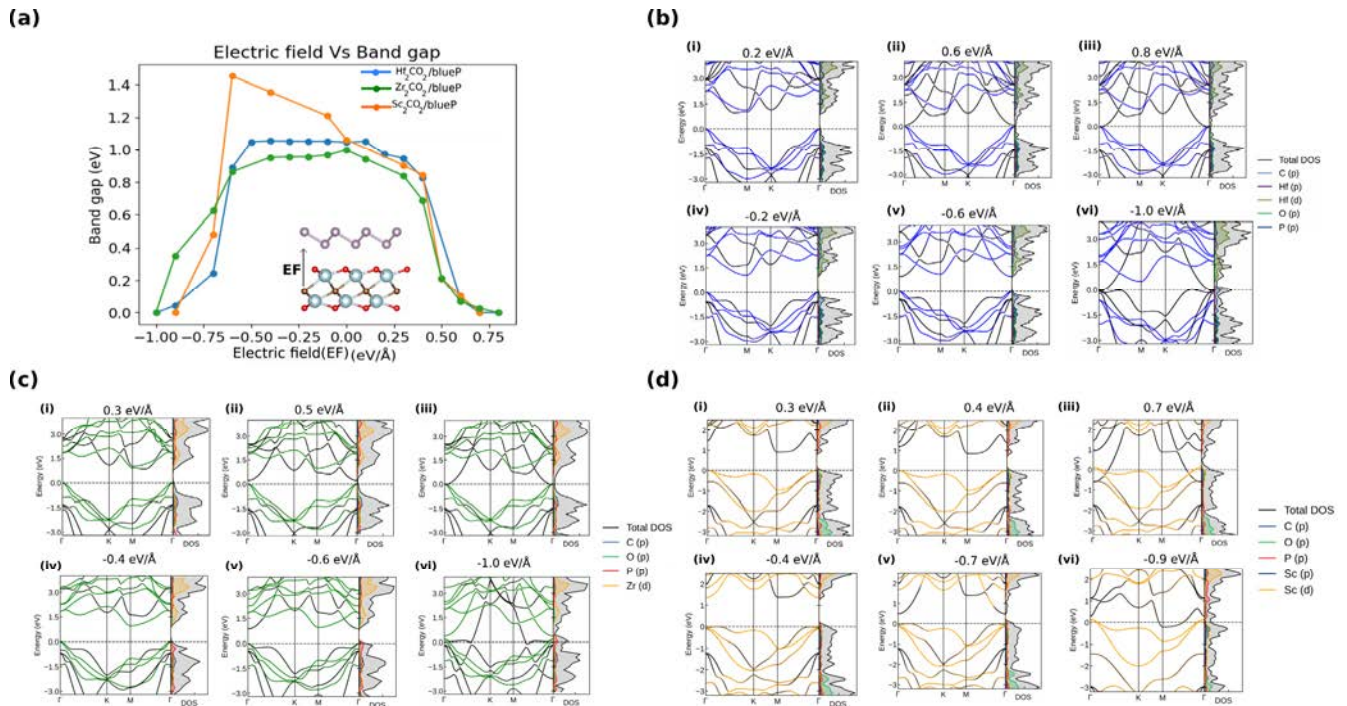


FIGURE 2. (a) Band gap variation of the MXene/blueP heterostructure under applied electric field. Change in band structure with applied electric field for (b) $\text{Hf}_2\text{CO}_2/\text{blueP}$, (c) $\text{Zr}_2\text{CO}_2/\text{blueP}$, and (d) $\text{Sc}_2\text{CO}_2/\text{blueP}$ heterostructures.

To investigate the effect of external parameters on the electronic properties of the MXene/blueP heterostructure, an electric field ranging from $-1.0 \text{ eV/\AA}$ to $+0.9 \text{ eV/\AA}$ was applied perpendicular to the plane. A positive field is applied from Mxene to blueP, and negative in the reverse direction. No structural distortion or bond length change is observed under the field. The band gap varies almost linearly for small electric fields as shown in Fig. 2 (a). In $\text{Sc}_2\text{CO}_2/\text{blueP}$, the band gap increases initially with a negative field, then decreases steadily and becomes metallic near $-0.9 \text{ eV/\AA}$. For positive fields, the gap reduces and vanishes at $+0.7 \text{ eV/\AA}$. This behavior arises from the interaction between the external and built-in electric fields, which either oppose or enhance each other. A transition from indirect to direct band gap occurs at $0.5 \text{ eV/\AA}$. In $\text{Zr}_2\text{CO}_2/\text{blueP}$ and $\text{Hf}_2\text{CO}_2/\text{blueP}$, the band gap remains largely unchanged under small electric fields but decreases at larger fields, leading to metallicity. For $\text{Zr}_2\text{CO}_2/\text{blueP}$, indirect-to-direct transitions occur at $0.5 \text{ eV/\AA}$ and $-0.6 \text{ eV/\AA}$, and type-I to type-II transitions occur at $0.3 \text{ eV/\AA}$ and $-0.6 \text{ eV/\AA}$. In $\text{Hf}_2\text{CO}_2/\text{blueP}$, indirect-to-direct transitions occur at $0.6 \text{ eV/\AA}$ and $-0.6 \text{ eV/\AA}$, while type-I to type-II transitions happen at $0.2 \text{ eV/\AA}$ and $0.6 \text{ eV/\AA}$. Figure 2 (b-d) shows the change of the band structure of the MXene/blueP heterostructure under varying electric fields. These results confirm the strong tunability of band structure and alignment in MXene/blueP heterostructures under external electric fields.

CONCLUSION

In summary, we have systematically investigated the electronic properties of $\text{Hf}_2\text{CO}_2/\text{blueP}$, $\text{Zr}_2\text{CO}_2/\text{blueP}$, and $\text{Sc}_2\text{CO}_2/\text{blueP}$ heterostructures using first-principles calculations, and explored their response to a perpendicular external electric field. All heterostructures exhibit indirect band gaps, with type-I alignment observed in $\text{Hf}_2\text{CO}_2/\text{blueP}$ and $\text{Zr}_2\text{CO}_2/\text{blueP}$ heterostructures, and type-II in the $\text{Sc}_2\text{CO}_2/\text{blueP}$ heterostructure. Upon applying an external electric field ranging from -1.0 to $+0.9 \text{ eV/\AA}$, significant tunability in the band gap was observed. Under an applied electric field, all MXene/blueP heterostructures undergo semiconductor-to-metal and indirect-to-direct band gap transitions, with $\text{Zr}_2\text{CO}_2/\text{blueP}$ and $\text{Hf}_2\text{CO}_2/\text{blueP}$ exhibiting a type-I to type-II band alignment change.

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Structural And Electronic Properties Of $\text{LaSn}_{3-x}\text{Ge}_x$ ($x = 0, 1, 2, 3$) Compounds: DFT Calculation

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Abstract. In this work, we investigate the effect of Ge substitution on the structural and electronic properties of LaSn_3 using density functional theory (DFT). The progressive substitution of Sn with Ge leads to lattice contraction while retaining parent cubic structure. All compounds remain metallic, with dominant contributions from La-*d* and Sn/Ge-*p* states near the Fermi level (E_F). The ground-state properties are obtained by using Birch–Murnaghan equation of state. The calculations reveal that LaGe_3 is thermodynamically and mechanically most stable composition with enhanced density of states (DOS) at Fermi level $N(E_F)$. These results indicate that Ge substitution effectively tunes the stability and electronic properties of LaSn_3 .

1. INTRODUCTION

Rare earth elements based binary compounds attracted significant attention in the realm of material science due to their diverse magnetic, electronic, thermal and optical properties arising from partially filled 4f orbitals. The localized nature of 4f electrons makes an accurate description of the electronic structure of RE compounds particularly challenging [1]. Among them, La-based compounds are particularly important as they lack occupied 4f electrons, making them suitable model systems for studying structure–property relationships. Structural, electronic and mechanical properties of nonmagnetic LaX_3 ($X = \text{Sn, Pb}$) compounds have been studied using DFT by Jisha et. al. [2]. Previous DFT studies have investigated the structural and electronic properties of LaX_3 ($X = \text{Sn, Pb}$) compounds [2], while experimental work has confirmed that LaSn_3 and related intermetallics crystallize in the cubic AuCu_3 -type structure [3]. However, the effect of elemental substitution in LaSn_3 remains largely unexplored. In particular, replacing Sn with Ge is expected to modify the structural and electronic properties due to differences in atomic size and bonding characteristics. In the present work, we report, for the first time, a systematic investigation of Ge doping in LaSn_3 . The structural and electronic properties of $\text{LaSn}_{3-x}\text{Ge}_x$ ($x = 0, 1, 2, 3$), corresponding to LaSn_3 , LaSn_2Ge , LaSnGe_2 , and LaGe_3 , are studied using the full-potential linearized augmented plane wave (FP-LAPW) method within the framework of DFT.

2. COMPUTATIONAL METHODS

The calculations were performed using FP-LAPW[5] method as implemented in WIEN2k code [6]. For the exchange-correlation functional, Perdew-Burke-Eraserhof (PBESOL) in the generalized gradient approximation (GGA) is used. LaSn_3 compound crystallizes in AuCu_3 -type structure with Wyckoff positions La = (0, 0, 0) and Sn = (0.5, 0.5, 0)[2]. The lattice parameter is optimized using volume optimization method. The calculations were performed over a mesh of 500 k-points. The core cut-off energy which separates of core and valence states was chosen as -0.6 Ry. The charge convergence was set to 10^{-4} Coulomb/cell and the wave functions in the interstitial region were expanded using plane waves with $RMTK_{max} = 8$, where K_{max} is the plane wave cut-off, and RMT is the smallest of all atomic sphere radii. The muffin tin radii (RMT) were chosen as 2.1 au for La, 1.9 au for Sn and 1.8 au for Ge. For Ge doping, $3 \times 1 \times 1$ supercell was constructed.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

LaSn₃ crystallizes in cubic $AuCu_3$ -type structure with space group $Pm-3m$. To study structural properties, we first performed volume optimization by calculating the ground state energies of LaSn₃ at different unit cell volumes. Then we applied Birch-Murnaghan equation of state[7] fit to energy vs. volume curve. This gave lattice constant 4.812 a₀, which is in good agreement with previous experimental as well as theoretical studies (See Table 1). To study the structural changes on replacing Sn with Ge, we constructed 3x3x1 supercell of LaSn₃ with three different doping configurations: LaSn₂Ge, LaSnGe₂ and LaGe₃. All these compounds were found to stabilize in parent cubic structure. The Birch-Murnaghan fitting for all of these compounds yielded ground state properties viz. lattice constant (a₀), optimized volume (V₀), bulk modulus (B) and its pressure derivative (B') as summarized in Table 1.

It can be observed that replacing Sn with Ge reduced lattice constant which is consistent with the smaller atomic radius of Ge compared to Sn. This lattice contraction leads to enhanced orbital overlap and stronger interatomic interactions. The value of bulk modulus which indicates mechanical stability is highest for LaGe₃. This can be attributed to the reduced lattice parameter and the increased directional bonding character introduced by Ge, which will strengthen the overall bonding. Whereas, LaSnGe₂ with least bulk modulus is most compressible possibly due to coexistence of unequal La-Sn and La-Ge bond lengths which will introduce local strain, thereby weakening the bond strength. The highest value of B' for LaGe₃ indicated that it possesses high resistance to compression under applied pressure.

TABLE 1. Calculated lattice constant (a₀), optimized volume (V₀), energy in Rydberg (Ry), bulk modulus (B) and its pressure derivative (B'), formation energy, DOS at the Fermi level N (E_F) for LaSn₃, LaSn₂Ge, LaSnGe₂ and LaGe₃ compounds .

Solids	Work	a ₀ (Å)	V ₀ (bohr ³)	Energy (Ry)	B (GPa)	B'	E _{formation} (Ry)	N(E _F) States/eV
LaSn ₃	Theo.	4.812	752.5503	-54070.0	60.4103	3.4264	-37074.43298	3.143
	Exp.	4.73 ^[3]						
		4.774 ^[4]						
LaSn ₂ Ge	-	4.711	705.5776	-45910.0	63.6734	4.5521	-37074.57008	3.065
LaSnGe ₂	-	4.592	642.166	-37749.9	60.0424	4.1685	-37074.58308	3.018
LaGe ₃	-	4.456	596.8789	-29589.9	69.3062	4.8386	-37074.58908	3.343

Theo. – Theoretical

Exp.—Experimental.

3.2 Formation Energy

The formation energy Ge doped LaSn₃ is given by the following reaction:

$$E_{\text{formation}} = [E_{\text{total}} (\text{LaSn}_{3-x}\text{Ge}) + E_{\text{total}} (x\text{Sn})] - [E_{\text{total}} (x\text{Ge}) + E_{\text{total}} (\text{LaSn}_3)]$$

where E_{total} represents the ground state energies of respective compounds. The calculated formation energies are tabulated in Table 1. LaGe₃ exhibits the most negative value among all compositions. This clearly indicates that LaGe₃ is thermodynamically the most stable phase in the series, owing to its stronger bonding interactions.

3.4 Electronic Properties

The electronic DOS and band structures of LaSn₃ and LaGe₃ along the high-symmetry directions of the Brillouin zone are shown in Fig. 2(a–d). All finite DOS and bands crossing at E_F indicate their metallic nature. The band structures remain qualitatively similar for all four compounds. The states at the Fermi level are mainly contributed by Sn-5p/Ge-4p and La-5d orbitals, indicating hybridization between these states. The DOS at E_F is found to be highest for LaGe₃, indicating a greater availability of electronic states for conduction. This suggests that LaGe₃ exhibits enhanced metallicity compared to the other compositions. The increased DOS at E_F is a result of stronger orbital overlap resulting from lattice contraction and improved bonding interactions.

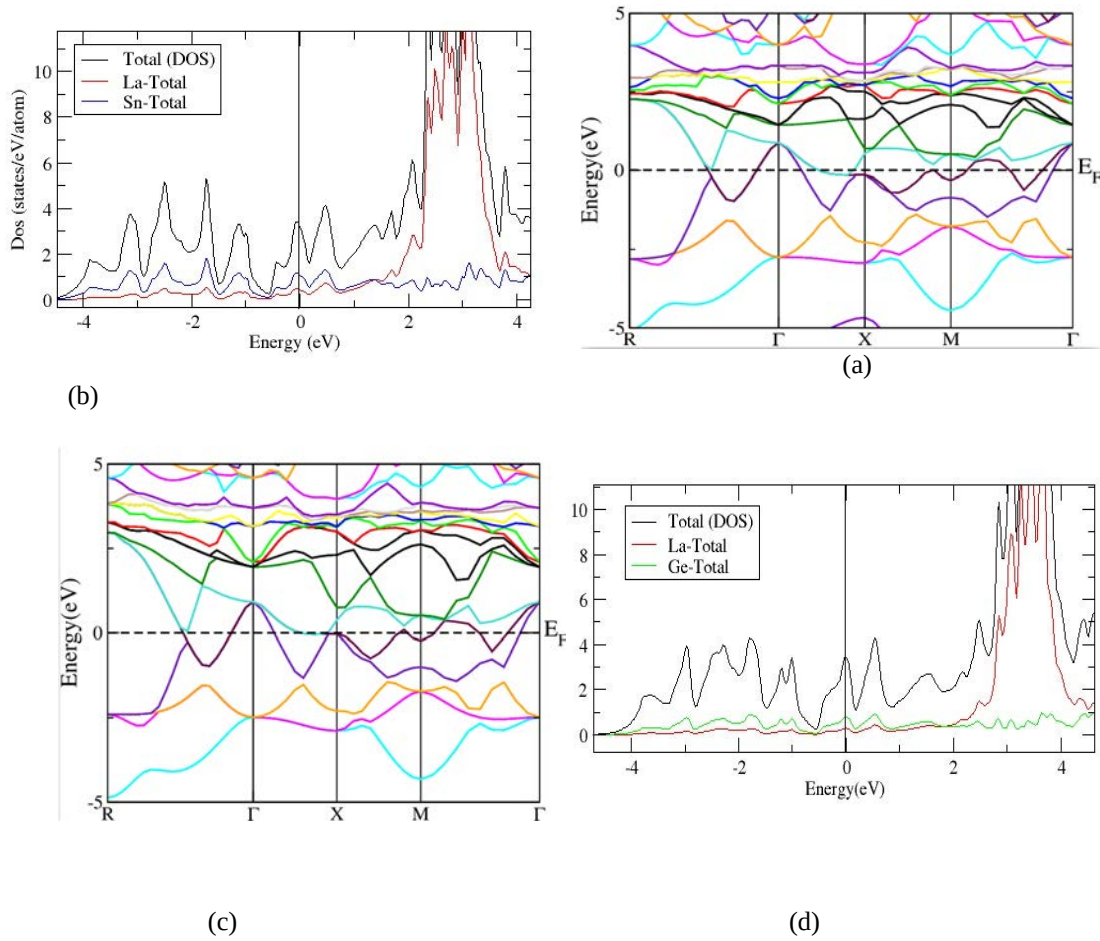


FIGURE 2 (a,b) DOS and Band structure of LaSn₃ **(c,d)** DOS and Band structure of LaGe₃

4. CONCLUSION

We have performed *ab-initio* calculations for the structural and electronic properties of Ge-substituted LaSn₃ compounds. All compounds remain stable in parent cubic structure and are metallic in nature. It is also observed that increasing Ge concentration leads to lattice contraction. LaGe₃ is identified as thermodynamically most stable composition in this series showing highest mechanical stability, resistance to compression and enhanced metallic character. Overall, Ge substitution is found to effectively tune the mechanical stability and electronic properties of LaSn₃, providing insights for the design of related intermetallic materials.

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First-Principle Investigation of the Dynamical Stability, Electronic Structure, Mechanical, and Thermo-Physical Properties of the Ni_3V Intermetallic Compound

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Abstract: First principle calculation was performed to study the structural, mechanical, thermo-physical, electronic and dynamical properties of Ni_3V intermetallic compound. The r phase and five possible geometrically closed pack structures- d0_{19} , d0_{22} , d0_{24} , d0_a and L1_2 were considered to determine the most stable structure of compound. Based on the energy of formation and cohesive energy, d0_a and d0_{22} structure were found to exhibits nearly same stability. Among them, d0_a is most stable, in this present study. The stable structure electronic, mechanic and thermo-physical were determined. The dynamic lattice stability of predicted structure was confirmed with phonon dispersion curve.

INTRODUCTION

The intermetallic compounds are widely used in high-temperature applications like aerospace components, turbine engine and nuclear reactor [1]. The Ni_3X based intermetallic compound are plays a crucial role in the structural stability in the extreme condition. Adding Vanadium, as transitional metal, it gives effective way to enhance the mechanical property, electronic property due to its unique electronic configuration and moderate atomic size. Specifically, Ni_3V has garnered significant interest due to its potential role as a strengthening phase in nickel-based superalloys, as well as its ability to form a variety of ordered crystal structures.

In this work, six known ordered crystal structure of Ni_3V in D0_{19} , D0_{22} , D0_{24} , D0_a , L1_2 and R-phase were chosen to study the stability using first principle calculation. The structural stability of each crystal structure is investigated through the energy of formation and cohesive energy. For the thermodynamically stable structure, mechanical, thermo-physical, dynamical, electronic property has been carried out.

COMPUTATIONAL METHODOLOGY

In this work, first principle calculation was performed using VASP software package with projected augmented wave with GGA-BLYP exchange correlation functional. The kinetic cutoff energy and smearing width were 500 eV and 0.12 eV respectively. The Monkhorst-Pack grids of k-points were optimized which varies with respect to structure. Valance electron configuration for pseudo-atoms was $3\text{d}^8 4\text{s}^2$ for Ni and $3\text{d}^3 4\text{s}^1$ for V. The geometry optimization of performed with respect energy and stress convergence of 5 meV and 100 MPa, respectively. Spin polarized calculation was performed. For dynamic stability of the structures were determined by Finite Displacement Method using phonopy and VASP software. The elastic constants of the structure were determined using energy strain relationship which supports for the determination of mechanical and thermos-physical properties.

RESULTS & DISCUSSION

A. Structural Stability

Figure 1 (a & b) shows the calculated energy of formation and cohesive energy of the chosen structure. All the structures have negative formation of energy in the order of $\text{L1}_2 > \text{D0}_{24} > \text{R-phase} > \text{D0}_{19} > \text{D0}_{22} > \text{D0}_a$. it indicates that D0_a structure (-22.62 kJ/mol) has lowest energy of formation which is thermodynamically stable than D0_{22} structure (-22.33 kJ/mol). The cohesive energy also the confirms that the atomic position and coordination number of

Ni and V in $D0_a$ structure have the higher the binding energy which actually decreases the volume of the structure too. The numerical value of cohesive energy for the $D0_a$ structure is 578.31 kJ/mole and for $D0_{22}$ structure is 578.02 kJ/mol. Experimentally, $D0_{22}$ structure is stable [2]. Present result contradicts the experimental result. Due to less difference in the energy of formation of these two structures and may be the favor of kinetic factor stabilize Ni_3V in $D0_{22}$ structure during solidification.

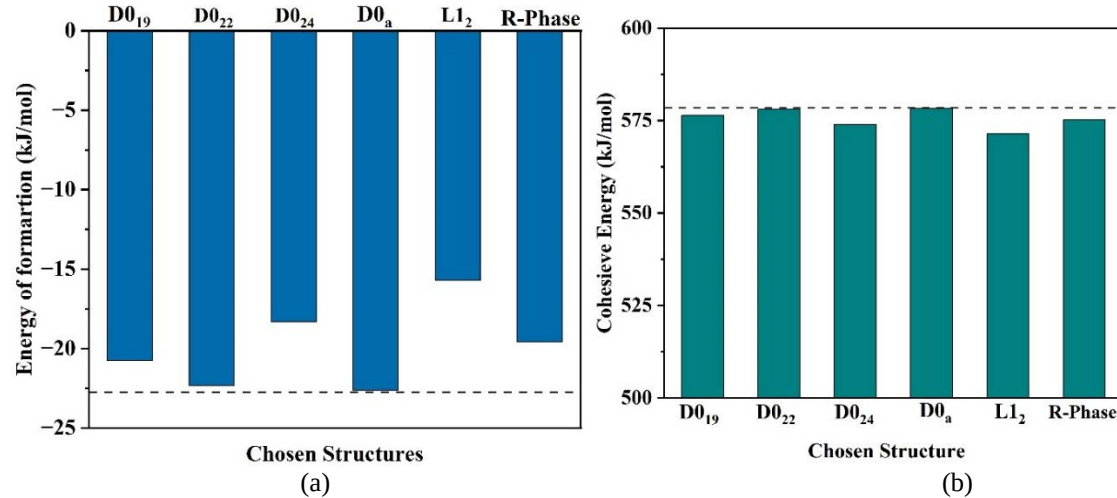


Fig.1. Comparison for Structural stability of chosen structures, (a) Energy of formation and (b) Cohesive Energy.

B. Mechanical Property & Thermo-physical Properties

The Ni_3V - $D0_a$ exhibits in orthorhombic crystal structure. Based on symmetry, orthorhombic has 9 independent elastic constants. The calculated values for elastic constants are as follows (in GPa): $C_{11} = 296$, $C_{22} = 313$, $C_{33} = 291$, $C_{12} = 115$, $C_{13} = 134$, $C_{23} = 124$, $C_{44} = 78$, $C_{55} = 57$ and $C_{66} = 48$. These elastic constants are satisfying the Cauchy-Bon criteria. The elastic moduli have been calculated using Voigt-Reuss-Hill (VRH) approximation. Using elastic moduli, Pugh's ratio, Poisson's ratio, hardness (Chen's and Tian's model) was calculated. The Pugh's ratio of the $D0_a$ structure greater than 1.75 which indicates the ductility in nature.

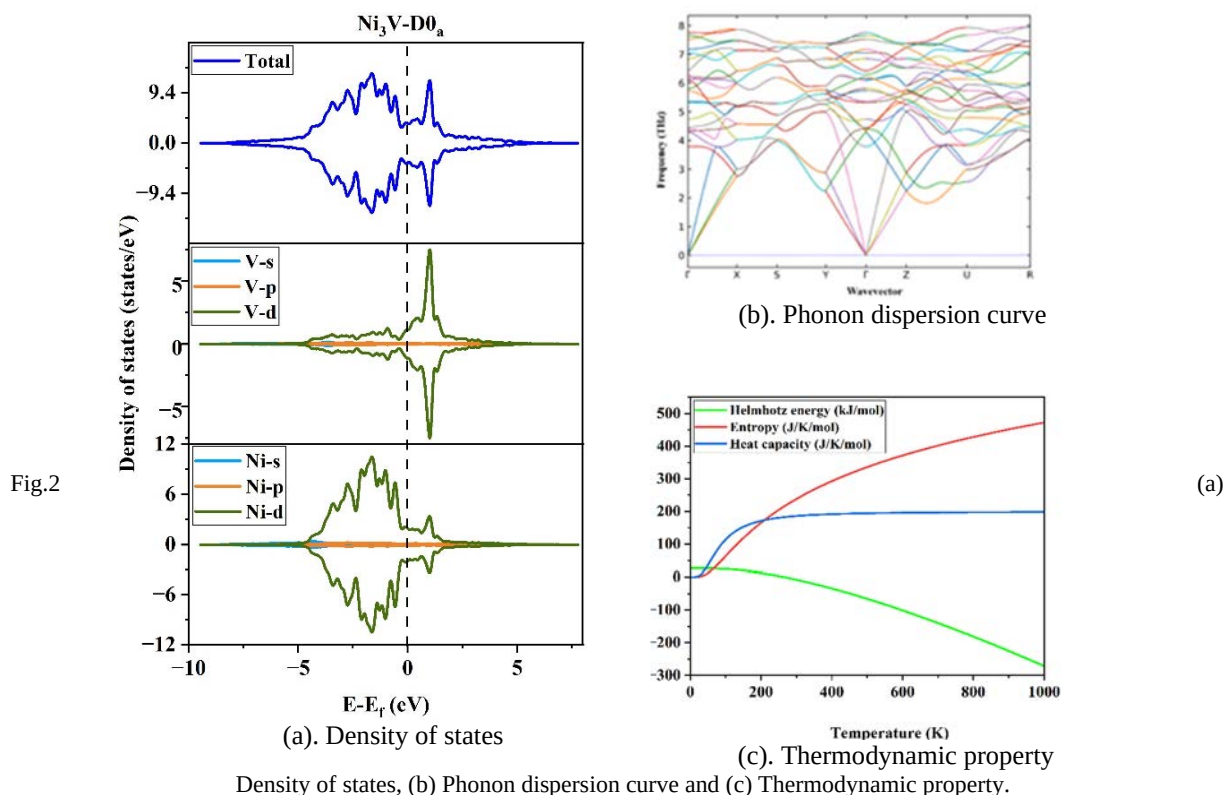
Using the relation between elastic modulus and thermo-physical properties, average sound velocity, Debye Temperature and thermal conductivity (Clarke and Cahil model) were calculated and listed in Table 1.

Table 1. Calculated Mechanical and Thermo-physical properties of binary stable structure.

Mechanical Properties				Thermo-physical Properties		
Bulk Modulus (GPa)	183	Pugh' ratio	2.69	Avg. Sound velocity (m/sec)	3207	
Shear Modulus (GPa)	68	Hardness (GPa)	Chen model	Debye Temperature (K)		406
Young's Modulus (GPa)	181		Tian Model	Thermal conductivity (W/m.k)	Clarke Model	0.99
Poisson's ratio	0.33				Cahil Model	1.96

C. Electronic Structure and Lattice Dynamic Stability

To understand the bonding characteristics, the partial density of states and total density of states stable $D0_a$ structure were calculated and shown in Fig.2 (a). The symmetry in bonding and antibonding, indicates that $D0_a$ is non- magnetic in nature. At fermi energy level, non-zero value confirms the metallic nature. It's clearly observed d-orbitals contribution is more in the case of Nickel and Vanadium. In addition, 3d orbital of Ni and V contributes to fermi surface. Figure 2 (b & c) shows the calculated the phonon dispersion curve and thermal properties such as Helmholtz energy, entropy and heat capacity at constant volume of $D0_a$, using $2 \times 2 \times 2$ supercell size of Ni_3V - $D0_a$. Absence of negative frequency indicates the dynamic stability of the structure.



CONCLUSIONS

In the present work, the stability of Ni_3V in geometrically closed pack structure such as L_{12} , D_{019} , D_{022} , D_{024} , D_{0a} , and in addition R phase were studied via DFT. It indicates, Ni_3V in D_{0a} structure is stable at 0K which differs from the experimentally stable D_{022} structure. The D_{0a} structure shows the electronic, mechanical and thermo-physical properties, indicates the metallic nature the structure is ductile in nature. Phonon studies confirmed the dynamical stability of the Ni_3V in D_{0a} structure.

ACKNOWLEDGMENT

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Formation Energy Prediction of Two-Dimensional Materials Using Machine Learning

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Abstract. The rapid development of two-dimensional (2D) materials has spurred the need for efficient screening of new stable compounds. In this study, we employ machine learning (ML) techniques to predict the formation energy of 2D dichalcogen (MXY), dihalide ($MX'Y'$) and chalcogenide MXX' ($M = \text{Sn, Pb, Sb, Bi}$; $X/Y = \text{O, S, Se, Te}$; $X'/Y' = \text{F, Cl, Br, I}$) single layers (SLs). The geometry optimization of all structures was performed using density functional theory-based electronic structure calculations. The dataset contains the formation energies of 144 Single layers (SLs). We have analyzed the calculated formation energies and found that all the designed SLs are energetically favorable. We use the chemical properties of the elements as descriptors for the prediction. The simplest statistical learning method, linear regression, is applied to 80% of the data, and predictions are made on the remaining 20%. The model performs well at predicting formation energy, as evidenced by an R^2 coefficient of 0.75.

INTRODUCTION

Two-dimensional (2D) materials have gained considerable attention due to their promising applications in electronics, energy storage, and catalysis. The newly emerged Janus layers, derived from traditional 2D SLs, have also attracted significant interest owing to their broken center-of-inversion and mirror-plane symmetries. This asymmetry in the structure generates a built-in electric field normal to the Janus layer surface. The built-in electric field enhances the carrier lifetime by driving them in opposite directions. Therefore, the 2D Janus SLs are well-suited for photocatalytic and photovoltaic applications. The formability of any 2D layer can be analyzed by calculating the formation energy. Formation energy is a thermodynamic parameter that quantifies the stability of a compound relative to its constituent elements in their stable reference states. Traditional methods like DFT, are accurate but computationally expensive for large-scale screening. Machine learning offers an alternative route by learning from known materials to predict the formation energy of new candidates with minimal computational cost. This work integrates first-principles calculations based on DFT with supervised machine learning to develop models for the prediction of formation energy of 2D dichalcogenide MXY , dihalide ($MX'Y'$), and chalcogenide MXX' ($M = \text{Sn, Pb, Sb, Bi}$; $X/Y = \text{O, S, Se, Te}$; $X'/Y' = \text{F, Cl, Br, I}$) SLs. Initially, we discuss the trends in formation energy obtained from DFT-simulated data. Next, we discuss feature selection and descriptor construction, followed by the results obtained with the linear regression model.

COMPUTATIONAL DETAILS

All the DFT calculations were performed using Vienna Ab-initio Simulation Package (VASP)[1]. Projected augmented wave (PAW) pseudopotentials have been used in the calculations. A plane-wave cutoff energy of 500 eV

was employed. Exchange-correlation effects were modeled using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). All the ions are relaxed until the total energy and force converge to 10^{-6} eV and 10^{-3} eV/Å, respectively. A vacuum layer of 20 Å is provided along the c direction to avoid interactions with neighboring images arising from periodicity. The van der Waals interactions were incorporated using the DFT-D3 method.

RESULT AND DISCUSSIONS

In our study, we have considered group-IVA and group-VA post-transition-metal (Sn, Pb, Sb, and Bi) dichalcogenide, dihalide, and chalcogenide structures. All the layers are designed in the 1T-phase in which the metal atomic layer is sandwiched between either two chalcogens (O, S, Se, Te) or halides (F, Cl, Br, and I) and one side chalcogen and the other side halide atomic planes. In a regular (Janus) metal-dichalcogenide or metal-halide SLs, the metal atom will be covered by two chalcogenide or halide atoms of the same (different) electronegativity. In chalcogenide SLs, one of the top and bottom atomic layers will always be a chalcogen atomic layer, whereas the other will always be a halide layer. By considering all the possible combinations, we designed 144 SLs. The formation energy E_f of any SL can be calculated as

$$E_f = E_{SL} - \sum_i n_i \mu_i$$

Here, E_{SL} , n_i and μ_i represent the total energy of the SL, the number, and the chemical potential of the elements in the unit cell of an SL, respectively. The chemical potential of an element is defined as the total energy per atom of its most stable bulk form. The calculated E_f for the group-IVA (Sn/Pb) and group-VA (Sb/Bi) based SLs is given in Fig. 1(a) and (b), respectively. To understand the correlation between the E_f of the Janus SLs and the non-Janus parent SLs, we have drawn the Janus SL versus E_f , and a comparison is made with the average E_f of the parent SLs. Here, we define parent SLs for a particular MXY Janus SL as MX_2 and MY_2 . The calculated E_f for all the designed SLs is negative, indicating that the SLs are energetically favorable. For both the group-IVA and group-VA based dihalide SLs, the E_f of the Janus and the average E_f of the parent SLs are almost equal.

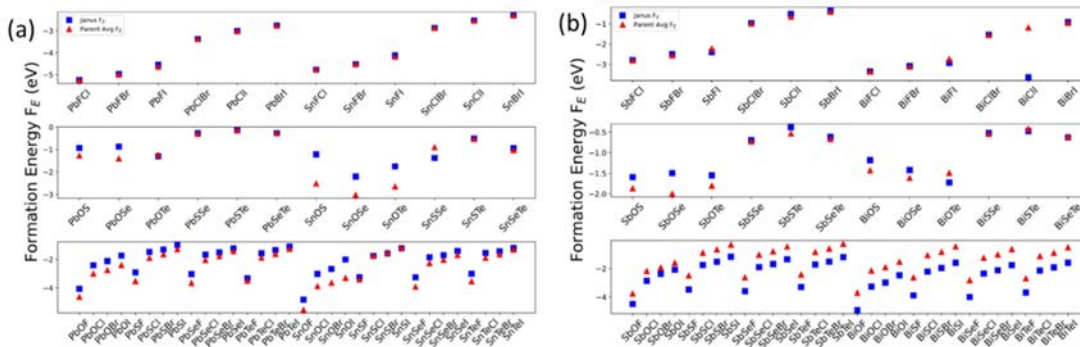


FIGURE 1. The calculated formation energies of (a) Sn- and Pb-based and (b) Sb- and Bi- based Janus SLs in comparison with their parent SLs across three distinct families of dihalides (top row), dichalcogenides (middle row), and chalcogenides (bottom row).

For accurate prediction of any property using an ML model, identifying the features that best describe the data is essential. Herein, we initially collect the elemental features namely, heat of gas-phase formation (HF), covalent radius (CR), specific heat (SP), electronegativity (EN), atomic radius (AR), atomic weight (AW), dipole polarizability (DP), electron affinity (EA), ionization energy (IE), heat of fusion (HS), and valency (VS) for each element. Since we are dealing with SLs with varied elemental compositions, we build compound descriptors based on the identified elemental chemical features. The selection of features and the design of the compound descriptors are done similarly to the work by Kumar et al. [2]. The compound descriptor for each of the SL is defined as $F_C = \frac{F_{X+Y}}{2} - F_M$ where, F_C is the compound descriptor, $\frac{F_{X+Y}}{2}$ is average of the elemental feature of chalcogen/halogen atoms and F_M is the elemental feature of the metal atom.

Using these identified compound descriptors, we train a linear regression model to predict E_f . Of the existing 144 datapoints, 80% (115) were used for training, with the remaining 20% (29) reserved for testing. Model performance was evaluated using RMSE and R^2 metrics, which were 0.56 eV (0.60 eV) and 0.75 (0.82) on the test (training) data. The scatter plot of DFT-calculated versus ML-predicted E_f is shown in Fig. 2. This simplest linear regression model serves as a baseline and provides insight into the linear relationships between features and formation energy. The equation representing the best-fitting linear regression model is as follows:

$$E_f = 0.33 HF + 0.32 SP - 0.24 CR + 0.19 EA + 0.14 AW - 0.05 EN + 0.36 AR - 1.27 IE + 0.08 HS - 0.16 DP + 0.10 VS - 2.09$$

Among all the features, the IE was found to be predictive of the E_f . However, the moderate RMSE and R^2 are partly due to data nonlinearity, which a linear regression model cannot fully capture. Many of the chemical and structural relationships governing formation energy are nonlinear. Thus, linear models tend to underestimate or misrepresent these complex patterns. This limitation emphasizes the need for nonlinear or more flexible machine learning approaches, such as support vector regression and random forest regression.

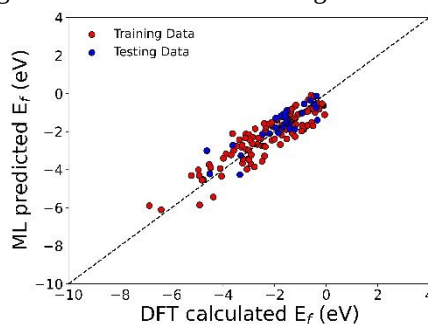


FIGURE 2. The comparison of DFT-calculated and ML-predicted formation energies using a linear regression model.

CONCLUSION

We have designed the 144 2D dichalcogen (MXY), dihalide ($MX'Y'$) and chalcohalide MXX' ($M = \text{Sn, Pb, Sb, Bi}$; $X/Y = \text{O, S, Se, Te}$; $X'/Y' = \text{F, Cl, Br, I}$) SLs and the structural optimization are performed. The formation energies of all the SLs are calculated and found to be negative, indicating their energetic stability. Later, we designed compound descriptors based on the elemental properties of the constituent elements in an SL. Using these compound descriptors, we trained a linear regression model and achieved an accuracy of 75%.

ACKNOWLEDGMENTS

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Multi-Paradigm Comparative Study of H₂ Ground and Excited State Potential Energy Curves Across Classical and Quantum Approaches

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Abstract. Characterizing the ground and low-lying excited-state manifolds of molecular hydrogen remains a critical prerequisite for calibrating emerging computational architectures. This study systematically investigates the H₂ Potential Energy Curves (PEC) across varying bond lengths using two distinct computational paradigms: classical ab initio quantum chemistry Full Configuration Interaction (FCI) via PySCF and quantum simulations using the Variational Quantum Eigensolver (VQE) for ground states and Variational Quantum Deflation (VQD) for excited states, simulated with Qiskit. Classical methods demonstrate characteristic behaviors: RHF exhibits an unphysical dissociation limit, UHF provides a qualitatively better description at stretched bond lengths, and FCI serves as the exact reference for both ground and excited states within the chosen basis set. VQE and VQD simulations yield ground- and excited-state energies in close agreement with exact diagonalization, particularly near the equilibrium bond length. This comparative study provides critical insights into the strengths, limitations, and potential synergies of classical and quantum approaches in computational chemistry.

INTRODUCTION

The hydrogen molecule (H₂) serves as a fundamental benchmark in quantum chemistry for evaluating computational methods, with the accurate determination of its ground-state energy at varying bond lengths being crucial for understanding chemical bonding and dissociation. This work explores the H₂ potential energy curve using a bipartite approach that combines established classical ab initio quantum chemistry methods and hybrid quantum-classical algorithms. Classical ab initio methods, such as Restricted Hartree-Fock (RHF), Unrestricted Hartree-Fock (UHF), and Full Configuration Interaction (FCI), form the foundation of molecular simulations.

The advent of quantum-coherent processors introduces a novel paradigm for circumventing the dimensionality bottlenecks inherent in traditional many-body fermionic simulations. The utility of VQE and VQD for the NISQ era stems from their hybrid architecture, which uses a classical optimizer to navigate the parameter space while relying on quantum-coherent processors for state preparation and measurement, effectively minimizing the depth of the quantum circuits required.

COMPUTATIONAL METHODS

This study employed two distinct computational approaches to the H₂ molecule's ground-state potential energy curve, both using the STO-3G basis set over bond lengths.

Classical Quantum Chemistry Calculations (PySCF)

Mean-field and configuration interaction benchmarks were established using the PySCF computational suite, facilitating a rigorous comparison of established electronic structure methodologies with their quantum counterparts. The fundamental goal is to solve the electronic Schrödinger equation:

$$\hat{H}\psi = E\psi \quad (1)$$

Hartree-Fock methods involve solving the self-consistent field equations, expressed through the Fock operator.

$$\hat{F}\psi_i = \epsilon_i\psi_i \quad (2)$$

FCI accounts for all possible electron configurations by diagonalizing the Hamiltonian matrix in the basis of Slater determinants.

$$HC = EC\epsilon_i\psi_i \quad (3)$$

Variational Quantum Eigen solver (VQE) and Variational Quantum Deflation (VQD) Simulations (Qiskit)

VQE simulations were conducted using Qiskit, IBM's open-source quantum computing SDK, to find the ground state energy of a given Hamiltonian by minimizing its expectation value over a parameterized trial wavefunction, iteratively refining the ansatz parameters navigating through high-dimensional Hilbert space, according to the variational principle.

$$E(\theta) = \langle \psi(\theta) | \hat{H} | \psi(\theta) \rangle \quad (4)$$

The VQD algorithm finds k^{th} excited state by minimizing an objective function that penalizes overlap with previously found lower-energy states, ensuring orthogonality given by:

$$C_k(\theta_k) = \langle \Psi(\theta_k) | \hat{H} | \Psi(\theta_k) \rangle + \sum_{i=1}^{k-1} \beta_i |\langle \Psi(\theta_k) | \Psi_i(\theta_i) \rangle|^2 \quad (5)$$

RESULTS AND DISCUSSION

FIGURE 1 illustrates the ground- and excited-state potential energy curves obtained from classical ab initio methods. The FCI method accurately captures electron correlation effects for both the ground and first three excited states, providing the most accurate potential energy surfaces among the classical methods.

The results from the quantum simulations are shown in FIGURE 2(a) and FIGURE 2(b). For the ground state, VQE (UCCSD) estimated energies show excellent agreement (as expected for H_2 in a minimal basis) with the exact diagonalization curve across the entire range of bond lengths. This demonstrates VQE's ability to achieve high accuracy comparable to that of classical exact methods for small systems, serving as a crucial proof-of-concept for quantum algorithms in chemistry. Similarly, VQD estimated energies for the ground and first three excited states show strong agreement with the corresponding curves from a classical Numpy Eigen Solver (classical exact solver), validating VQD's ability to accurately resolve multiple excited states.

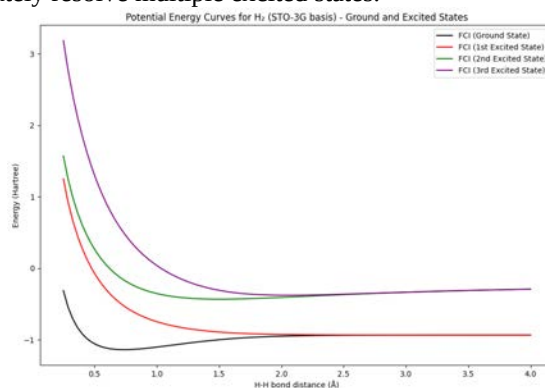


FIGURE 1. Potential Energy Curves for H_2 generated by FCI method using STO-3G basis set.

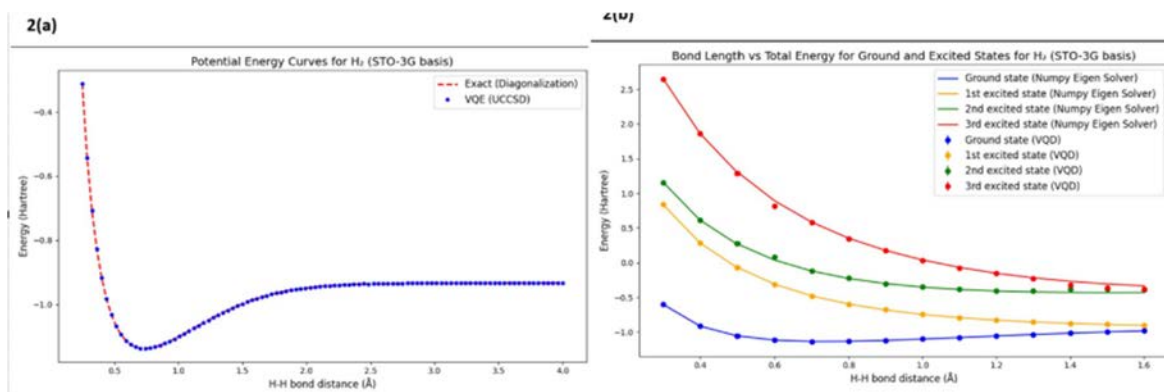


FIGURE 2. Ground and Excited State Energy Curves for H_2 generated by VQE and VQD using STO-3G basis set.

CONCLUSION

This study successfully calculated the H_2 ground state potential energy curve and the first three excited states using classical ab initio methods and quantum simulations. Results showed FCI's accuracy as a benchmark for both ground and excited states. The VQE and VQD simulations demonstrated promising agreement with exact energies for both ground and excited states, particularly near equilibrium, validating their potential for molecular energy calculations across multiple states.

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Vertical heterostructures of ferroelectric BaTiO₃ and topological insulator square tellurene

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Abstract. Herein, we design the BaTiO₃-square tellurene (BTO-Te) van der Waals heterostructure (vdWH) and discuss its structural and electronic properties. BTO is the most studied perovskite oxide, explored for catalytic, piezoelectric, and optoelectronic devices, as well as multi-layer ceramic capacitors. On the other hand, square Te acts as a topological insulator, which has found applications in spintronics. The ultralow lattice mismatch between these layers will be promising for the design of the vdWH. We considered the two surface terminations of BTO: the Ti- and Ba-terminations. The binding energy of the designed vdWH is negative, indicating that it is energetically feasible. To date, the square Te monolayers have not been realized experimentally. The observed negative binding energy indicates that the BTO-001 surface can act as a good substrate for the growth of square Te. We have performed electronic structure calculations including spin-orbit coupling and observed a metallic nature for the two surface terminations, which are promising for electronic device applications.

INTRODUCTION

BaTiO₃ (BTO) is a well-known perovskite oxide that exhibits strong photocatalytic, piezoelectric, ferroelectric, pyroelectric, and optical properties. Even though BTO was discovered more than 70 years ago, the material remains fascinating and is being explored for various applications. The Te monolayers were discovered in 2017 in distinct crystal phases. Since their discovery, due to their thickness-dependent electronic properties and narrow band gap, these layers have been widely explored for photodiode and photodetector applications. In addition, the β -Te monolayers show high thermoelectric performance with a ZT of 6.3. The square Te is a topological insulator with its semi-Dirac Hamiltonian, which can be used in spintronic applications.

The design of vertically stacked heterostructures leads to various fascinating phenomena arising from charge redistribution between different materials. Among various interfaces, oxide perovskites with 2D SL interfaces are of particular interest [1]. The two-dimensional electron gas at the interface of oxide-based heterostructures, arising from oxygen vacancies, will be useful for quantum devices. In this study, by making BTO-Te vdWH, we investigate the structure, binding energy, charge transfer, and electronic properties under two different surface terminations.

COMPUTATIONAL DETAILS

Density functional theory-based calculations are performed using the Vienna Ab initio Simulation Package (VASP) [2]. The projected augmented wave method is used to incorporate the electron-ion interactions. The plane-wave energy cutoff is set to 500 eV. All the calculations are performed within the generalized gradient approximation [3]. The structural optimization is performed until the energy and force convergence tolerances reach 10⁻⁶ eV and 10⁻³ eV/Å, respectively. The DFT-D3 method is used to account for van der Waals interactions. To design the BTO-Te

vdWH, the bulk-BTO is cleaved along the (001) direction. To avoid interactions between images arising from periodic boundary conditions, a 20 Å vacuum layer is provided along the direction normal to the interface.

RESULTS AND DISCUSSION

Before designing the BTO-Te 3D-2D vdWH, we studied the basic electronic properties of the tetragonal bulk BTO and the square Te SLs. The optimized structures of BTO and Te are given in Fig. 1 (a-b and d-e). The lattice parameters of BTO and Te are 3.99 Å and 4.01 Å, respectively. From the electronic band structure calculation, it is found that both have an indirect band gap of 1.77 eV and 0.31 eV, respectively. The lattice mismatch between the layers is calculated and observed to be 2.76%.

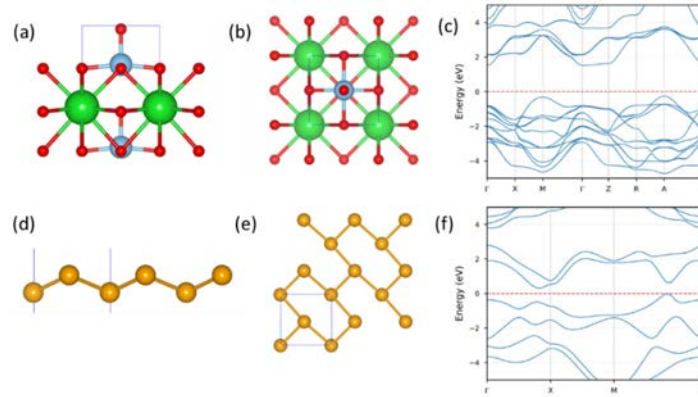


FIGURE 1. The perpendicular (a and d), cross-sectional (b and e) views, and the electronic band structure (c and f) of the optimized bulk BTO and square Te SL. The green, blue, red, and orange colors represent the Ba, Ti, O, and Te atoms, respectively.

The low lattice mismatch between the bulk BTO and 2D Te single layer (SL) satisfies the criterion for designing the vdWH. The vdWH is designed in two distinct configurations, as shown in Fig. 2(a) and (b): one with the Ti and the other with the Ba atomic-layer termination at the interface. The other termination for the BTO surface is always the Ba atomic plane. In-plane relaxation is performed to optimize the vdWH by fixing the BTO lattice constant and straining the Te SL by 2.76%. After the relaxation, it is found that the lattice constants are slightly changed to 4.01 Å and 4.03 Å for Ti-terminated and Ba-terminated vdWH. The optimized distance between the BTO and Te layers is

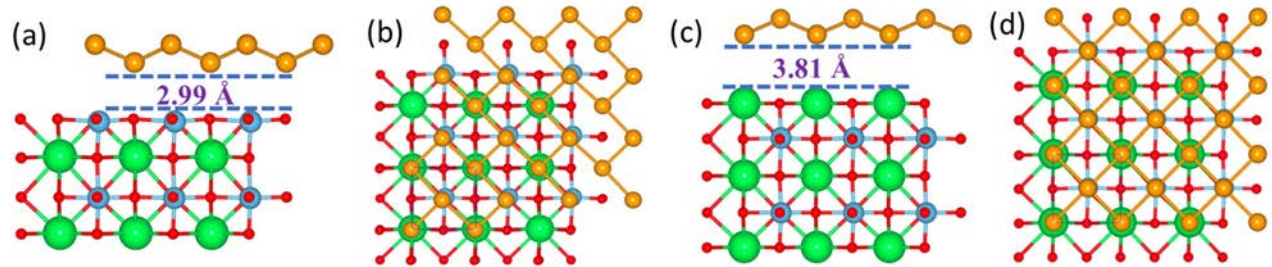


FIGURE 2. The perpendicular (a and c) and cross-sectional (b and d) views of the designed BTO-Te vdWH when the interface termination is Ti and Ba atomic planes. The green, blue, red and orange colors represent the Ba, Ti, O and Te atoms respectively.

found to be 2.99 Å and 3.81 Å, respectively, for Ti and Ba-terminated vdWH. To check the energetic feasibility of the vdWH, we calculate the binding energy E_b using the following formula

$$E_b = E_{vdWH} - E_{BTO} - E_{Te}$$

Here, E_{vdWH} , E_{BTO} and E_{Te} represents the total energies of the BTO-Te vdWH, BTO surface, and Te SL, respectively. The calculated E_b for the Ti- and Ba-terminated configurations are found to be -0.36 eV and -0.34 eV. The negative binding energies for the vdWH confirm its formability. To understand the charge redistribution quantitatively, we perform the Bader charge analysis. In the Ti- and Ba- terminated vdWHs, the observed electron transfer is 0.02e from Te SL to BTO and -0.09e from BTO to Te SL. Thus, based on the surface termination, the built-in electric field in the vdWH switched.

After confirming the energetic stability of the BTO-Te vdWH, we calculate the GGA-level electronic properties and compare them with those of bulk BTO and the square tellurene SL. Unlike the BTO and Te, the vdWH are found to be metallic. From the layer-resolved density of states, it is found that the Te states near the Fermi level dominate the vdWH under both metallic surface terminations. This kind of metallic interface can be promising for electronic devices.

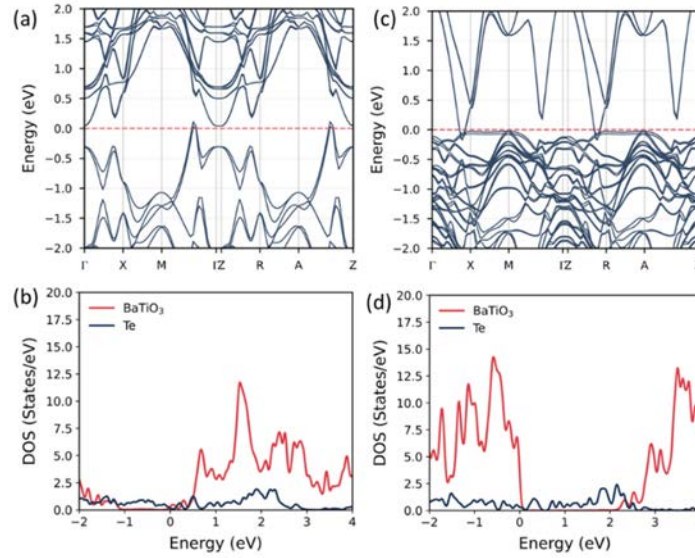


FIGURE 3. The GGA + SOC electronic band structure and layer-resolved density of states (LDOS) of the BTO-Te vdWH with the Ti-termination (a and b) and Ba-termination (c and d) at the interface. The Fermi-level is set to zero.

CONCLUSION

In summary, we have designed the vdWH BTO-Te with two surface terminations and studied their structural and electronic properties. The negative binding energy suggests that both surface terminations are energetically favorable, indicating that BTO can serve as a substrate for the growth of square-Te layers. From the electronic property study, we found that the narrow bandgap of square tellurene drives the vdWH under Ti- and Ba-termination towards a metallic state and that it can be applied in electronics and spintronics.

ACKNOWLEDGMENTS

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Electrical Resistivity of Compound Forming Na-Pb Liquid Alloy

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Abstract. The liquid alloys of alkali metals with lead are of great interest due to compound forming tendency. Sodium-Lead (Na-Pb) system is one of them. One of the features of compound formation is exhibited by a high value of electrical resistivity ($\sim 464 \mu\Omega\text{cm}$ in the case of Na-Pb); hence, a capable theoretical model should be able to reproduce results in its proximity. Well known theoretical model due to Faber and Ziman can not reproduce very high value of electrical resistivity and hence some modification is required to reproduce the correct resistivity isotherm. In the present work, we have coupled the model potential formalism with the t-matrix formulation. Finite phase shifts are calculated using a model potential instead of the Muffin-Tin (MT) potential. The effective valence is treated as a parameter to reproduce the experimental resistivity of pure Na and Pb. The results are in excellent agreement with the experimental results. Present results suggest that compared to the conventionally used approaches such as Faber-Ziman and $2k_F$ scattering model, coupling model potential with t-matrix formalism can reproduce qualitative results of compound forming liquid alloys.

INTRODUCTION

Theoretical study of liquid alloys of alkali metals with lead is of immense interest due to the compound formation tendency. The compound formation in such a system is exhibited by characteristics behavior of several properties such as peak in the mutual diffusion coefficient [1], very high value of electrical resistivity [2] and negative value of temperature coefficient of resistivity [3] around compound forming concentration. As far as the electrical resistivity of liquid alloys of alkali metals with lead is concerned, it is observed that the electrical resistivity of Li-Pb alloy is around $438 \mu\Omega\text{cm}$ [4], that of Na-Pb alloys is $464 \mu\Omega\text{cm}$ [5], that of K-Pb alloys is $978 \mu\Omega\text{cm}$ [6], that of Rb-Pb alloys is $2200 \mu\Omega\text{cm}$ [3] and that of Cs-Pb alloys is $7000 \mu\Omega\text{cm}$ [3] near the compound forming concentration. Meijer et al [3] have observed that the values of electrical resistivity of alkali metal-lead alloys exceeds the limiting value of metallic behavior. It is very difficult for conventional theoretical models such as Faber-Ziman (FZ) [7] or $2k_F$ scattering model [8] to reproduce such high values of electrical resistivity. The reason behind the limitation of FZ model in reproducing the electrical resistivity of compound forming alloys is very well discussed in our recent publication [4] and hence we are not repeating it here. Similarly, $2k_F$ scattering model sometimes overestimates the values of electrical resistivity of such systems [4]; may be because the $2k_F$ scattering model calculates the electrical resistivity in terms of the finite mean free path. The compound formation concentration in alkali metal-lead alloys is not unique but varies. Whereas compound formation is observed in Li-Pb and Na-Pb alloys at around 20% Pb concentration [4,5], a similar feature is observed in Cs-Pb and Rb-Pb alloys at the equi-atomic composition [3]. Most recently, Abdullaev et al. [1] have confirmed the compound-forming tendency in liquid Na-Pb alloys through an experimental study of the mutual diffusion coefficient of Na-Pb alloys, specifically around a 20% Pb concentration. Thakur et al [2] have reported the results of the theoretical study of electrical resistivity of liquid Na-Pb alloys using *ab initio* pseudopotential that reproduces the eigenvalues and wavefunctions very well. Thakur et al [2] have calculated the electrical resistivity of liquid Na-Pb alloys using the interatomic potential obtained through second-order perturbation theory. Recently, we had calculated the electrical resistivity of liquid Li-Pb alloys using model potential formalism coupled with t-matrix formulation [4], in which we have used an alternative approach mentioned in the second section of this work. The results were in very good agreement with the experimental results. Motivated by these facts and our results of the Li-Pb system [4], we have further applied the same method to calculate the electrical resistivity of liquid Na-Pb alloys. The paper is organized as follows. The next section 2 deals with the theoretical formulation, followed by results and discussion in section 3, and the work is finally concluded in section 4.

Method of Computation

While using the t-matrix formulation, the most common method is to obtain the finite phase shifts using the Muffin-Tin (MT) potential [9]. However, in our approach, we have computed the finite phase shifts of pure Na and Pb up to second order using the model potential formalism [4]. The reason behind using this approach is that it allows us to incorporate various forms of model potentials in the actual calculation. One can calculate the t-matrix form factors of pure Na and Pb using these values of phase shifts. Further, using the Ashcroft-Langreth partial structure factors [10] coupled with the t-matrix form factors, one can calculate the electrical resistivity in the entire concentration range using the following equation (1) [4, 9].

$$\rho_{el} = \frac{\pi \Omega_0}{k_F^2} \int_0^1 \left(\frac{q}{2k_F} \right)^3 d \left(\frac{q}{2k_F} \right) |T_{alloy}|^2 \quad (1)$$

Here, Ω_0 is the effective atomic volume, k_F is the wave number and T_{alloy} is the effective t-matrix of the binary alloy, which is calculated using equation (2).

$$|T_{alloy}|^2 = c_i \cdot |t_i|^2 [1 - c_i + c_i a_{ii}(q)] + c_j \cdot |t_j|^2 [1 - c_j + c_j a_{jj}(q)] + c_i \cdot c_j (t_i^* t_j + t_i t_j^*) [a_{ij}(q) - 1] \quad (2)$$

Here, c_i and c_j are the concentrations of pure Na and Pb, respectively such that $c_i + c_j = 1$. $a_{ii}(q)$, $a_{jj}(q)$ and $a_{ij}(q)$ are the three AL partial structure factors corresponding to Na-Na, Pb-Pb and Na-Pb interaction. t_i and t_j are the t-matrix form factors of pure Na and Pb, respectively. In the present work, we have used empty core model due to Ashcroft [11] to incorporate electron-ion interaction and dielectric screening function due to Ichimaru and Utsumi [12], which satisfies the compressibility sum rule in the long wavelength limit. Further, for determining phase shifts of pure Na and Pb, we have used Percus-Yevick (PY) hard sphere structure factor [13]. Rather than treating core radius as a potential parameter, we have used valence of pure Na and Pb as parameters in the calculation. We have obtained core radius for Na and Pb from the known density [4]. Experimental values of density of pure Na and Pb are used in the present calculations [4, 14]. Further, we assumed that phase shifts are independent of alloy concentration. Further, we have ignored the contribution of band energy while calculating the phase shifts. One of the reasons behind treating valence of pure Na and Pb as parameters of the calculations is that anomaly in the density of states near Fermi surface of non-crystalline materials like liquid metal alloys is related to the reduction of valence [4]. Since, the compound formation tendency is observed in the liquid Na-Pb alloy, it is more likely that effective valence may reduce from the ideal value and hence we have treated valence of Na and Pb as parameters in the present work. More details about present work can be found in our recent work [4]. All the calculations are carried out at 700K temperature.

Results and Discussion

In the present work, firstly, we obtained the phase shifts up to second order using model potential formalism instead of MT potential. We have not plotted the presently calculated phase shifts here. But it is clear that the zeroth order phase shift contribute more compared to first and second order phase shift. By fitting the presently calculated electrical resistivity with the experimental results, we obtained $Z = 0.8$ for Na and $Z = 2.4$ for Pb. The reduction in the valence of the non-crystalline materials is already discussed in detail in Ref. [4]. Further, we have estimated the core radius from the experimental density [4,14]. Thus, there is only one parameter of the potential namely valence. Presently calculated t-matrix form factors of Na and Pb are shown in Fig. 1(a). There is not data available for comparison. While calculating electrical resistivity of Na-Pb alloys, we assumed that phase shifts of Na and Pb are independent of alloy concentration. However, since partial structure factors are strongly dependent on alloy concentration, we have obtained the AL partial structure factors for each concentration separately. Finally, the presently calculated concentration dependent electrical resistivity of Na-Pb alloys is plotted in Fig. 1(b) as a function of Na concentration along with the available experimental [5] and other theoretical results [5]. It is clearly observed from Fig. 1(b) that the presently calculated values of electrical resistivity are in excellent agreement with the experimental results [5]. It is clearly seen that the values reported in Ref. [5] using FZ formulation are consistently low compared to the experimental values. The maximum value of electrical resistivity in the experimental database is around $464 \mu\Omega \cdot \text{cm}$, which is generally beyond the metallic behavior. Presently calculated results are not only in very good agreement around the maximum value but also in the entire concentration range.

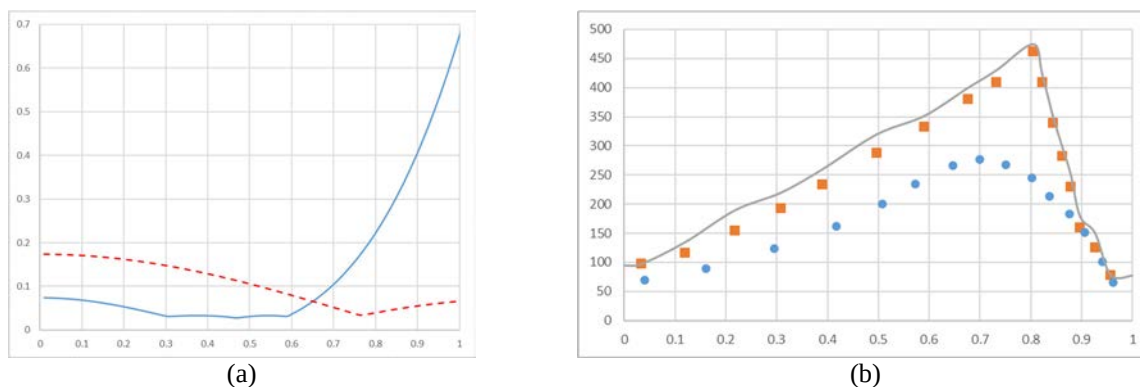


FIGURE 1. (a) Presently calculated t-matrix form factor (R_y) of pure Na (full line) and Pb (dashed line) as a function of wave vector q (au). (b) Presently calculated electrical resistivity of Na-Pb alloys as a function of Na concentration (full line) along with the experimental results [5] (squares) and FZ results [5] (filled circles). Results of complex formation model [2] are not plotted here to avoid complication in reading graph.

Conclusion

In the present work, we have reported the results of our theoretical study of electrical resistivity of compound forming Na-Pb liquid alloys using model potential formalism coupled with t-matrix formulation. The results are in very good agreement with the experimental results. Present method of computing electrical resistivity does not include any fitting process except electrical resistivity of pure Na and Pb with respect to valence. We believe that presently used method can be extended to study electrical transport properties of other compound forming non-crystalline systems as well, with low computational cost.

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Crystallinity and Structural Properties of Tussar and Bivoltine Silk Fibers through X-ray Diffraction [XRD]: A Comparative Study

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Abstract. Silk is a natural, high-strength protein fiber, consisting of a fibroin core and sericin coating. It is characterized by high crystallinity, biocompatibility, and sheen, making it valuable for textiles and biomedical applications. X-ray diffraction (xrd) is used to identify its crystalline structures. This study investigates the effect of irradiation on the crystalline and structural properties of tussar and bivoltine silk fibers using x-ray diffraction analysis. Descriptive statistics revealed that while the primary diffraction peak ($2\theta \approx 20\text{--}21^\circ$) remained unchanged, significant differences in diffraction intensity were observed between the control and irradiated samples. Tussar silk displayed a marked reduction in crystallinity and crystallite size after 5 min irradiation, with only partial recovery at 10 min. In contrast, bivoltine silk maintained a stable crystallite size and exhibited enhanced diffraction intensity and reduced lattice defects at higher exposure, indicating irradiation-induced molecular reorganization. The crystallographic parameters, including crystallite size, d-spacing, microstrain, and dislocation density, confirmed these observations, with bivoltine silk showing greater structural resilience compared to tussar silk. Williamson–hall plots further demonstrated that bivoltine silk accommodated irradiation effects through reduced lattice strain and improved lattice perfection at 10 min exposure.

INTRODUCTION

Silk, a natural protein fiber, has long been valued for its exceptional combination of strength, softness, and luster [1]. Among silk varieties, Tussar and Bivoltine fibers are distinguished by their unique properties and diverse applications. Tussar silk, sourced from larvae of various *Antheraea* species, is prized for its rich, golden texture [2], while Bivoltine silk, produced by *Bombyx mori* cocoons, is smoother and exhibits high tensile strength suitable for performance textiles [3]. Understanding the structural properties of these fibers is critical for optimizing their use across textile, biomedical, and industrial applications. XRD is a powerful technique to probe crystalline architecture, enabling insights into molecular arrangement and degree of crystallinity—key factors impacting tensile strength, elasticity, dye uptake, and thermal behavior [4]. Prior research has established that crystallinity profoundly influences silk fiber performance [5]. This study delivers a comparative XRD analysis of Tussar and Bivoltine silk fibers under varying irradiation (0, 5 min, and 10 min), highlighting differences in peak positions, intensities, breadths, crystallite sizes, microstrain, and dislocation density. Through this comprehensive structural evaluation, the work aims to elucidate how irradiation modulates crystalline order and potential mechanical stability of silk fibers, enabling informed material selection and processing strategies in textile science.

MATERIAL AND METHOD

The X-ray diffraction (XRD) analysis of silk fibers was carried out for the samples of Tussar and Bivoltine for Raw samples (Controlled), 5 Minutes Irradiated samples and 10 Minutes irradiated samples. Each sample undergoes a standard diffraction protocol to ensure the accuracy and reproducibility of results. Tussar and Bivoltine silk fibers were procured from certified sources to maintain sample purity and batch-to-batch consistency. The raw fibers were initially cleaned with distilled water to remove any surface impurities and residual contaminants, followed by air drying at room temperature. Dried fibers were exposed to microwave irradiation to understand the variation in the crystalline structure and study the properties of the silk fibers with various time intervals. The raw and irradiated

samples were tested individually. The silk fiber was mounted on the sample holder, ensuring a flat and even surface to facilitate uniform X-ray exposure during data acquisition. XRD measurements were performed using X-ray diffractometer equipped with a Ni-filtered Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). Instrument calibration was carried out prior to scanning using a standard silicon sample. Diffraction patterns were recorded in the 2θ range of $5^\circ - 60^\circ$ with a step size of 0.02° and a scanning speed of $1^\circ/\text{min}$ under operating conditions of 40 kV and 30 mA. Each sample was scanned to ensure reproducibility. The acquired diffraction profiles were analyzed using SmartLab Studio-II software for peak identification and baseline correction and calculated various parameters like

The crystallite size (D) was calculated using the Scherrer Equation 1,

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where, K is the shape factor (0.9), λ is the X-ray wavelength, β is the Full Width at Half Maximum (FWHM) of the diffraction peak (in radians), and θ is Bragg angle (half of the 2θ peak position).

The Crystallinity Index (CI) of the silk fibers was determined by comparing the integrated intensity of the crystalline peaks with the amorphous region according to the Segal method using Equation 2. These analyses enabled quantitative evaluation of the crystalline and amorphous domains present in the Tussar and Bivoltine silk fibers.

Crystallinity Index (CI)

$$CI (\%) = \frac{I_{\text{crystalline}} - I_{\text{amorphous}}}{I_{\text{crystalline}}} \times 100 \quad (2)$$

Where: $I_{\text{crystalline}}$ = intensity of the main crystalline peak (e.g., $2\theta \approx 20^\circ$ for silk)

$I_{\text{amorphous}}$ = intensity at the minimum between crystalline peaks (amorphous halo)

The parameters estimated for the samples of Tussar and Bivoltine for Raw samples (Controlled), 5 Minutes Irradiated samples and 10 Minutes irradiated samples for comparative study of Crystallinity and Structural Properties.

RESULT AND DISCUSSION

The XRD analysis of the Tussar silk samples, as presented in Table 1, reveals that distinct variations in the diffraction intensity values among the raw and irradiated samples, while the diffraction angles remained constant across treatments. The 2θ angle values, with a median of 32.5° and consistent minimum (5°) and maximum (60°) across all samples, suggest that the fundamental crystalline lattice planes of the silk fibroin remained structurally unaltered by irradiation. This stability in diffraction angles indicates that the crystalline unit cell parameters of Tussar silk are resistant to the low-dose irradiation treatments employed. Analysis of Tussar silk also revealed that consistent diffraction angles ($\sim 32.5^\circ$ median) across control and irradiated samples, indicating stable crystalline lattice parameters unaffected by irradiation. However, intensity—an indicator of crystallinity—dropped from mean 394.1 (control) to 292.9 (5 minutes irradiation), partially recovering to 315.5 at 10 minutes. This pattern suggests chain scission and structural fragmentation followed by limited recrystallization. In contrast, the diffraction intensity, which is closely related to the degree of crystallinity, exhibited notable differences.

TABLE.1. Descriptive statistics of Tussar silk samples

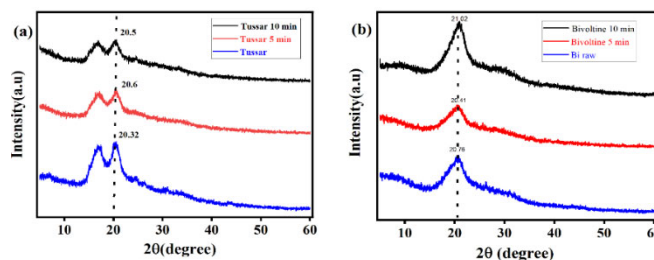
easures	Bivoltine silk samples					
	Control		5 Min. Irradiation		10 Min. Irradiation	
	Angle (2θ)	Intensity	Angle (2θ)	Intensity	Angle (2θ)	Intensity
Min	5	95	5	88	5	101
1 st Qu	18.75	167	18.75	142	18.75	205
Median	32.5	322	32.5	263	32.5	393
Mean	32.5	360.3	32.5	289.4	32.5	409.8
3 rd Qu	46.25	517	46.25	404	46.25	544
Max	60	95	60	708	60	1191

The statistics of the Bivoltine silk samples show in the Table 2. that the diffraction angles (2θ) remain unchanged across the control and irradiated samples, with median and mean values consistently at 32.5° . The control sample exhibited a mean intensity of 360.3 and a maximum intensity of 708, indicating a relatively ordered crystalline structure. After 5 minutes of irradiation, the mean intensity decreased to 289.4, suggesting partial disruption of the crystalline regions. Interestingly, the 10-minute irradiated sample showed a substantial increase in mean (409.8) and maximum (1191) intensities compared to the control, suggesting irradiation-induced reorganization or enhancement of crystalline domains at higher exposure. This indicates irradiation-induced structural reorganization and enhanced β -sheet crystalline alignment in Bivoltine fibers.

TABLE.2. Descriptive statistics of Bivoltine silk samples

Measures	Tussar silk samples					
	Control		5 Min. Irradiation		10 Min. Irradiation	
	Angle (2 θ)	Intensity	Angle (2 θ)	Intensity	Angle (2 θ)	Intensity
Min	5	92	5	83	5	91
1 st Qu	18.75	170.5	18.75	144.5	18.75	156
Median	32.5	355	32.5	276	32.5	295
Mean	32.5	394.1	32.5	292.9	32.5	315.5
3 rd Qu	46.25	541.5	46.25	397	46.25	443
Max	60	1109	60	740	60	719

When comparing the two silk varieties, Bivoltine silk exhibited a higher recovery and even enhancement of diffraction intensities at 10 minutes of irradiation, unlike Tussar silk, which showed only a minor recovery but remained below the control level. This indicates that Bivoltine silk fibroin structures may be more responsive to irradiation-induced molecular rearrangements, leading to an increase in crystalline order at higher exposure times. The XRD patterns from figure 1. Indicates that Bivoltine and Tussar silk fibers (control, 5 min, and 10 min irradiated) exhibit distinct changes in diffraction intensity, while the diffraction angles remain largely constant. For Bivoltine silk, the control sample shows moderate crystalline peak intensity around 20–22° (2 θ), which decreases after 5 min of irradiation, indicating partial disruption of crystalline domains. However, at 10 min irradiation, the peak intensity is significantly enhanced,

**FIGURE.1.** XRD patterns of Tussar and Bivoltine silk samples

suggesting irradiation-induced structural reorganization that increases crystallinity. Conversely, Tussar silk shows a more pronounced reduction in peak intensity after 5 min irradiation, and although there is some recovery at 10 min, the intensity remains lower than the control, indicating a net decrease in crystalline order. The presence of sharp peaks in both silk types confirms the coexistence of crystalline β -sheet structures with amorphous regions, with Bivoltine silk demonstrating greater resistance and adaptability to irradiation effects compared to Tussar silk.

CONCLUSION

The XRD analysis of Tussar and Bivoltine silk fibers under varying irradiation treatments clearly demonstrates that the two silk types exhibit distinct structural responses. Both fibers maintained their characteristic β -sheet crystalline peaks around 20–21° (2 θ), with only minor shifts in d-spacing, indicating that the fundamental crystalline lattice remained largely intact. However, significant differences were observed in crystallite size, diffraction intensity, and lattice strain. Tussar silk showed a pronounced reduction in crystallinity and crystallite size after 5 min irradiation, with only partial recovery at 10 min. In contrast, Bivoltine silk maintained stable crystallite size across all treatments and exhibited enhanced crystallinity and reduced lattice defects at 10 min irradiation, suggesting irradiation-induced molecular reorganization rather than structural degradation.

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Dual Spin-Dependent Band Alignment In $\text{CrCl}_3/\text{CrHO}_2$ 2D Heterostructure For Photocatalysis: A DFT Study

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Abstract. This work presents the Two-dimensional spin-filtered Heterostructure present significant opportunities for next generation photocatalytic technologies. In this work we explore the photocatalytic potential of a $\text{CrCl}_3/\text{CrHO}_2$ Heterostructure for water splitting using first principles calculations. This system demonstrates a distinctive dual band-alignment behavior, exhibits type-I (straddling) alignment in a specific spin channel and type-II (staggered) alignment for the opposite spin channel. Such spin-dependents alignments result to efficient spatial charge separation, which is crucial for enhancing photocatalytic activity. The synergy of strong spin filtering, favorable band edge positions which enhanced charge separation indicate that the $\text{CrCl}_3/\text{CrHO}_2$ heterostructures is highly promising for spin-polarized photocatalysis and advanced water splitting applications.

INTRODUCTION

We construct a Two-dimensional (2D) van der Waals (vdW) heterostructures by vertically stacking different monolayers exhibits highly tunable electronic, optical and magnetic properties. Here, we propose a two-dimensional (2D) van der Waals heterolayers of CrCl_3 and CrHO_2 , a chromium trihalide, exhibits intrinsic ferromagnetism along with semiconducting properties, while CrHO_2 is a chromium based oxyhydride with complementary electronic properties, suitable for Hetero-structure design. We Employ density functional theory (DFT) within SIESTA framework, we investigate the spin polarized electronic structure and photocatalytic potential of the $\text{CrCl}_3/\text{CrHO}_2$ Hetero-structures **Our results reveal spin-dependent type-I and type-II band alignments [1], enabling efficient spin-selective charge separation. This dual alignment behavior suggests that the $\text{CrCl}_3/\text{CrHO}_2$ heterostructure is a promising material for spin-polarized photocatalysis and water-splitting applications.**

COMPUTATIONAL DETAILS

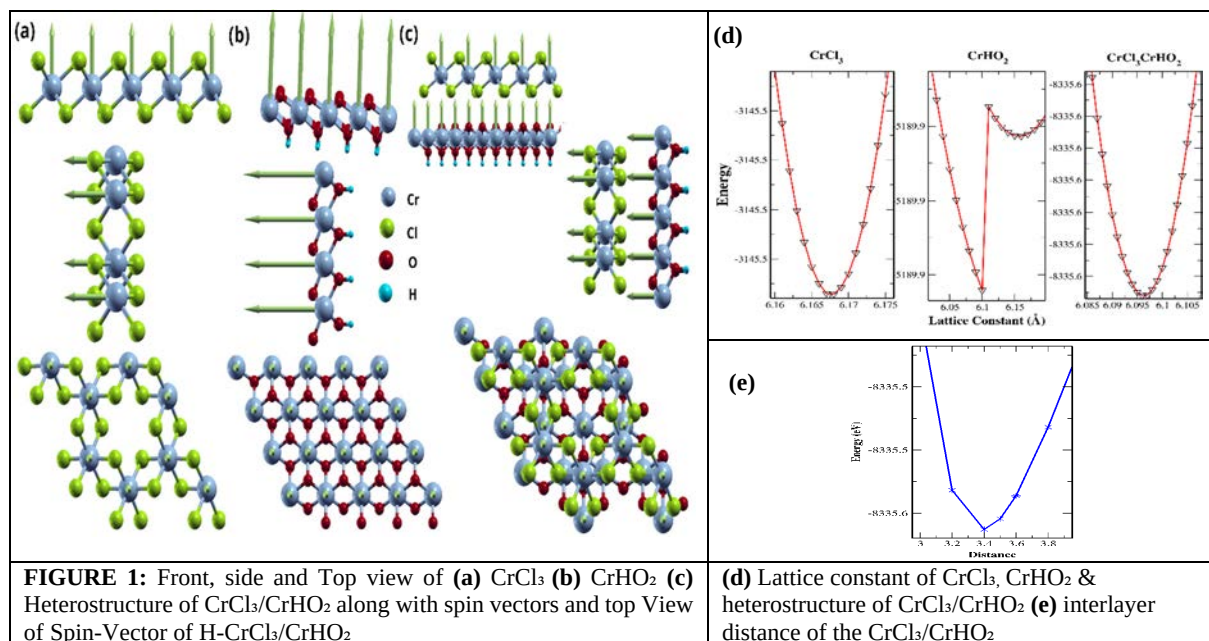
We performed all the simulation using the localized atomic orbital basis set within the DFT framework as implemented in SIESTA[2]. We used norm-conserving pseudopotentials to model core-valence interactions and applied the PBE functional of GGA for exchange-correlation interactions. The Brillouin zone was sampled using a $15 \times 15 \times 1$ Monk-horst-Pack mesh, with 800 Ry cutoff. To avoid unwanted interactions between layers, a 20 Å vacuum was added along the z-axis. Structural relaxation with forces converges at 0.01 eV/Å was done at fixed cell volume, optimizing only atomic positions.

RESULTS AND DISCUSSION

Structural properties

The relaxed geometries of the individual 2D monolayers CrCl_3 , CrHO_2 and the heterostructure of $\text{CrCl}_3/\text{CrHO}_2$ are shown in **FIGURE 1(a-c)**. Both monolayers maintain stable planar geometries and the stacked heterostructure exhibits a clean interface without structural distortion. The optimized lattice constants are 6.168 Å for CrCl_3 [3], 6.09 Å for CrHO_2 , and 6.10 Å for the heterostructure is illustrated in **FIGURE 1(d)**. To evaluate thermal and structural stability, we calculated the binding energies of the monolayers. CrCl_3 and CrHO_2 show binding energies of -2.3636 eV and -4.0892 eV respectively, as listed in **TABLE 1**, suggesting that Both materials are indicating structurally

robust and energetically favorable, moreover, the calculated formation energy of the heterostructure is -3.7308 eV, indicating that the stacking of CrCl₃ and CrHO₂ is strongly energetic stable and thermodynamically stable.



Electronic and Magnetic Properties

All considered system shows magnetic behavior with their spin moment as present in **TABLE 1**. The ideal CrCl₃ and CrHO₂ isolated monolayers shows magnetic moment of 6.0 μ_B and 12.0 μ_B , with combined heterostructure gives rise to a combined spin moment of 18 μ_B . The observed magnetism is primarily arising from Cr atoms, as illustrated in the **FIGURE 2**. Where the Cr D-orbitals accounts for the majority of the total magnetic moments. The work function calculations further indicate pronounced spin-dependent behavior, CrHO₂ is characterized by the highest work function (-4.699), followed by heterostructure (-5.1382) and CrCl₃ (-5.808 eV). The variation in work function enables efficient inter layers charge transfer through the interface.

TABLE 1: The optimized lattice parameter (a), binding energy (E_b), energy band gap (E_g) and work function (Φ) for the 2D structures of CrCl₃, CrHO₂ and their eterostructure

Materials	a (Å)	E_b (eV)	E_{for} (eV)	E_g (eV)	(Φ) (eV)	μ (μ_B)
2D CrCl ₃	6.168, (6.056) ^[3]	-2.3636	—	1.414(↑), 4.37(↓), [2.06(↑) 4.63(↓)] ^[4]	-5.808	6.0
2D CrHO ₂	6.010	-4.0892	—	1.404(↑) 4.051(↓)	-4.699	12.0
CrCl ₃ /CrHO ₂	6.096	—	-3.7308	1.348(↑) 3.566(↓)	-5.138	18.0

The spin-resolved electronic band structures and the corresponding total and projected density of states (T/PDOS) for all systems are presented in **FIGURE 2**, with the spin-dependent band gaps summarized in **TABLE 1**. As illustrated in **FIGURE 2(a-c)**, the CrCl₃/CrHO₂ heterostructure demonstrate a distinct a spin-dependent band alignment. For the spin up channel valance band maximum (VBM) and conduction band minimum (CBM) confined to the CrHO₂ layers indicating type-I (straddling) alignment well suited for the optoelectronic applications such as LED. In contrast the spin down channel reveals a type-II (staggered) band alignment, where electrons are localized in the CrCl₃ layers while the holes are confined on CrOH₂. This efficient separation of charge carriers enhanced interlayers charge transfer and substantially improves photocatalytic functionality.

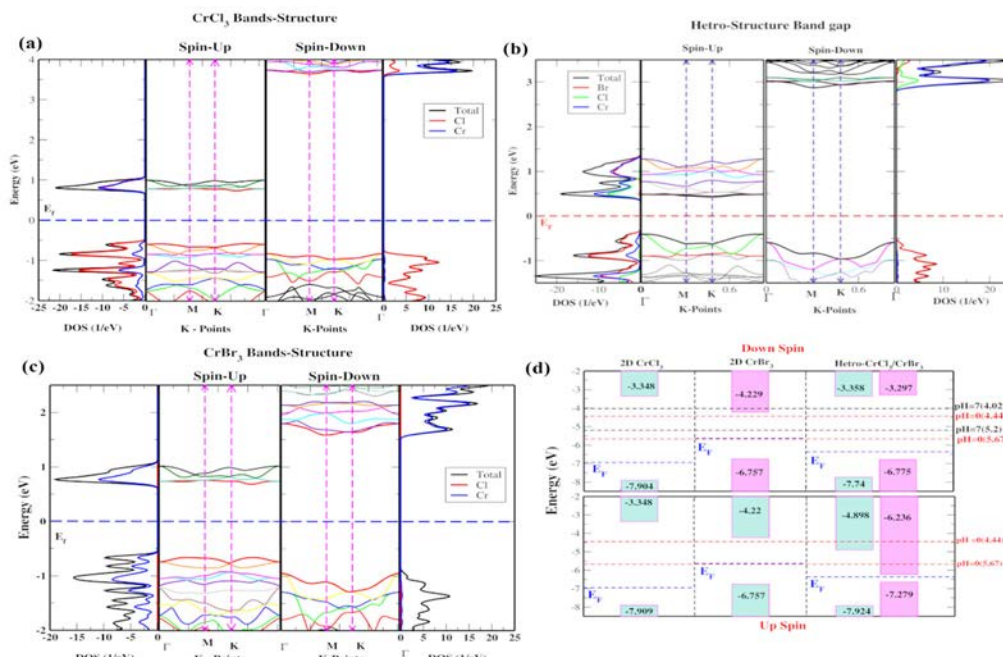


FIGURE 2. Electronic Spin-Up and Spin-Down bands structures and Density of states of (a) CrCl₃, (b) CrHO₂,

Such dual spin-controlled behavior confers exceptional, versatility to the heterostructure. It promotes spin selective separation of charge carriers. Which makes the material a promising candidate for spin-polarized photocatalysis, particularly water splitting reactions, while simultaneously offering strong potential for emerging optoelectronics devices [5]. The tunability of electronics properties through spin and interlayers interactions highlighting its relevance for next generation clean energy technologies

CONCLUSION

Taken together, our DFT-based spin polarised investigation reveals that the CrCl₃/CrHO₂ heterostructure features unique dual band-alignment behaviour, revealing type-I alignment in the spin-up channel and type-II band alignment in the spin down channel. Such spin-dependent electronic alignment drives efficient charge separation, with electrons predominantly occupying CrCl₃ and holes distribution favouring CrHO₂, such behaviour demonstrates strong potential of the materials for next generation spin polarised photocatalysis making it particularly suitable for solar energy conversion and water splitting applications.

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Study of Hysteresis Scaling Exponent Behavior in Fe Modified BaTiO₃

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Abstract. In the present work, ferroelectric hysteresis dynamics have been studied for Fe-modified Barium titanate (BaTi_{0.98}Fe_{0.02}O₃). A comparative study has been carried out with respect to the behavior of the internal bias field present in the sample. The cause of ageing in the present sample is due to the charge imbalance between Fe³⁺ and Ti⁴⁺. We have studied the hysteresis scaling exponent behavior by considering $\langle A \rangle \propto E^n$ and $\langle A \rangle \propto (E + E_i)^n$, respectively, where A is the area of the hysteresis curve, E is the applied field, and E_i is the internal bias field. It has been found that the relation $\langle A \rangle \propto (E + E_i)^n$ holds for aged samples.

INTRODUCTION

The evolution of the hysteresis loop as a function of temperature, frequency, applied field, etc., has gained significance since it provides important details about ferroelectric materials, which can be utilized in a variety of applications, i.e., memory devices, actuators, etc. [1, 2]. The hysteresis area $\langle A \rangle$, defined as the dynamic hysteresis, which is dependent on the frequency and the field amplitude, has emerged as a significant factor in various applications where performance is linked with the signal's frequency and the amplitude. As a result, the scaling behavior is an important factor for predicting the behavior of high-frequency hysteresis in various devices [2,3,4].

The formula used for scaling power law is given as

$$\langle A \rangle \propto f^m E^n T^{-\gamma} \sigma^p \quad (1)$$

Here, A represents the hysteresis area, f indicates the frequency, E denotes the applied field, T signifies the temperature, σ stands for stress, and m, n, γ, p are the exponents, which depend upon symmetries, dimension, etc. [1, 3, 4]. The past literature [1-5] discusses the scaling factor and its significance in the investigation of various ferroelectric materials, including ceramics, thin films, single crystals, and liquid crystals. However, in the literature, the evolution of pinched hysteresis loops is rare and not explored in detail. Such a pinched loop is the consequence of an oxygen vacancy present in the ferroelectric material and has been well studied in the literature for its potential application [4]. In the present work, we have incorporated the oxygen vacancy in BaTiO₃ (BTO) by the introduction of a small amount of Fe³⁺ at the Ti⁴⁺ site.

When Fe³⁺ is substituted at the Ti⁴⁺ site, due to charge compensation, the oxygen vacancy is formed. This vacancy, along with the dopant ions, forms the defect dipole, which is not switchable with respect to the applied electric field, unlike the intrinsic electric dipole. This leads to the ageing effect, such as the pinching of the P-E loop and reduced remnant polarization [5, 6]. In contrast, this phenomenon is absent in pure BTO (in general) due to the absence of defect dipole. Essentially, due to the presence of the defect dipole, the hysteresis dynamics are likely to be different from pure BTO. In the present work, we have explored the dynamic hysteresis behavior of the pinched loop by considering the effect of the internal bias field (E_i). The XRD analysis, Dielectric, and P-E measurements of the sample were studied and will be reported elsewhere [7].

EXPERIMENTAL DETAILS

For the synthesis of $\text{BaTi}_{0.98}\text{Fe}_{0.02}\text{O}_3$ by the solid-state reaction method, the stoichiometric amounts of Barium Carbonate (BaCO_3), Titanium oxide (TiO_2), and Iron oxide (Fe_2O_3) were weighed and ground for 4-6 hours. The mixed powder was then calcined at 1100°C for 12 hours. The calcined powder was made into pellets after grinding for a few hours. The pellet was sintered at 1250°C for 5 hours. The X-Ray Diffraction (XRD) patterns were detected by Bruker's D8 Advance diffractometer with x-ray wavelength of 0.154 nm ($\text{Cu K}\alpha$). P-E loop measurement was done by using the M/s Radiant Premier-II system.

RESULT AND DISCUSSION

The X-ray pattern (not shown here) shows the single-phase behavior of the present studied sample associated with the tetragonal structure. The obtained room temperature P - E loop for the maximum applied field is shown in the inset of Figure 1(a). It shows the pinched loop, which depicts the presence of an unswitchable defect dipole present in the $\text{BaTi}_{0.98}\text{Fe}_{0.02}\text{O}_3$. The internal bias field, E_i , is basically the shift along the electric field axis from the symmetric position. The evolution of the pinched hysteresis loop as a function of applied field is plotted in Figure 1 (a). The obtained scaling exponents are presented in Table 1. The plot is separated into two regions as $E < 30\text{ kV/cm}$ (Region I) and $E > 30\text{ kV/cm}$ (Region II), on the basis of the best fit to the data. The value of the exponent n is calculated for $\langle A \rangle \propto E^n$. The obtained value of the scaling exponent shows the different behavior for low and high applied fields.

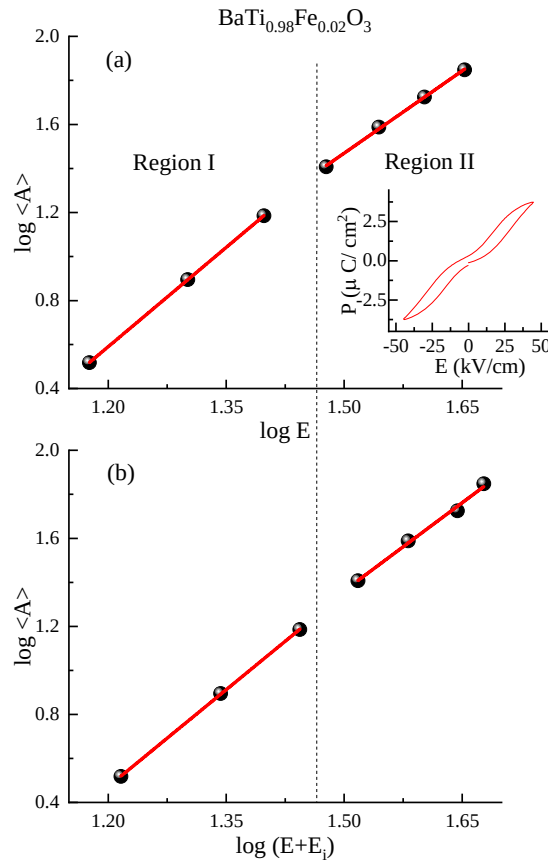


FIGURE 1. (a) Double logarithm plot between the hysteresis area and the applied field (E). (b) Double logarithm plot between the hysteresis area and $E + E_i$, where E is applied field and E_i is internal bias field.

However, in the above procedure, we have not taken into account the internal bias field due to the defect dipole. For such samples, internal bias field is always there along with the applied electric field while measuring the hysteresis curve. Therefore, the relation $\langle A \rangle \propto (E \pm E_i)^n$ holds for our present studied sample. Figure 1(b) shows the scaling

exponent behavior with the inclusion of the internal bias field. The obtained scaling exponents are shown in Table 1. A similar trend has been observed with respect to the applied field in two different regions. However, the obtained value of scaling exponent n for the low field region is the same with respect to E and $E + E_i$, whereas it is slightly different at high field. A possible explanation for this can be understood in terms of the effect of a high electric field on the behavior of the defect dipole.

In summary, the present work reveals the importance of the inclusion of an internal bias field in studying dynamic hysteresis for aged ferroelectric materials.

TABLE 1. The value of the exponent n for the low field and high field regions.

Value of n calculated from $\langle A \rangle E^n$		Value of n calculated from $\langle A \rangle (E + E_i)^n$	
Low field region ($E < 1.5 \text{ kV/cm}$)	High field region ($E > 1.5 \text{ kV/cm}$)	Low field region ($E < 1.5 \text{ kV/cm}$)	High field region ($E > 1.5 \text{ kV/cm}$)
3.000 ± 0.006	2.492 ± 0.056	2.934 ± 0.027	2.660 ± 0.152

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Signature of Stacking Faults and Dislocations in Single Crystal Neutron Diffraction data of Tris-Sarcosine Calcium Bromide

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Abstract. Tris-sarcosine Calcium chloride (TSCC) is a very well-studied hydrogen bonded ferroelectric crystal, Tris-sarcosine Calcium bromide (TSCB) is isostructural to TSCC. These crystals exhibit ferroelastic behaviour at room temperature. These crystals are almost always twinned with (0 1 1) and (0 3 1) planes acting as twin planes. We have performed single crystal neutron diffraction investigations on TSCB, we report here the effects of twinning on the peak shapes of Bragg reflections recorded from a TSCB crystals

INTRODUCTION

Tris-sarcosine calcium chloride ($((C_3H_7NO_2)_3CaCl_2)$) is one of the most extensively studied amino acid-based ferroelectrics [1] which is known to undergo a paraelectric to ferroelectric phase transition at $T_c = 127$ K with crystal symmetry changing from $Pmna$ to $Pm2_1a$ at T_c . An isostructural crystal is obtained when chlorine atoms of TSCC are replaced by bromine, Tris-sarcosine calcium bromide ($((C_3H_7NO_2)_3CaBr_2)$) crystals thus obtained do not undergo any ferroelectric phase transition and their crystal symmetry remains $Pmna$ down to 0K. Both TSCC as well as TSCB crystals have pseudo-hexagonal symmetry when viewed along the “a” axis (figure-1a) and these two-crystal exhibit ferroelastic behaviour at room temperature [2] i.e. they exhibit a spontaneous strain and it can switch between different stable states (ferroelastic domains) in response to mechanical stress. In this manuscript we describe the preliminary results of peak shape analysis performed on single crystal neutron diffraction data obtained from a twinned single crystal of TSCB at room temperature.

EXPERIMENT

Large single crystals of TSCB were grown from aqueous solutions of sarcosine and calcium bromide in 3:1 stoichiometric proportion. Earlier crystal growth and structure studies on TSCC have shown that almost all crystals of TSCC as well as TSCBr grown from aqueous solutions are twinned. Twinning is a result of the pseudo-hexagonal symmetry of these crystals, there are three kinds of twin domains present in these crystals namely domain I, II and III that are separated by (011) twin planes (figure-1b). The (031) twin planes were also observed in these crystals.

A clear crystal of TSCB of approximate dimension 3X3X3mm was loaded on a goniometer which was mounted on the four-circle single crystal neutron diffractometer with BF_3 point detector located at Dhruva Reactor at Trombay. Integrated neutron counts for about 536 Bragg reflections were recorded in the symmetrical setting of the diffractometer using θ - 2θ coupled step scan mode (0.1° step in 2θ). Data consisted of 303 unique (h k l) reflections up to $\sin \theta/\lambda = 0.35 \text{ \AA}^{-1}$ with cell parameters $a=9.241 \text{ \AA}$, $b=17.696 \text{ \AA}$, $c=10.356 \text{ \AA}$, only 95 reflections had significant intensity above 4σ level, indicating that the single crystal was weakly diffracting most likely due to presence of twinning and other crystal defects. Individual Bragg peaks were plotted and their peak shapes were analyzed.

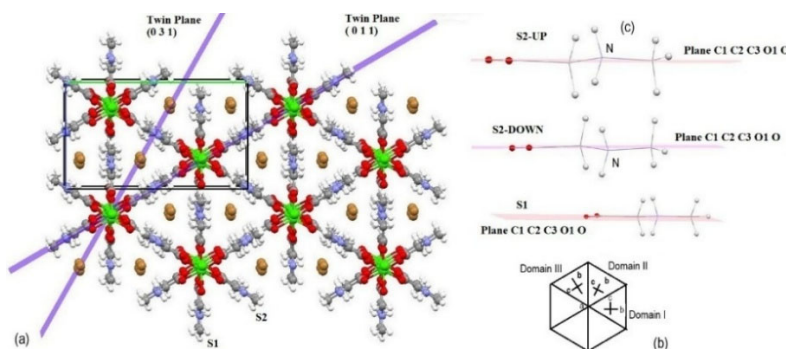


FIGURE 1. Crystal structure of TSCB, S1 and S2 are two types of sarcosine molecules, S1 is planar whereas S2 is slightly non-planar with S2-UP and S2-DOWN being two type of S2 with Nitrogen (N) atom above and below the molecular plane. Three types of domains present in TSCB crystal are also shown.

DISCUSSION

Defects within crystals are known to induce strong distortions in the diffraction patterns [3,4]. One-dimensional defects, or two-dimensional defects cause microstrains, especially when the atoms around the defects need to be slightly displaced in order to match the lattices. As a consequence, the lattice d-spacings are contracted or expanded around the defect, this variation of d-spacings translates into variation of diffraction angle, which leads to the modification in the shapes of diffraction peaks obtained from such strained crystals. Twinning in a crystal is a type of stacking fault where a portion of a crystal lattice is a mirror image of the rest, the plane across which the lattice is mirrored is called the twin plane, twin regions are separated by a region across the twin mirror plane called the twin boundary which can have some degree of structure mismatch with the rest of the crystal.

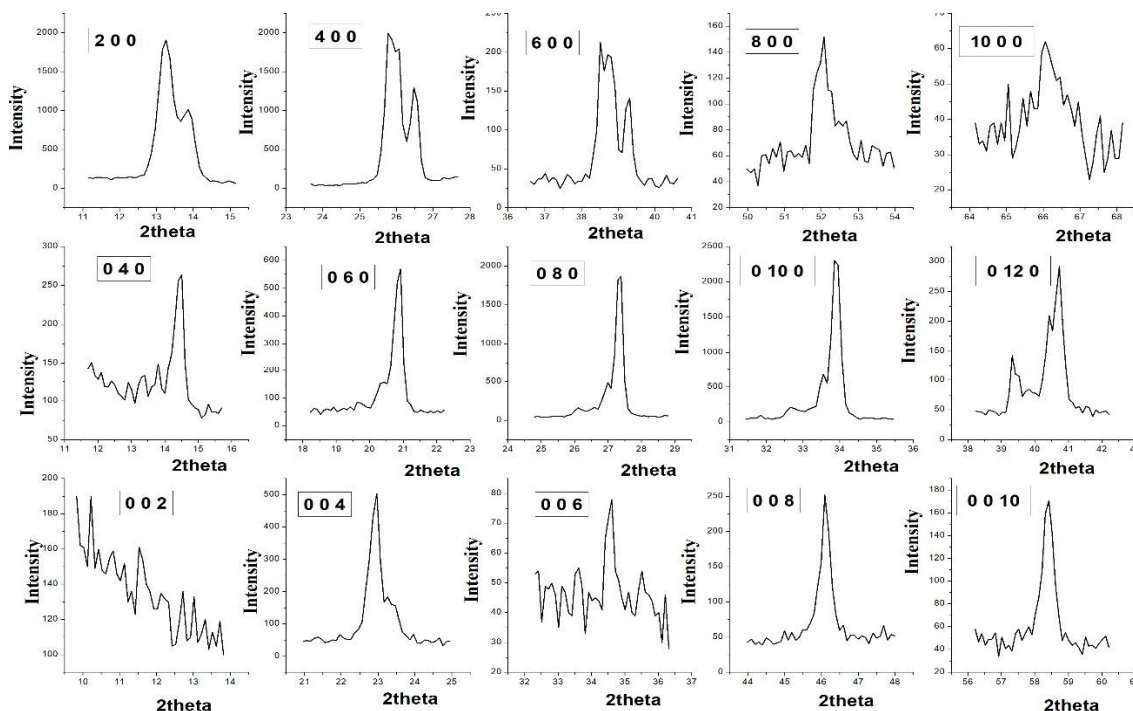


FIGURE 2. Axial Bragg peaks from TSCB

Looking at the crystal structure of TSCB [5] one finds that there are two types of sarcosine molecules present in unit cell, first type labelled S1 has an exactly planar structure (figure-1c) and it lies on a mirror plane, whereas the second type labelled S2 (figure-1c) occupies a general position, it is nearly planar the position of its Nitrogen (N)

atom deviates from the molecular plane containing the rest of the non-hydrogen atoms. Depending on whether N atom lies above or below the molecular plane S2 molecule can have up or down state (figure-1). All sarcosine molecules have their centers of gravity at a height near either $a/4$ or $3a/4$. Erroneous packing of S1, S2-UP and S2-down molecule around the (011) and (031) planes give rise to various twin domains in the crystals of TSCC [2], since TSCB are isostructural to TSCC both the crystals have similar microstructures.

The Bragg peak profiles obtained after neutron diffraction from a large twinned crystal of TSCB were examined keeping the above-mentioned structural description in mind. Peaks profiles for axial reflections ($h00$) ($0k0$) & ($00l$) show significant peak asymmetry (figure-2) indicating the presence of high-density of defects within the crystal. MD Simulation results by Kumar et al [3] have shown that the presence of edge dislocations in single crystals results in diffraction peak asymmetry with peak splitting, increase in dislocation density increases the distance between the split peaks. Comparing the peak profiles of axial reflections of TSCB crystal we conclude that ($h00$) type reflections show maximum peak asymmetry with most peaks showing some degree of peak splitting, this indicates that the dislocation density is highest in a-planes that are perpendicular to both the twin planes (011) and (031). It is known that in crystal when the twin boundary does not cross the entire crystal it is restricted by a dislocation [6], presence of a large number of dislocations in a-planes points towards the existence of complicated network of twin boundaries throughout the crystal.

In a multidomain crystal depending on the combination of domains and domain boundaries, a plethora of different features are observed in the diffraction patterns. Timmer and Wollschläger [7] theoretically demonstrated this by calculating diffraction patterns (figure-3a) from one-dimensional binary array with periodic domain boundaries, due to the presence of domain superstructure new features like diffraction spot splitting and emergence of superstructure diffraction peaks are observed in the simulated patterns. In case of our multidomain TSCB crystal we observed splitting of diffraction peaks from the twin planes (figure-3b). In all likelihood splitting of diffraction peaks from the twin planes of TSCB is a consequence of destructive interference between adjacent domains.

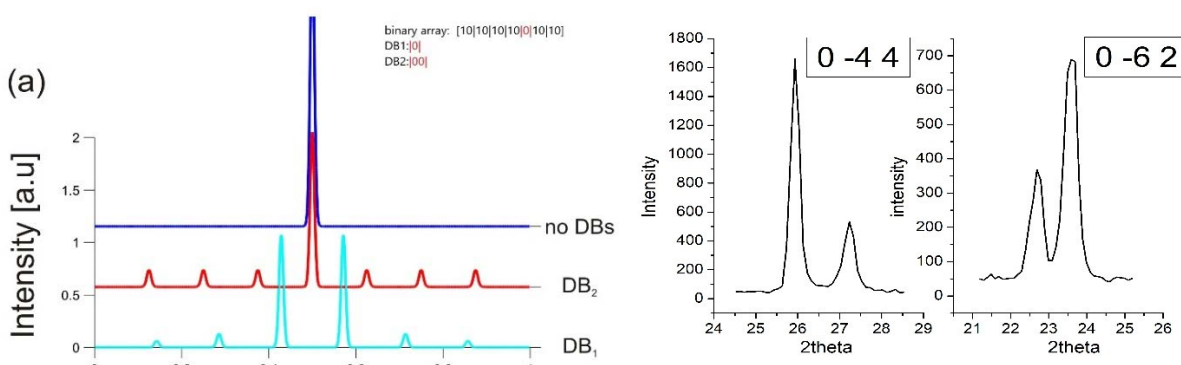


FIGURE 3. (a) Calculated diffraction patterns [7] from one-dimensional binary array with periodic domain boundaries. (b) Splitting of diffraction peaks from the twin planes of TSCB

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Study of Dielectric & Ferroelectric Behavior in Mn Modified BaTiO₃

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Abstract. In the present work, Mn-doped barium titanate, BaTi_{1-x}Mn_xO₃ (x=0.02, 0.05), was studied by means of x-ray diffraction, ferroelectric, and dielectric measurements. Phase-coexistence (tetragonal and hexagonal) has been observed for both compositions. For x= 0.02, a pinched type of ferroelectric hysteresis loop has been observed due to the presence of defect dipole. The origin of the defect dipole can be understood in terms of the generation of oxygen vacancies, created by the charge imbalance of Ti⁴⁺ and Mn³⁺. The transition temperature for x= 0.02 sample comes out to be 395 K. For x= 0.05 sample, typical paraelectric behavior has been observed in *PE* loop at room temperature. However, the transition temperature comes out to be 391 K in temperature-dependent dielectric data, essentially associated with a small fraction of tetragonal phase.

INTRODUCTION

BaTiO₃ (BTO) is one of the most studied ferroelectric materials due to its fascinating dielectric, piezoelectric, and ferroelectric properties over a broad temperature range and the ease of tunability of these properties by suitable doping [1]. BTO exhibits various phase transitions below 120 °C with polarization in different crystallographic directions. The advantage of BTO over Pb(Zr,Ti)O₃, (PZT) is associated with the environmental hazard. PZT has higher piezoelectric properties compared to BTO, but faces challenges due to the toxicity related to Pb [1]. However, it has been found that in aged BTO (single crystal), large functional properties have been found which are comparable with PZT [2]. From the application point of view, it is desirable to have such large functional properties in polycrystalline/ceramic-based Pb-free ferroelectric materials. Therefore, in the present work, we have investigated the structural, dielectric, and ferroelectric behavior of Mn-doped BTO polycrystalline. A comparative study, BaTi_{1-x}Mn_xO₃ (x=0.02 and 0.05), has been taken into account for the same.

EXPERIMENTAL DETAILS

For the synthesis of BaTi_{1-x}Mn_xO₃ (x=0.02, 0.05), we have employed the solid-state method. Stoichiometric amounts of BaCO₃, TiO₂, and MnO₂ have been used for the studied compounds. The required mixture of the above-mentioned precursor was ground using an agate mortar and pestle. The initial grinding was done for 3 hours. After that, the mixed powder was calcinated at 1100 °C for 12 hours. Calcinated powder was further ground for 2 hours, and pellets were prepared from the ground powder using a hydraulic press. The pellets were sintered at 1300 °C for 5 hours. For x-ray diffraction measurement, a Bruker D8 Advance x-ray diffractometer was used. The wavelength of the used x-ray was 1.54 Å (Cu K_α). For the measurement of temperature-dependent dielectric properties, we have used Keysight-E4980AL equipment integrated with a high temperature furnace. Ferroelectric hysteresis loops were measured by M/s Radiant Premier-II system.

RESULT & DISCUSSION

X-Ray diffraction data

Figure 1(a) show the x-ray pattern of $x=0.02$ sample. It has been observed that it exhibits both the tetragonal and hexagonal phases. The corresponding indices related to tetragonal and hexagonal phases are also shown in Figure 1 (a). The x-ray pattern corresponding to $x=0.05$ is shown in fig1(b) and it also shows the coexistence of hexagonal and tetragonal phases. Both the above x-ray pattern is well matched with the literature [3-5].

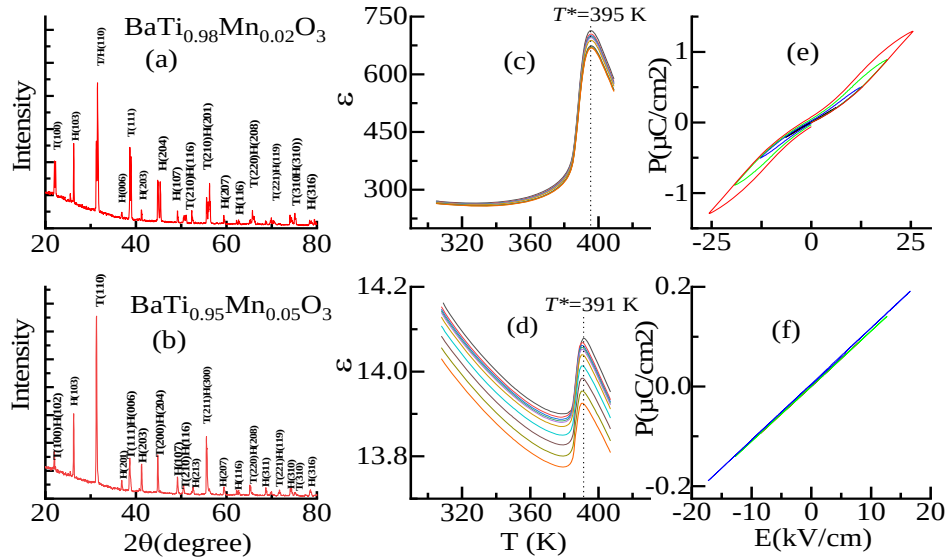


FIGURE 1. XRD pattern along with its miller indices for (a) $\text{BaTi}_{0.98}\text{Mn}_{0.02}\text{O}_3$ and (b) $\text{BaTi}_{0.95}\text{Mn}_{0.05}\text{O}_3$. The plot of dielectric constant as a function of temperature and frequency for (c) $\text{BaTi}_{0.98}\text{Mn}_{0.02}\text{O}_3$, and (d) $\text{BaTi}_{0.95}\text{Mn}_{0.05}\text{O}_3$. Room temperature PE plot of (e) $\text{BaTi}_{0.98}\text{Mn}_{0.02}\text{O}_3$ and (f) $\text{BaTi}_{0.95}\text{Mn}_{0.05}\text{O}_3$ as a function of applied electric field.

Dielectric Behavior

The temperature dependence of dielectric behaviour for Mn-doped BTO was measured at frequencies between 1 kHz and 1000 kHz over a temperature range of 300-410 K. Fig1(c) represent the temperature dependent dielectric behaviour of $x=0.02$ sample and it has been observed that the transition temperature comes out to be at 395 K. Further frequency independence has been observed around the transition temperature which signify the true ferroelectric nature of the studied compound.

Fig. (d) shows the dielectric behavior corresponding to the $x=0.05$ sample, and the associated transition temperature was obtained at 391 K, which is also frequency independent. The room temperature value of the dielectric constant of $x=0.05$ sample comes out to be higher compared to its value at transition temperature, unlike $x=0.02$ sample. For pure hexagonal BTO, there are two transitions, one at 74 K and another at 222 K. The low temperature transition (74 K) is associated with the ferroelectric transition, while the higher one corresponds to the structural phase transition [5]. Since the present sample consists of both hexagonal and tetragonal phases, the transition corresponding to 391 K may be associated with the tetragonal phase.

Ferroelectric Behavior

The room temperature ferroelectric hysteresis loop has been measured as a function of applied electric field (7 kV/cm, 12 kV/cm, 19 kV/cm, 25 kV/cm) and shown in Fig. 1(e) and Fig. 1 (f) for $x=0.02$, and $x=0.05$, respectively. The pinch type of hysteresis curve has been observed for the $x=0.02$ sample and can be understood in terms of the generation of a defect dipole. As we have doped Mn^{3+} at Ti^{4+} site, there is generation of oxygen vacancy as a result of charge imbalance. These defect dipoles are not switchable if we reverse the applied electric field, and hence there is an internal biased field associated with the sample. In the present case, for the high applied electric field, the internal bias comes out to be 1.053 kV/cm. For $x=0.05$ sample at room temperature, a linear P-E loop has been observed, depicting the paraelectric behavior of the studied sample.

In summary, the present work reports the ferroelectric and dielectric behavior of Mn-modified BTO. For small doping ($x=0.02$), it shows room temperature ferroelectricity with a pinched loop. For higher composition ($x=0.05$), paraelectric behavior has been observed at room temperature. Temperature-dependent Dielectric behavior of $x=0.02$ is consistent with ferroelectric behavior. However, for $x=0.05$ they are not consistent and need further measurement to explain this anomalous behavior.

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Flexible High-Performance Nanogenerator for Self-Powered Pressure Sensors Using BaTiO₃/PVDF

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Abstract. Flexible piezoelectric nanogenerators (PENGs) have become promising viable power sources for self-powered wearable electronics by converting ambient mechanical energy into electricity. Herein, we present a lead-free PENG device based on a BaTiO₃ (BTO) nanoparticle-embedded polyvinylidene fluoride (PVDF) nanocomposite film. Dielectric measurements revealed a significant increase in dielectric constant from 8.1 to 15.6 with BTO addition. Polarization-electric field (P-E) measurements confirmed enhanced ferroelectric behaviour, with the PVDF/3 wt% BTO composite exhibiting a spontaneous polarization (P_s) of ~ 0.76 $\mu\text{C}/\text{cm}^2$ and an enhanced efficiency of 67.6% at 300 kV/cm. The potential of fabricated PENG being used for energy harvesting applications was demonstrated by it providing an output voltage of ~15 V when it was tapped with the finger.

INTRODUCTION

The growing demand for clean energy and the limitations of fossil fuels have made the development of sustainable energy harvesting technologies essential. Among these, piezoelectric nanogenerators (PENGs) are especially significant. [1-2]. However, limited electrical output and a lack of suitable piezoelectric materials pose challenges for practical applications. To address this, research has been focused on developing materials that combine strong piezoelectricity with flexibility. Polyvinylidene fluoride (PVDF), a flexible, semi-crystalline polymer, is widely used due to its inherent piezoelectric and ferroelectric properties. Its β -phase has the strongest piezoelectric response and is distinguished by all-trans (TTTT) dipole alignment [3]. Ceramic fillers promote β -phase formation due to their ferroelectricity and high dielectric constants. BTO, a lead-free, chemically stable, and easily processed ceramic, is especially favoured. With piezoelectric coefficients of 350 - 460 pC/N depending on synthesis, it serves as a promising eco-friendly alternative to lead-based materials [4]. In this study, perovskite BTO nanoparticles are incorporated into PVDF to stabilize the β -phase, resulting in a flexible PENG that delivers ~15 V under finger tapping that can also effectively charge small capacitors.

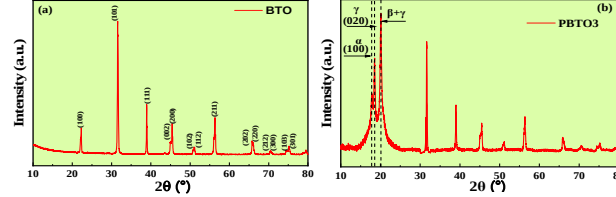
EXPERIMENTAL SECTION

BaTiO₃ (BTO) powder was synthesized via the sol-gel method using stoichiometric amounts of barium acetate and titanium isopropoxide. Each precursor was dissolved separately in a solvent mixture of ethanol, DI water, and propanol. The solutions were combined and mixed at room temperature till they formed a gel. This gel was dried at 120 °C. Then, calcination was performed at 1100 °C for 8 hours to obtain nanosized BTO powder. The obtained powder was ultrasonicated for 6 hours. PVDF solution (8 wt%) was prepared in N, N-dimethylformamide (DMF), into which 3 wt% BTO was added and stirred vigorously for 10 hours. Solution casting of pure PVDF and BTO-PVDF mixtures was done onto pre-cleaned glass slides. They were then dried for 4 hours at 120°C. The resulting films were peeled off after cooling and labelled PBTO 0 (pure PVDF) and PBTO 3 (3 wt% BTO). The PENG device was fabricated by sandwiching a 2×2 cm² PBTO 3 film in between copper electrodes and encapsulated in Polydimethylsiloxane (PDMS). Copper wires were attached to both electrodes.

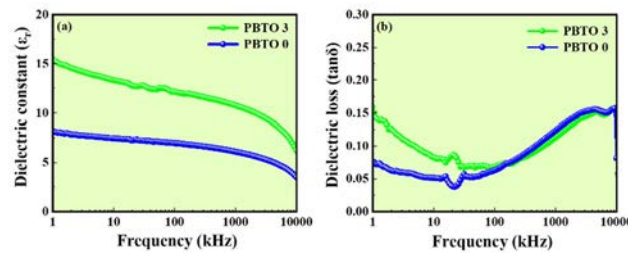
RESULTS AND DISCUSSION

X-ray diffraction (XRD) was used to analyze the crystalline structure of the synthesized BTO nanopowder and the PBTO 3, as depicted in Fig. 1(a-b). The BTO powder exhibits diffraction peaks consistent with the JCPDS card (PDF #85-0368), confirming the tetragonal perovskite phase [5]. In the composite film, peaks from both BTO and PVDF confirm the successful integration. Diffraction maxima at 2θ of 17.6° , 18.5° , and 20.1° point to the (100) plane of the α -phase, the (020) plane of the γ -phase, and overlapping contributions from the γ - and β -phases of PVDF [6].

FIGURE 1. XRD patterns of (a) BTO nanoparticles, (b) PBTO 3.



The dielectric properties of PBTO 0 and PBTO 3 films were evaluated at room temperature from 1 kHz to 10 MHz, as depicted in Fig. 2(a-b). PBTO 3 consistently shows a higher dielectric constant than PBTO 0, indicating the



enhancing effect of BTO nanoparticle incorporation. At 1 kHz, PBTO 0 exhibits a dielectric constant of 8.1, while PBTO 3 reaches 15.6, nearly a twofold increase due to the high permittivity of BTO and enhanced interfacial polarization at the filler polymer interface. A decreasing trend in dielectric constant with frequency is observed, attributed to the diminishing influence of space charge and Maxwell-Wagner-Sillars (MWS) polarization. Similarly, the loss tangent increases with BTO addition, ascribed to localized conductive regions formed within the PVDF matrix [7].

FIGURE 2. (a) Dielectric constant and (b) dielectric loss of PBTO 0 and PBTO 3.

The ferroelectric characteristics of PBTO 0 and PBTO 3 were examined under varying electric fields as shown in Fig. 3(a-b). The P-E hysteresis loops confirmed typical ferroelectric behaviour, with PBTO 3 exhibiting a higher polarization than PBTO 0. The maximum polarization ($P_{\max}$) values for PBTO 0 and PBTO 3 were found to be $0.29 \mu\text{C}/\text{cm}^2$ and $0.76 \mu\text{C}/\text{cm}^2$, respectively. This significant enhancement can be attributed to the presence of ceramic particles with strong ferroelectric characteristics. They likely serve as heterogeneous nucleation centers. These centers can facilitate the formation of ferroelectric domains, thereby boosting overall ferroelectric characteristics of the composite films [8]. To determine the energy storage performance, values of remanent polarization (P_r), $P_{\max}$, and Coercive field (E_c) were utilized to calculate theoretical energy density [9]. The recoverable energy densities (W_{rec}) of PBTO 0 and PBTO 3 calculated at 300 kV/cm are 14.23 and $85.1 \text{ mJ}/\text{cm}^3$, respectively, and their efficiencies (η) are 22.2% and 67.6%. This demonstrates an increase in efficiency of over three times upon the inclusion of BTO nanoparticles in PVDF.

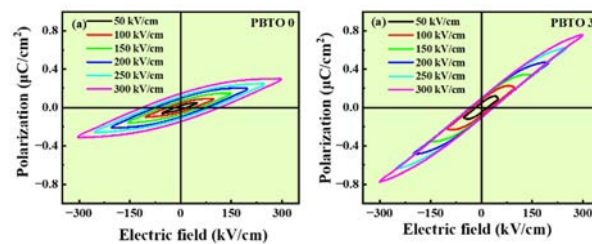


FIGURE 3. P-E loops of (a) PBTO 0 (b) PBTO 3.

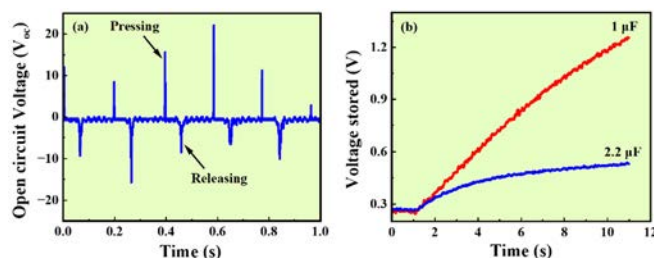


FIGURE 4. (a) Energy harvesting from finger tapping (b) Charging curves of different capacitors.

The PENG device was assessed for its performance under gentle finger tapping. An open circuit voltage of about 15 V was obtained, as shown in Fig. 4a. Figure 4b illustrates the charging performance of the PENG device. By using a full-wave rectifier, the nanogenerator's alternating current (AC) output was transformed into a direct current (DC) output. In 11 seconds, repeated finger tapping charges 47 μF and 100 μF capacitors to 1.2 V and 0.5 V, respectively. The working mechanism of the PENG device is illustrated in Figure 5. When no force is applied (Fig. 5(i)), dipoles are oriented in a random direction. As a result, no net voltage is produced. When mechanical force is applied (Fig. 5(ii)), polarization occurs, and dipoles get aligned. This generates a potential difference across the copper electrodes and induces the charge flow. When force is removed (Fig. 5(iii)), the dipoles relax, creating a reverse potential that drives the charges back [2]. This cyclic process facilitates continuous mechanical-to-electrical energy conversion.

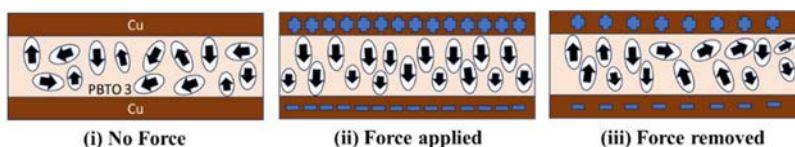


FIGURE 5. Working mechanism of PENG.

CONCLUSION

BaTiO₃/PVDF nanocomposite films were successfully developed using sol-gel synthesis and solution casting technique. The addition of BTO nanoparticles promoted β -phase formation in PVDF, leading to enhanced functional properties. PBTO 3 achieved a maximum polarization of 0.76 $\mu\text{C}/\text{cm}^2$. It also exhibits energy storage density of 85.1 mJ/cm^3 along with an efficiency of 67.6% at 300 kV/cm . This marks nearly a threefold improvement compared to PBTO 0. The piezoelectric nanogenerator produced an output voltage of about 15 V when tapped by a finger. It effectively charged capacitors, showing that it is well-suited for flexible energy harvesting and storage applications.

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Magneto-electric Coupling In CZFMO-Embedded P(VDF-TrFE) Composites For Self-powered Electronics And Magnetic Energy Scavenging

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Abstract. The present research focuses on the development and characterization of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_{1.7}\text{Mn}_{0.3}\text{O}_4$ (CZFMO)-embedded poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] composites for magnetic energy harvesting applications. Initially, the structural and vibrational properties of the composites were analyzed using X-ray diffraction (XRD) and Fourier-transform infrared (FTIR) spectroscopy, respectively. Subsequently, dielectric measurements were performed to evaluate the dielectric constant and loss behavior of the composites. Among the samples, the composite containing 0.5 wt.% CZFMO exhibited an appreciable magnetoelectric (ME) voltage coefficient of 52.31 mV/(cm·Oe). Finally, the energy harvesting capability of the optimized composite was investigated. The output voltage demonstrated a proportional response to increasing magnetic field strength, rising from 0.3 V to 0.9 V as the applied magnetic field increased from 0.9 mT to 2.7 mT. These results highlight the potential of CZFMO/P(VDF-TrFE) composites in low-field magnetic energy harvesting applications.

INTRODUCTION

The world's population has increased several times since the start of the industrial revolution, and this growth is predicted to continue at the same rate in the foreseeable future. Researchers worldwide are searching for alternative renewable energy sources due to the depletion of fossil fuel supply and the harm they contribute to the environment [1]. Small-scale energy scavenging at a level adequate to run low-power electronic devices has also drawn attention from the research community in addition to large-scale energy harvesting. Ferroelectric polymers like polyvinylidene fluoride (P(VDF)) and its copolymers, such as polyvinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) and polyvinylidene fluoride-hexafluoropropylene P(VDF-HFP), have gained increasing attention in research due to their compatibility with low-temperature processing techniques, enabling the fabrication of flexible materials with reduced leakage current and dielectric loss [2]. In recent years, considerable efforts have focused on achieving magneto-electric coupling between ferroelectric P(VDF) and well-dispersed ferromagnetic nanoparticles. However, limited research has been directed toward exploring such coupling in its copolymers[3]. Because of its favourable magnetostriction characteristics, $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_{1.7}\text{Mn}_{0.3}\text{O}_4$ (CZFMO) has been chosen for the ferromagnetic phase. In this work, we have fabricated a magneto-electric nano-generator (MENG) by incorporating CZFMO into P(VDF-TrFE) and demonstrated its ability to harvest energy from weak magnetic fields.

EXPERIMENTAL SECTION

The CZFMO ferrite nano-particles were synthesized via sol-gel method using appropriate amount of initial precursors such as Cobalt(II) nitrate hexahydrate, Zinc(II) nitrate hexahydrate, Manganese(II) nitrate tetrahydrate and Iron(III) nitrate nonahydrate into deionized water. The solution was then chelated with 50g citric acid to ensure water solubility of metal ions and their uniformity throughout the solution. The mixture was then heated to a temperature of 80 C to get a dry porous mass called xerogel. The xerogel was then subjected to pre-calcinations step to decompose the organic citric acid, leaving behind a loose metal oxides powder. This powder was then calcinated in the range of 800C for 4hrs to get a homogenous powder of nano-crystalline spinel ferrite. Then suitable amount of P(VDF-TrFE) powder (purchased from Piezotech S.A.S. (France)) was weighed and dissolved into 3ml MEK (Methyl Ethyl Ketone) with the help of magnetic stirrer. Separately prepared 1.2 mg CZFMO powder was added into 0.5ml MEK and put into sonication for about 4hrs. The neat P(VDF-TrFE) and P(VDF-TrFE)/0.5CZFMO (0.5C) films then casted in hot air oven, kept at 120C for 2hr.

RESULTS AND DISCUSSION

Fig. 1(a) displays the FTIR spectra of both the neat P(VDF-TrFE) film and the P(VDF-TrFE) film incorporated with CZFMO, named 0.5C. Three characteristic absorption peaks corresponding the 506 cm^{-1} can be associated to the $-\text{CF}_2$ wagging and bending vibrations, while peaks at 1288 cm^{-1} and 843 cm^{-1} are attributed to $-\text{CF}_2$ symmetric stretching vibrations. These vibrations are closely associated with dipole orientation in the films, indicating dipole alignment along the b-axis [4]. Since these peaks are indicative of the β -phase, one can clearly observe that there is no alteration of the β -phase with the addition of CZFMO filler in the P(VDF-TrFE) matrix.. Further, this observation is supported by the XRD pattern's (**fig. 1(b)**), which shows similar type of the pattern for both neat and composite films, without any additional impurity phase. This indicates non-

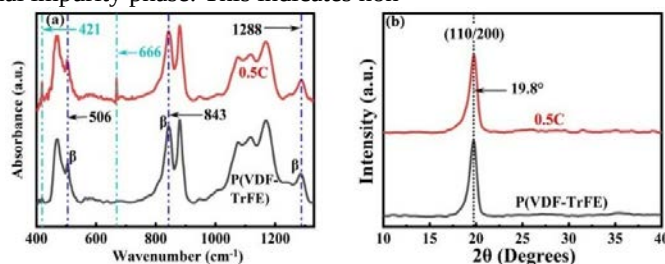


FIGURE 1. (a) FTIR spectra and (b) XRD patterns of neat P(VDF-TrFE) and P(VDF-TrFE)/0.5CZFMO composite films at room temperature.

-disruptive incorporation of CZFMO into the P(VDF-TrFE) matrix. The dielectric constant and loss behaviour of the synthesized films at room temperature as a function of frequency are shown in **fig. 2(a-b)**. At lower frequencies, a clear interfacial polarization effect is observed, as indicated by the decreasing dielectric constant with increasing frequency. This behaviour likely results from dipoles struggling to keep up with the rapidly alternating electric field at higher frequencies [5]. Interestingly, the CZFMO incorporated film shows a lower dielectric constant (ϵ) of about 11.8 at 1 kHz. The likely reason for this reduction is that the conductivity of CZFMO is much more than that of parent P(VDF-TrFE), so they provide conductive pathways through the film [5]. However marginal increase in the dielectric loss is observed in composite film as compared to neat P(VDF-TrFE) as shown in **fig. 2(b)** at 1 kHz.

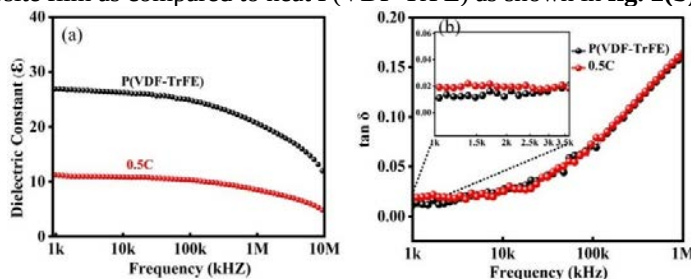


FIGURE 2. (a) The Dielectric Constant (ϵ) and (b) Dielectric loss ($\tan \delta$) behavior of neat P(VDF-TrFE) and P(VDF-TrFE)/0.5CZFMO composite films at room temperature.

The magneto-electric voltage behaviour (α_{ME} coefficient) of the film is investigated under varying DC magnetic fields with the help of experimental set-up shown in **Fig. 3(a)**. **Fig. 3(b)** presents the variation of α_{ME} coefficient at constant AC magnetic field of 10 Oe and frequency of 1 kHz, as a function of applied DC magnetic field strength. The film shows a pronounced magneto-electric response $\alpha_{ME} \sim 52.31\text{ mV/cm}\cdot\text{Oe}$ at a DC magnetic field of 500 Oe, highlighting its strong magneto-electric coupling, which is primarily attributed to the incorporation of CZFMO into the PVDF-TrFE matrix.

To evaluate the magnetic energy harvesting capability of the 0.5C composite, the electrodes were deposited on both side of the film using silver paste to form the magneto-electric nano-generator (MENG). Then the film has been positioned at the centre of a Helmholtz coil to ensure exposure to the maximum magnetic flux density (**fig. 4(a)**). The resulting induced voltage is measured with respect to varying magnetic field strengths and the output voltage responded proportionally from 0.3 mV to 0.9 mV with the increasing available magnetic field from 0.9 mT to 2.7 mT as shown in **fig. 4(b)**.

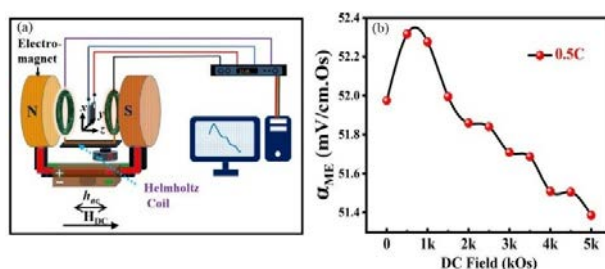


FIGURE 3. The Schematic of ME coupling measurement set-up and the coupling coefficient α_{ME} behavior with varying dc magnetic field at constant ac magnetic field of 10e at 1 kHz.

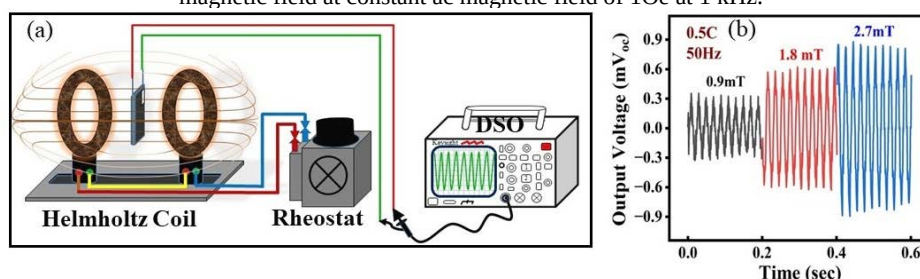


FIGURE 4. (a)The Schematic of Magnetic energy harvesting set-up and (b) the magnetic energy harvesting performance of P(VDF-TrFE)/0.5CZFM0 composite based MENG.

CONCLUSION

This study systematically investigates the FTIR, XRD, dielectric, magneto-electric (ME) coupling, and magnetic energy harvesting characteristics of neat P(VDF-TrFE) and its composite with 0.5 wt.% CZFMO. FTIR and XRD analyses confirm the formation of high-quality films with a dominant β -phase content in both the neat and composite samples, without the emergence of any secondary phases. Upon incorporation of CZFMO, the dielectric constant decreases from 28 to 11, accompanied by a slight increase in dielectric loss. A notable ME coupling coefficient α_{ME} of approximately 52 mV/cm·Oe is achieved at 0.5 wt.% CZFMO loading. Furthermore, magnetic energy harvesting experiments using a Helmholtz coil demonstrate an open-circuit voltage output of ~0.9 V under a low magnetic field of 2.7 mT, highlighting the composite's efficient magnetic-to-electric energy conversion capability.

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Microstructure–Property Correlation in Microwave-Sintered NBSTS-BT Ceramics for Enhanced Dielectric Energy Storage

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Abstract. The pursuit of sustainable and efficient dielectric materials has steered attention toward lead-free ferroelectric ceramics. Achieving multifunctional performance in lead-free dielectrics remains a major challenge. In this study, innovative processing of $0.94(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.75}\text{Sm}_{0.25}\text{Ti}_{0.95}\text{Sc}_{0.05}\text{O}_3-0.06\text{BaTiO}_3$ ceramics through microwave sintering significantly enhances energy storage behavior. Under a high field of 221.5kV/cm, the microwave-sintered ceramics achieve high recoverable energy density $\sim 0.93\text{J}/\text{cm}^3$ and high $\eta \sim 80.86\%$, outperforming conventionally sintered counterparts. FESEM micrographs indicate dense and uniform microstructure of MS ceramics. A high dielectric constant ~ 1600 and ~ 1100 is observed for CS and MS ceramics, respectively. These findings suggest microwave sintering as a rapid and efficient route to enhance energy storage performance.

INTRODUCTION

The advancement of renewable energy technologies has highlighted the need for efficient energy storage systems for stable power delivery [1]. Although dielectric capacitors provide superior power density, their limited storage capacity continues to motivate material innovation. The energy storage is evaluated using the equations [2]:

$$W_s = \int_0^{P_{max}} E dP \quad (1)$$

$$W_r = \int_{P_r}^{P_{max}} E dP \quad (2)$$

$$\eta\% = \frac{W_r}{W_s} \times 100 \quad (3)$$

where W_s , η , W_r , E , P , P_m , and P_r denote total energy density, efficiency, recoverable energy density, electric field, polarization, maximum and remnant polarization, respectively. Achieving high energy storage requires both large ΔP ($P_m - P_r$) and high breakdown strength (E_b). The toxicity of lead-based dielectrics highlights the need for sustainable Pb-free energy-storage materials [3]. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) is suitable for pulse capacitors, but high P_r and leakage current restricts energy storage performance [4]. The A/B site engineering in BNT promotes enhanced energy storage. Cao et al. [5] reported a W_r of $0.65\text{J}/\text{cm}^3$ at 65 kV/cm in $0.7(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-0.3\text{SrTiO}_3$ ceramics fabricated by solid-state method. Herein, $0.94(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.75}\text{Sm}_{0.25}\text{Ti}_{0.95}\text{Sc}_{0.05}\text{O}_3-0.06\text{BaTiO}_3$ ceramics were prepared by microwave and conventional sintering, followed by systematic structural and electrical characterization.

EXPERIMENTAL

The solid state route was utilized to fabricate $0.94(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.75}\text{Sm}_{0.25}\text{Ti}_{0.95}\text{Sc}_{0.05}\text{O}_3-0.06\text{BaTiO}_3$ (NBSTS-BT) using pristine raw powders Na_2CO_3 (>99.5%), BaCO_3 (99.9%), TiO_2 (>99%), Bi_2O_3 (99%), Sm_2O_3 (99.9%), Sc_2O_3 (99.9%) procured from Sigma Aldrich. Stoichiometric measurements were done and then ball milled in acetone medium for 24 hours. The Air-dried powders were calcined at 850°C for 3 hours. Pellets with dimensions of $10\text{ mm} \times 1\text{ mm}$ were processed by adding 5 wt% PVA. Two sintering routes were employed: microwave sintering at 1150°C for 40 min ($20^\circ\text{C}/\text{min}$), and conventional furnace sintering at 1100°C for 3 h ($2.5^\circ\text{C}/\text{min}$). The crystal structure was examined using Advance X-ray diffractometer (Model-D8). Reitveld analysis was carried out using Fullprof software. The

microstructure was investigated using field emission SEM [FE-SEM; SU8010 SERIES HITACHI]. Grain size was computed via ImageJ software. The dielectric studies were done using impedance analyzer [Keysight, E4990A], and the P-E loop system [Marine India] was employed for ferroelectric measurements.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) was utilized to determine the phase structure of the NBSTS-BT ceramics. Fig. 1(a) displays XRD pattern of NBSTS-BT ceramic samples in the 2θ range 10° – 80° . The samples were prepared using two different sintering techniques and no secondary phases were detected, confirming the formation of a single-phase composition. To gain further insight into the crystal structure, Rietveld refinement was carried out, and it reveals the presence of pseudocubic phase with $Pm-3m$ space group, consistent with literature [6, 7], as depicted in Fig. 1(b, c). The Rietveld refinement of both ceramics shows an excellent fit (χ^2 values close to 2).

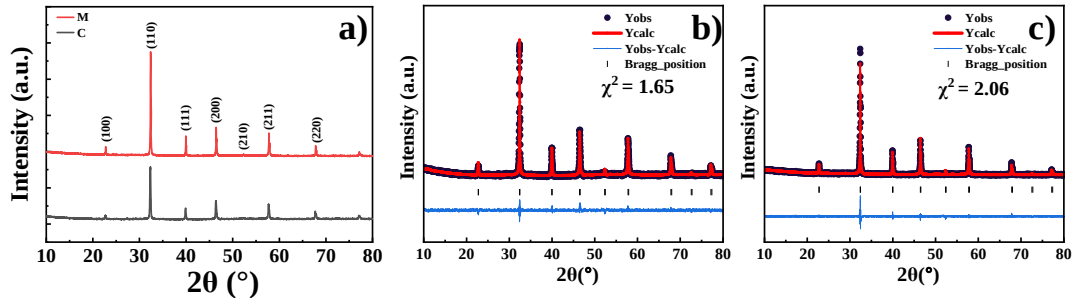


FIGURE 1. a) XRD patterns of both CS and MS NBSTS-BT ceramics, rietveld refinement b) CS c) MS.

Figure 2(a-b) presents the FESEM micrographs of the NBSTS-BT ceramics and the inset depicts the average grain size (AGS). The MS ceramics exhibit dense packing and fine grains as compared to CS ones. The AGS came out to be $0.59\mu\text{m}$ for the CS sample and $0.19\mu\text{m}$ for the MS sample. According to the relationship $E_b \propto 1/G^{1/2}$, a fine grain size is favourable for attaining higher E_b , which is essential for enhanced energy storage performance. The finer microstructures in MS ceramics likely contribute to enhanced breakdown strength [8].

Figure 3(a-b) illustrates the dielectric studies across broad temperature (30°C – 400°C) range. The dielectric constant (ϵ_r) initially increases with temperature, reaching a maximum at T_m (ferroelectric-paraelectric phase transition) and then decreases upon further increasing the temperature. For the CS sample, the maximum dielectric constant (ϵ_{max}) ~ 1600 , while for the MS, it is ~ 1100 , likely due to its smaller grain size. Additionally, both samples exhibit a diffuse dielectric peak that slides toward higher temperatures as the frequency increases, revealing relaxor nature [9]. Fig. 4(a, b) illustrates the P-E loops of both CS and MS NBSTS-BT ceramics samples at 20Hz, respectively. Both samples exhibit well saturated P-E loops along with a high breakdown strength (E_b). It is observed that the MS sample demonstrates a high $E_b \sim 221.50\text{kV/cm}$, with P_r and P_s values of $\sim 1\mu\text{C/cm}^2$ and $\sim 10\mu\text{C/cm}^2$, respectively.

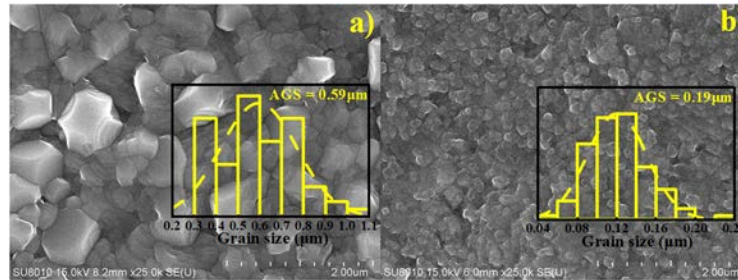


FIGURE 2. FE-SEM micrograph of NBSTS-BT for a) CS ceramic, b) MS ceramic

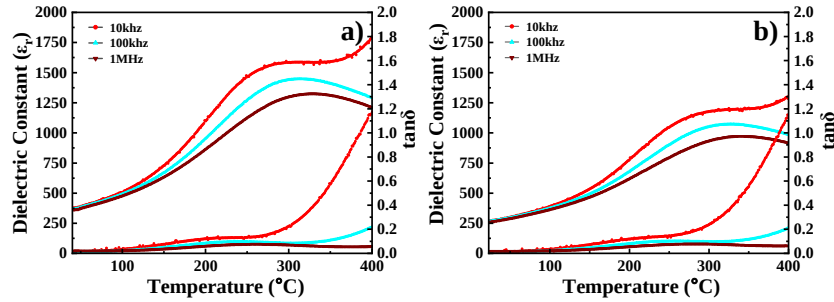


FIGURE 3. Temperature dependent dielectric studies (30° - 400°C) of NBSTS-BT ceramics for a) CS, b) MS.

The observed slim P - E loops are a hallmark of relaxors, which are widely utilized in applications requiring efficient energy storage [10]. The calculated W_s , W_r and η for the MS ceramic are $1.15\text{J}/\text{cm}^3$, $0.93\text{J}/\text{cm}^3$ and 80.86% , respectively, on the other hand, for the CS one, these values are $0.77\text{J}/\text{cm}^3$, $0.52\text{J}/\text{cm}^3$ and 67.53% , respectively. It is evident that the samples prepared via MS approach are exhibiting better properties as compared to the CS ones.

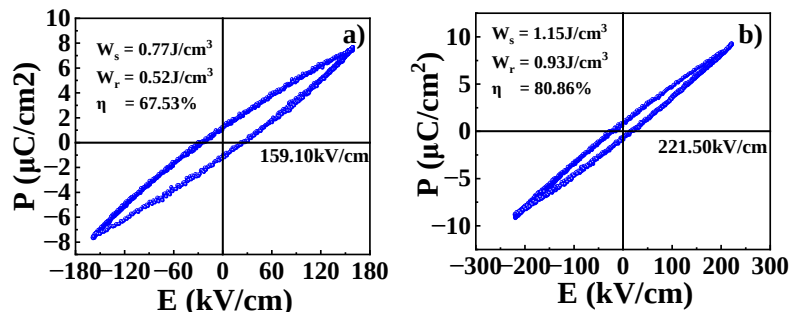


FIGURE 4. Dipolar P - E Loops of NBSTS-BT ceramics for a) CS ceramic, b) MS ceramic at 20Hz.

CONCLUSION

In summary, this work signifies that microwave sintering is an efficient technique for significantly boosting the energy storage behavior of lead-free NBSTS-BT ceramics. Microwave sintering enables faster densification and leads to a more compact and homogeneous microstructure, which directly contributes to higher energy storage response. The microwave-sintered sample exhibits a high $W_r \sim 0.93\text{J}/\text{cm}^3$ and excellent $\eta \sim 80.86\%$ at $\sim 221.50\text{ kV}/\text{cm}$. Despite lower dielectric constant (~ 1100), microwave-sintered ceramics exhibit superior overall performance. These results highlight the critical role of micro-structural tailoring in achieving superior energy storage performance.

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Microwave-Assisted Sintering of KNN-Based Relaxors: Local Structure Homogeneity and Nanodomain Engineering for High Energy Storage Efficiency

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Abstract. Microwave sintering represents an advanced technological innovation that significantly accelerates the synthesis process in bulk ceramics, thereby enhancing time efficiency. Herein, we synthesized $0.875\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{-}0.125\text{Bi}(\text{Zr}_{0.98}\text{Sr}_{0.02})\text{O}_3$ via conventional as well as microwave sintering and analyzed both for energy storage properties. X-Ray Diffraction (XRD) Refinement demonstrates tetragonal structure with P4mm symmetry for both samples. From dielectric studies with temperature, $\epsilon_{\text{max}} \sim 1481$ is observed in the conventionally sintered sample with $T_m \sim 405^\circ\text{C}$. FESEM studies imply that the grain size of ceramics obtained via microwave sintering is finer than that of conventional sintering. Slimmer P-E loops with elevated maximum polarization $P_{\text{max}} \sim 20 \mu\text{C}/\text{cm}^2$, reduced remnant polarization, $P_r \sim 3 \mu\text{C}/\text{cm}^2$ leads to a high recoverable energy density $\sim 0.89 \text{ J}/\text{cm}^3$ with 70 % efficiency in the microwave-sintered sample. Hence, this study underscores the potential use of microwave sintering in boosting the energy storage capabilities.

INTRODUCTION

Renewable energy sources require efficient storage systems, and dielectric capacitors along with chemical energy storage devices have emerged as crucial, stable, and easily maintained solutions, with dielectric materials forming their core for effective energy storage [1-2]. Among the various dielectric materials studied so far, lead-free ceramic dielectric capacitors have remained an indispensable component of energy storage devices due to their excellent mechanical and thermal characteristics. In general, the energy storage characteristics are determined by the combined influence of P_{max} , P_r and electric field (E). Hence, achieving high energy storage performance necessitates both significant ΔP and elevated breakdown strength (E_B) [3]. Relaxor-ferroelectrics are preferred due to their superior energy storage characteristics. Among them, $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ -based systems have been identified as strong contenders. However, the extended sintering times in conventional processes lead to porosity in KNN samples, hindering their functional properties [4–5]. Consequently, sintering conditions must be precisely tailored to ensure densification and performance of these ceramics. In this study, $0.875\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 - 0.125 \text{ BiZr}_{0.98}\text{Sr}_{0.02}\text{O}_3$ ceramics were synthesized using both conventional and microwave sintering, and their energy storage properties were comparatively evaluated.

EXPERIMENTAL METHOD

$0.875 \text{ K}_{0.5}\text{Na}_{0.5}\text{NbO}_3 - 0.125 \text{ BiZr}_{0.98}\text{Sr}_{0.02}\text{O}_3$ ($0.875\text{KNN-}0.125\text{BZS}$) ceramics were synthesized by using precursors of Na_2CO_3 powder (99.5%), K_2CO_3 powder (99%), Nb_2O_5 powder (99.99%), Bi_2O_3 (99.9%), SrCO_3 (98%) and ZrO_2 powder (99%) procured from Sigma Aldrich. The precursor powders were weighed stoichiometrically and ball-milled for 8h using zirconia balls in isopropyl alcohol (IPA). The resultant slurry was dried and then calcined (850°C for 4h) in an alumina crucible. The dried powder was blended with 2 wt% PVA binder and compacted into pellets having a diameter of 10 mm followed by cold isostatic pressing (CIP). The green pellets were then sintered via (a) conventional air sintering (1120°C - 2h) & (b) microwave sintering (1120°C - 40 min) followed by applying Ag paste.

RESULTS & DISCUSSION

Figure 1(a-c) provides insights into crystalline structure of KNN-BZS ceramics sintered via (a) conventional and (b) microwave sintering, as obtained from X-ray Diffraction Rietveld refinement. The XRD patterns confirm the perovskite phase, with minimal secondary phases observed in the conventionally sintered sample (Fig.1(b)), while the microwave-sintered sample exhibits a completely single-phase nature (Fig.1(c)). The refinement results demonstrate that the incorporation of BZS into the KNN matrix induces a structural transformation from orthorhombic to tetragonal symmetry for both samples [6, 7]. The tetragonal phase stabilization through BZS doping is anticipated to strengthen the ferroelectric properties of KNN-BZS ceramics, which is crucial for their energy storage applications.

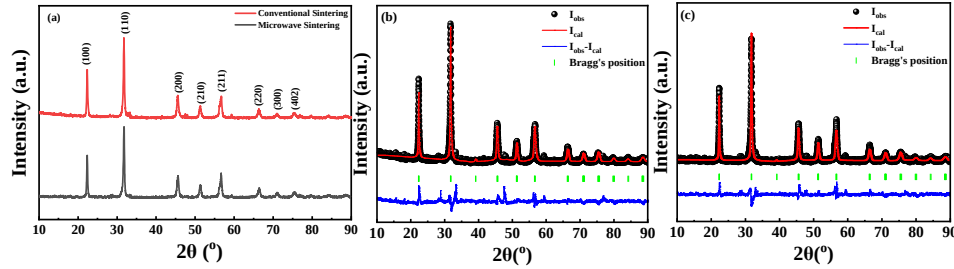


FIGURE 1. Rietveld Profile for 0.875KNN-0.125BSZ ceramics sintered (a) conventionally (b) via microwave.

Figure 2(a-b) demonstrates the micrograph images & distribution of grain size obtained via Field emission scanning electron microscopy (FE-SEM) of the as sintered pellets. Grain size analysis was performed using ImageJ software. The average grain size (AGS) for the conventionally sintered ceramic is found to be $0.669\mu\text{m}$, while that for the microwave sintered sample is $0.632\mu\text{m}$. The electric breakdown strength of the ceramics is inversely dependent on grain size [8]. Due to the smaller average grain size (AGS) in the microwave-sintered sample, a higher grain boundary density is observed. These grain boundaries act as effective barriers to motion of domain walls and electrical breakdown, thereby predicting the enhanced E_B for microwave-sintered samples.

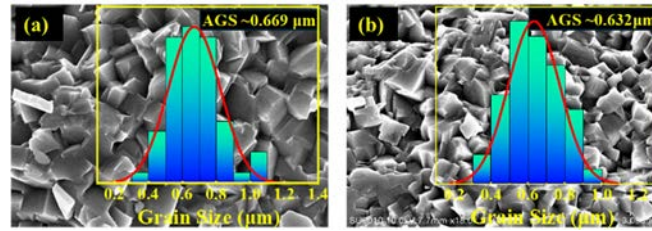


FIGURE 2. Micrographs of FE-SEM for 0.875KNN-0.125BSZ ceramics sintered (a) conventionally (b) via microwave.

Dielectric properties of both the samples have been investigated and are presented in Fig.3. Both samples show broadened dielectric peaks, confirming a diffuse phase transition and the emergence of relaxor ferroelectric (RFE)

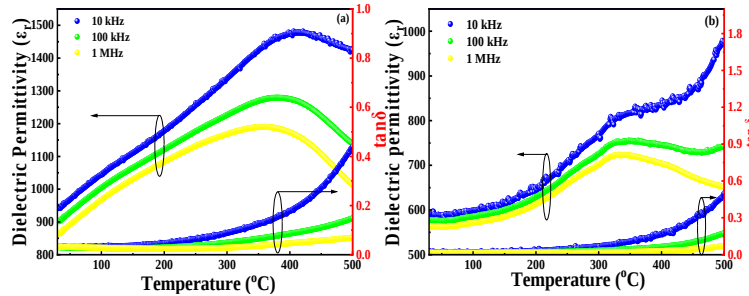


FIGURE 3. Dielectric studies for 0.875KNN-0.125BSZ ceramics sintered (a) conventionally (b) via microwave sintering. characteristics [9]. Consequently, a diffused dielectric anomaly at T_m is observed. For the conventionally sintered sample, T_m is approximately 405°C , whereas it decreases to around 326°C in the microwave-sintered sample. Additionally, frequency-driven shift of T_m towards higher temperature with an increase in frequency further substantiates the relaxor behaviour of the materials.

Figure 4(a-b) depicts the ferroelectric properties of KNN-BZS ceramics, as evaluated by room temperature Polarization-Electric Field (P-E) loop recorded at 20 Hz. Both samples exhibit slim P-E loops, characteristic of relaxor ferroelectric behaviour. The low hysteresis loss observed in these samples can be attributed to the emergence of polar nanoregions (PNRs) via breakage of long-range ferroelectric order, which facilitates smooth domain switching [10]. The P_{max} value for the microwave-sintered sample is approximately $20 \mu\text{C}/\text{cm}^2$ Fig.4(a), significantly higher than that of the conventionally sintered sample ($\sim 12 \mu\text{C}/\text{cm}^2$) Fig.4(b). In contrast, the remanent polarization (P_r) is lower for the microwave-sintered sample ($\sim 3 \mu\text{C}/\text{cm}^2$). This substantial difference between P_{max} & P_r , enables $W_{rec} \sim 0.89 \text{ J}/\text{cm}^3$. Furthermore, lower P_r results in higher energy storage efficiency for the microwave-sintered sample reaching $\sim 70\%$.

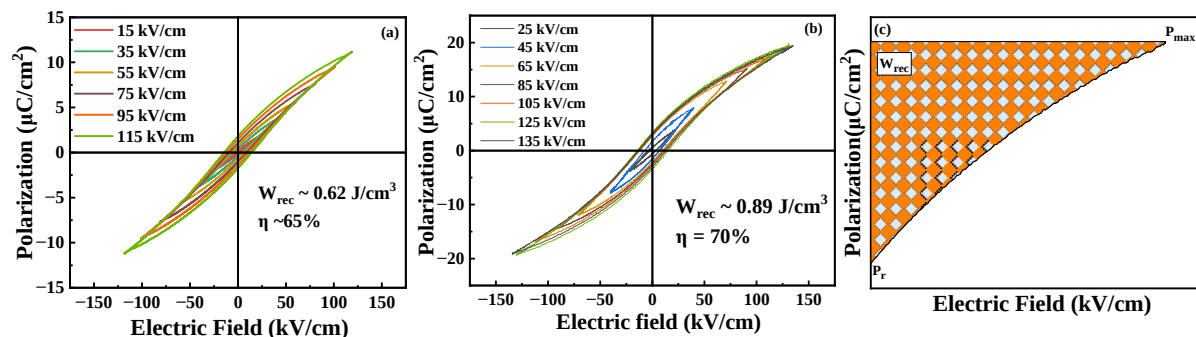


FIGURE 4. P-E loops for 0.875KNN-0.125BSZ ceramics sintered (a) conventionally (b) using microwave sintering.

CONCLUSION

This study systematically compares the microstructural, dielectric and ferroelectric properties of 0.875KNN-0.125BZS ceramics synthesized via conventional and microwave sintering techniques. Microwave sintering was found to produce ceramics with finer grain size, enhanced breakdown strength, augmented P_{max} , minimal P_r , and improved W_{rec} ($\sim 0.89 \text{ J}/\text{cm}^3$) and η ($\sim 70\%$) compared to conventional sintering. These enhancements are attributed to rapid and uniform heating during microwave sintering, leading to better densification and microstructural control. Overall, the results indicate that microwave sintering offers a viable and efficient route for synthesizing high-performance KNN based dielectric ceramics well suited for energy storage applications.

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Structural and Frequency-Dependent Dielectric Properties of HfO₂ & Sr-doped HfO₂ Ceramics Synthesised via Hydrothermal Method for Energy Applications

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Abstract. HfO₂ and Sr-doped HfO₂ nanoparticles were synthesized via the hydrothermal method and subsequently calcined at 500°C for 5 hours. X-ray diffraction analysis confirmed the orthorhombic phase structure with space group (Pbcm). Photoluminescence spectra reveal the creation of defects and radical species. The room temperature dielectric measurement revealed a high dielectric constant and low dielectric loss. The Nyquist plot of ceramics shows the significant grain boundary contributions to the impedance behaviour. The AC conductivity analysis (σ_{ac}) reveals that the dominant charge transport mechanism is governed by hopping mechanism.

INTRODUCTION

The demand for high-performance, miniaturized, and multifunctional devices drives the ongoing advancement of the microelectronics industry. This progress relies heavily on the development and integration of cutting-edge materials with tuned properties. Recently, the HfO₂ nanoparticles have garnered momentous attention due to its high dielectric constant and wide band gap (5.7 eV) with admirable thermal stability and compatibility with silicon-based technology. Additionally, HfO₂ exhibits crystalline phase variation reliant on the temperature, and its functional properties are closely associated with the condition of the synthesis method used. These features make HfO₂ a prominent material for the next-generation high-performance electronic and optoelectronic devices. Many methods have been adopted to synthesize the HfO₂ nanoparticles till now, such as sol-gel, hydrothermal, coprecipitation, solvothermal, and microwave-assisted methods [1]. There are many studies have been carried out on the synthesis of HfO₂ nanoparticles, comparatively, scarcer studies have focused on the structural, dielectric, and optical properties of hydrothermally synthesized HfO₂ nanoparticles, which offer the advantage of low-temperature processing. In the present study, HfO₂ and Sr-doped HfO₂ nanoparticles were synthesized via a hydrothermal route.

SYNTHESIS

The HfO₂ nanoparticles are synthesised via the hydrothermal method using HfCl₄ (0.5M, 35.5mL) and NaOH (7 M, 35.5 mL) solutions. The NaOH solution is added drop by drop into the HfCl₄ solution under constant magnetic stirring for 30 minutes, and the resulting mixture is then transferred to a 100 mL Teflon-lined autoclave and heated at 120 °C for 6 hours. For the Sr-doped HfO₂ samples, the same process is followed with addition of an aqueous solution of SrCl₂ (0.1M, 10mL). The resulting white precipitate is washed with the deionized water and ethanol (3 cycles, 10,000 RPM, 5 min each), dried until a fine powder is obtained, and then calcined at 500 °C for 5 hrs. The final calcined powder is mixed with PVA and then pressed into cylindrical pellets (1 mm thickness and 8 mm diameter) using a KBr press under 2-ton pressure. The pellets are then sintered at 1000 °C for 10 hrs to achieve densification.

RESULTS & DISCUSSIONS

Powder X-ray diffraction analysis

The crystal structure of both the pristine HfO₂ and Sr-doped HfO₂ nanoparticles is investigated using XRD. The samples are labelled as HM0 (undoped HfO₂ nanoparticles) and HM1 (Sr-doped HfO₂ nanoparticles). Figure 1(a) represents the XRD patterns of both samples, with diffraction peaks are observed at 30.56°, 35.33°, 50.80°, 60.35°, 63.50°, and 74.55° corresponding to the (111), (200), (202), (131), (222), and (004) planes, respectively. The XRD

peak patterns of the Sr-doped HfO_2 reveal no extra peaks, suggesting successful incorporation of the Sr ions into the HfO_2 matrix without forming a secondary phase. A slight shift in peak position of the doped sample further support the integration of the Sr ions in the host matrix. The average crystallite size and microstrain of the HfO_2 and Sr-doped HfO_2 nanoparticles are estimated utilizing the Williamson-Hall method [2]. The av. crystallite size of the HM0 and HM1 are 7 nm and 5 nm, and the corresponding microstrains are 4.1×10^{-3} and 3.3×10^{-3} , respectively. The reduction in crystallite size upon Sr doping may be ascribed to the substitution of a smaller ionic radius compared to Hf, which may induce lattice distortion and restrict crystal growth. Figure 1(b) illustrates the Rietveld refinement of the XRD pattern of HM0, analysed using Fullprof software with pseudo-Voigt peak analyzer function. The refinement confirms the orthorhombic phase (Pbcm). The goodness of the fitting is judged by the small Chi. sqr. value. The Chi. Sqr. value of the HM0 sample is 1.78, indicating a good agreement between the observed and calculated pattern.

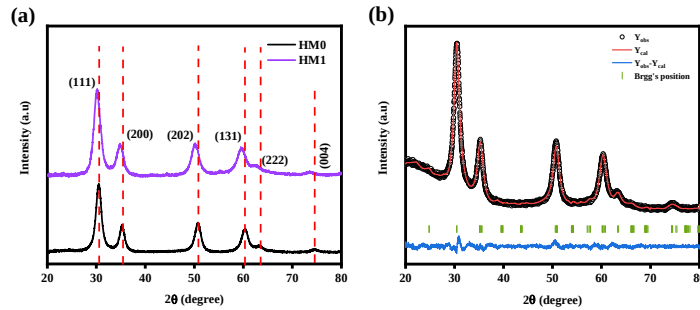


FIGURE 1. (a) X-ray diffraction peak patterns of the HfO_2 & Sr-doped HfO_2 nanoparticles, (b) Rietveld refinement XRD of HfO_2 nanoparticles.

Photoluminescence spectra

PL spectra are a very pivotal tool for studying the defect states of oxide materials. The defects of both the samples, HfO_2 and Sr-doped HfO_2 nanoparticles, are investigated by utilizing an excitation wavelength of 541 nm at room temperature. Figure 2(a) shows PL spectra of the HM0 and HM1 samples; both samples reveal the same emission peaks at 280.57 nm, 400.09 nm, 447.56 nm, 472.04 nm, and 540.76 nm, respectively. These emission peaks originate from the self-trapped excitons, radicals and defects in the samples [3].

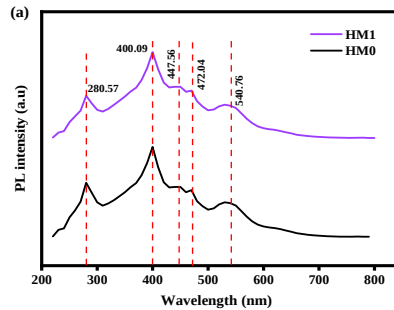


FIGURE 2. (a) Photoluminescence spectra of HfO_2 and Sr-doped HfO_2 nanoparticles.

Dielectric properties

Figure 3(a) shows the frequency-dependent dielectric constant of the HM0 and HM1 samples measured at room temperature, exhibiting the typical dielectric behaviour of ceramics. These types of dielectric characteristics can be elucidated by the Maxwell-Wagner theory, where space charge accumulation at grain boundaries leads to a high dielectric constant at lower frequencies [4]. The red line fitting over the experimental data corresponds to the Havriliak-Negami model, revealing the charge relaxation in the prepared samples [5]. Figure 3(b) illustrates the dielectric loss ($\tan \delta$) of the samples, with the low dielectric loss having a relaxation peak around 1 KHz frequency. This peak is attributed to the alignment of intrinsic dipole moments with the applied field, signifying the dipolar relaxation behavior [6]. The Debye relaxation characteristics are also further analyzed using Nyquist plot. Figure 3(c) presents the Nyquist plot for HM0 and HM1 samples along with an inset showing the equivalent circuit model. Both

HM0 and HM1 samples display a clear semicircle arc with a slight spike at lower frequencies, indicating a deviation from the ideal Debye relaxation, which signifies the influence of the bulk and grain boundaries in the prepared samples [7]. The low-frequency spike may arise from the space charge accumulation at the electrode material interface or grain boundaries.

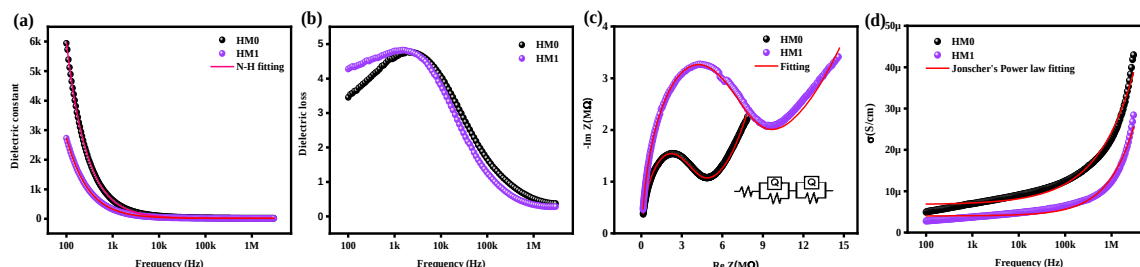


FIGURE 3. (a) Dielectric constant, (b) dielectric loss, (c) Nyquist plot, and (d) Ac conductivity of the HfO₂ & Sr-doped HfO₂ nanoparticles measured at room temperature.

The AC conductivity (σ_{ac}) of HM0 and HM1 ceramics was measured to investigate the transport properties. Figure 3(d) represents the frequency-dependent AC conductivity, with the red line showing the fitting based on Jonscher's Power Law. The AC conductivity increases gradually with the frequency, which is ascribed to the hopping of localized charge carrier's presence in the prepared samples. The AC conductivity at higher frequency ($f > 100\text{kHz}$) can be elucidated with Jonscher's Power Law fitting, suggesting that the hopping charge carriers play a significant role in the electrical conduction process in HM0 and HM1 ceramics [2].

CONCLUSIONS

The HfO₂ and Sr-doped HfO₂ nanoparticles with an orthorhombic structure were synthesized via a hydrothermal method. The introduction of Sr ions into the HfO₂ lattice leads to a reduction of average crystallite size, ascribed to the smaller ionic radius of Sr compared to Hf ions. Photoluminescence (PL) spectra confirmed the presence of intrinsic defects in the prepared samples. Dielectric measurement revealed that Sr doping slightly reduced the dielectric constant, along with low dielectric loss. These properties suggest that the synthesized ceramic materials are promising materials for application in energy storage devices, microwave applications, and electromagnetic shielding in defence and electronic industries.

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Structural Phase Transition in $K_xNa_{1-x}NbO_3$

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Abstract. Lead-free ferroelectric ceramic system $K_xNa_{1-x}NbO_3$ ($x = 0.45, 0.50$ and 0.55) have been prepared by solid-state reaction technique by varying K/Na ratio. Their crystal structures have been investigated by room temperature XRD and Raman spectroscopy. Rietveld refinement analysis on XRD data suggest the monoclinic crystal structure having Pm space group for $K_{0.45}Na_{0.55}NbO_3$ and orthorhombic crystal structure with $Amm2$ space group for both $K_{0.5}Na_{0.5}NbO_3$ and $K_{0.55}Na_{0.45}NbO_3$ respectively. The composition driven structural phase transition of the $K_xNa_{1-x}NbO_3$ is seen by the splitting of the mode near 191 cm^{-1} as well. The presence of prominent central peak (CP) reveals the order-disorder nature of the ferroelectric phase transition of the $K_xNa_{1-x}NbO_3$.

INTRODUCTION

Among various lead-free alternatives, potassium sodium niobate ($K_{0.5}Na_{0.5}NbO_3$, abbreviated as KNN) ceramics have emerged as promising candidates, owing to their high remnant polarization, high Curie temperature, and moderate piezoelectric properties.^{1, 2} However, optimizing the performance of KNN-based ceramics requires a thorough understanding of how compositional variations influence their structural and functional properties. The solid solution of $KNbO_3$ and $NaNbO_3$ form $K_xNa_{1-x}NbO_3$ within the solid solubility limit.² In the ideal KNN composition, the A-site is equally occupied by K^+ and Na^+ ions. The variations of K/Na ratio can lead to local structural distortions, the formation of secondary phases, and modifications in long-range crystallographic symmetry, all of which directly affect the material's electrical properties. This study aims to systematically investigate the effects of varying K and Na stoichiometry around $K_{0.5}Na_{0.5}NbO_3$ on both the local structure (using Raman Spectroscopy) and the global structure (using XRD analysis) of the ceramics.

EXPERIMENTAL TECHNIQUES

Polycrystalline ceramics of $K_xNa_{1-x}NbO_3$, ($x = 0.45, 0.50$, and 0.55) synthesized by conventional solid-state reaction method. K_2CO_3 (99% Alfa Aesar), Na_2CO_3 (99.5% Sigma Aldrich), Nb_2O_5 (99.99% Sigma Aldrich) used as precursors. The detailed synthesis procedure has been followed as per our previous article.² The calcination was carried out at $875^\circ\text{C}/6\text{h}$ followed by sintering at $1125^\circ\text{C}/3\text{h}$. Structural analysis performed using X-ray diffractometer (RIGAKU/ULTIMA IV) in 2θ range (20° - 100°) at a scan rate of 2° min^{-1} with step size of 0.01° . The RT Raman spectra of the sintered pellets were collected using micro-Raman spectrometer (INVIA, RENISHAW, UK).

RESULTS AND DISCUSSION

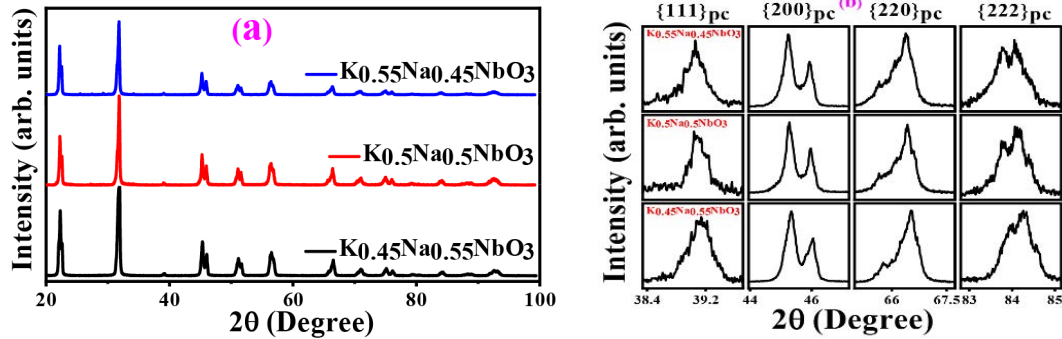


FIGURE 1. (a) Room temperature XRD pattern of $K_xNa_{1-x}NbO_3$ (b) Evolution of pseudocubic Bragg profiles of $\{111\}_{pc}$, $\{200\}_{pc}$, $\{220\}_{pc}$, $\{222\}_{pc}$ obtained from room temperature XRD

The XRD patterns of $K_xNa_{1-x}NbO_3$ ($x = 0.45, 0.50$ and 0.55) are shown in fig. 1(a). The existence of sharp and well-defined peaks indicates its highly crystalline structure without any pyrochlore phase confirming the formation of single-phase perovskite structured material. The compositional emergence of the XRD profiles of four pseudo-cubic (pc) reflections ($\{111\}_{pc}$, $\{200\}_{pc}$, $\{220\}_{pc}$, and $\{222\}_{pc}$) are shown in fig. 1(b). The variations in the pc reflections indicate that structural phase transition occurs across the compositions by varying K/Na ratio. The best method for determining tetragonal, orthorhombic, and rhombohedral crystal structures is to examine the splitting of $\{h00\}_{pc}$, $\{hh0\}_{pc}$, and $\{hhh\}_{pc}$.² For an orthorhombic crystal structure, $\{h00\}_{pc}$ and $\{hhh\}_{pc}$ are expected to get splitted. It is evident that $K_{0.5}Na_{0.5}NbO_3$ and $K_{0.55}Na_{0.45}NbO_3$ exhibit the doublet character of their $\{200\}_{pc}$ and $\{222\}_{pc}$. Moreover, it is also observed that for $K_{0.5}Na_{0.5}NbO_3$ and $K_{0.55}Na_{0.45}NbO_3$, the $\{200\}_{pc}$ reflection around 45° splits into 200 and 020 such as the intensity of 200 peak is double that of 020, which is the typical nature of orthorhombic crystal structure. However, for $K_{0.45}Na_{0.55}NbO_3$, the peak splitting of $\{222\}_{pc}$ reflection around 85° is not clearly visible due to broadening of pseudo-cubic reflections. This information suggests that its crystal structure is different from orthorhombic and hence we have considered the lower symmetry monoclinic crystal structure. Baker *et al.* reported the transition of monoclinic to orthorhombic phase around $x = 0.5$ for $K_xNa_{1-x}NbO_3$ and hence $K_{0.45}Na_{0.55}NbO_3$ is supposed to be in monoclinic phase at room temperature.³ In view of that, we have fitted the XRD data of $K_{0.45}Na_{0.55}NbO_3$ with monoclinic structure (SG: Pm) and $K_{0.5}Na_{0.5}NbO_3$ and $K_{0.55}Na_{0.45}NbO_3$ with orthorhombic (SG: $Amm2$) using Rietveld refinement analysis as shown in fig. 2(a).

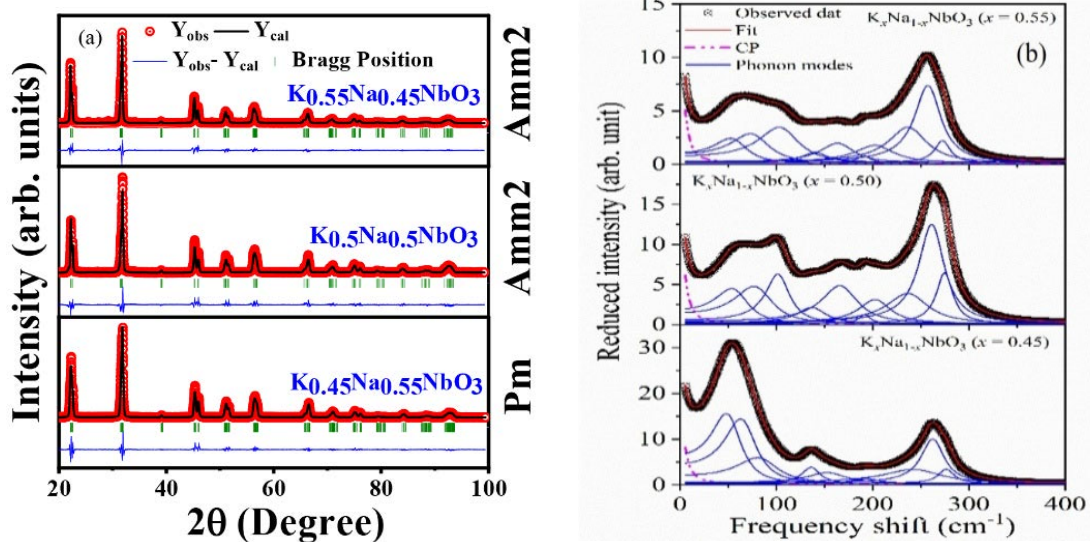


FIGURE 2. (a) RT Rietveld refined XRD pattern of $K_xNa_{1-x}NbO_3$ and (b) Fitted low frequency Raman scattering spectra of $K_xNa_{1-x}NbO_3$. The Raman spectra are fitted using the combination of Lorentzian central peak (CP) and damped harmonic oscillators (DHOs) model.

Rietveld refinement performed by FULLPROF suit to accurately determine the structural phase transitions. The diffraction data for $\text{K}_{0.45}\text{Na}_{0.55}\text{NbO}_3$ is best fitted using monoclinic structure (S.G.: *Pm*), whereas the patterns for $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ and $\text{K}_{0.55}\text{Na}_{0.45}\text{NbO}_3$ are refined using orthorhombic structure (S.G.: *Amm2*). Good agreement between experimental and simulated profiles yielded, indicated by χ^2 value of 3.36, 3.05, and 2.91 for $x = 0.45, 0.50$, and 0.55 , respectively. The refined lattice parameters are obtained after refinement are as follows: $\text{K}_{0.45}\text{Na}_{0.55}\text{NbO}_3$ (*Pm*): $a = 4.0096$ (2) Å, $b = 3.9475$ (1) Å, $c = 3.9945$ (2) Å, $\beta = 90.33$ (0)°, $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (*Amm2*): $a = 3.9602$ (2) Å, $b = 5.6604$ (3) Å, $c = 5.6956$ (3) Å and $\text{K}_{0.55}\text{Na}_{0.45}\text{NbO}_3$ (*Amm2*): $a = 3.9561$ (2) Å, $b = 5.6554$ (3) Å, $c = 5.6891$ (2) Å. Due to the *Pm* monoclinic symmetry of $\text{K}_{0.45}\text{Na}_{0.55}\text{NbO}_3$, its unit cell volume is approximately half that of the orthorhombic phases (*Amm2*). We have also investigated reduced Raman scattering spectra to understand the composition driven structural phase transition of $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ ceramics.⁴ Raman spectra of the $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ can be rationalized by the vibrational modes of coordination polyhedrons and isolated cations. The vibrational modes come from the internal NbO_6 octahedron modes and the K^+/Na^+ cations translational modes. The NbO_6 octahedron vibrational modes consist of $A_{1g}(\nu_1) + E_g(\nu_2) + 2F_{1u}(\nu_3, \nu_4) + F_{2g}(\nu_5) + F_{2u}(\nu_6)$,² where $A_{1g}(\nu_1)$, $E_g(\nu_2)$, and $F_{1u}(\nu_3)$ are stretching modes, and the rest of the modes are bending. In the frequency range lower than around 200 cm^{-1} , Raman modes may be attributed to rotation of the octahedron and the translational modes of the K^+/Na^+ cations. However, in the high-frequency range of $200\text{--}900\text{ cm}^{-1}$, Raman modes can be assigned due to internal vibrational modes of the octahedron. The ν_6 mode related to NbO_6 octahedron may also appear in the low frequency range, and peaks around $137\text{--}142\text{ cm}^{-1}$ corresponds to ν_6 mode in this study. The translational modes of K^+/Na^+ cations appear at around $55\text{--}83\text{ cm}^{-1}$, whereas the mode near 192 cm^{-1} is associated to NbO_6 octahedron versus K^+/Na^+ cations. The rotational mode of the NbO_6 octahedron may appear at around 103 cm^{-1} . Raman modes near $247\text{--}263\text{ cm}^{-1}$ can be assigned to the ν_5 mode. The modes at about 440 cm^{-1} , 548 cm^{-1} , 620 cm^{-1} , and 710 cm^{-1} are denoted as ν_4 , ν_2 , ν_1 , and ν_3 modes of the NbO_6 octahedron, respectively. The mode near 859 cm^{-1} is commonly treated as the coupled $\nu_1 + \nu_5$ mode. The high frequency Raman spectra are not shown here, and the detailed Raman scattering results will be reported elsewhere. In monoclinic phase, the lowest frequency mode, which are attributed to lattice distortions and sensitive to structural phase transition, appears near 55 cm^{-1} as shown in fig. 2(b). As can be seen in fig. 2(b), the shape and size of the peaks near $55\text{--}83\text{ cm}^{-1}$ significantly change with compositions, denoting the substitution of the K ions with Na ions. It is worth noting that the mode near 192 cm^{-1} , which is attributed to K^+/Na^+ cations versus NbO_6 octahedron, splits into two with increasing K contents. The splitting of the mode may be due to increase of local distortion of the NbO_6 octahedron, which breaks the symmetry results in structural transition from monoclinic to orthorhombic phase of the $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$. This finding is supported by the XRD analysis as well. The common feature of order-disorder nature of the ferroelectric phase transition is the existence of CP, whereas the displacive nature is marked by the presence of soft mode phenomena. It is difficult to make a comment regarding the soft mode nature of the lowest frequency mode due to the lack of temperature dependent Raman scattering spectra. However, the prominent CP is found in this study, denoting the order-disorder nature of the ferroelectric phase transition of the $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$.

CONCLUSION

$\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ ($x = 0.45, 0.50$ and 0.55) ceramics are prepared by solid-state reaction technique. From Rietveld refinement analysis, it is concluded that $\text{K}_{0.45}\text{Na}_{0.55}\text{NbO}_3$ is best fitted with monoclinic structure (S.G.: *Pm*) whereas orthorhombic structure (S.G.: *Amm2*) is stabilized for $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ and $\text{K}_{0.55}\text{Na}_{0.45}\text{NbO}_3$. The order-disorder nature of the ferroelectric phase transition of the $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$ is observed by the existence of the prominent CP.

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Structural Characteristics and Dielectric Features of Lead-Free BKT-BST Submicrorods

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Abstract. In the present work, the synthesis protocol, structural characteristics and dielectric behavior of lead-free submicrorods composed of $0.75\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ - $0.25\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BKT-BST). Structural analysis reveals a predominantly tetragonal phase with minor distortion in TiO_6 octahedral unit. Morphological observations confirm the formation of highly dense submicrorods. Room temperature dielectric spectra show that the BKT-BST submicrorods exhibit significant dielectric constant with low dissipation, making them a potential candidate for microelectronics application.

INTRODUCTION

Lead based dielectric and ferroelectric compounds have serious environmental issues. Therefore, the recent research has been concentrating on developing a novel lead-free ferroelectric and dielectric materials for advanced electronic devices [1], [2]. They have capabilities to show high dielectric constant, low dissipation, and significant polarization [3]. $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ (BKT) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST) are lead free ferroelectric materials with perovskite structure [4], [5]. BKT display relatively high Curie temperature ($T_c \sim 380^\circ\text{C}$) [5], [6]. On the other hand, BST show a promising application as multilayer ceramic capacitors due to its potential dielectric features and environmental compatibility though it possesses Curie temperature at ambient temperature. The relative dielectric permittivity for BST at room temperature is reported about 650 at 1 kHz [7], [8] it shows high dielectric constant, low loss tangent, cost effective synthesis and higher thermal stability [9]. It can be very interesting to explore the structural and dielectric feature when BKT and BST are combined in the form of solid solution. In line with this objective, the solid solution of $0.75\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ - $0.25\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BKT-BST) is developed by using sol-gel method. The deep investigations on its structural, morphological and dielectric characteristics are carried out and studied.

EXPERIMENTAL DETAILS

BKT-BST solid solution was prepared by sol-gel technique. High purity grade of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, KNO_3 , $\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$ were used as precursors. Initially metal nitrates were dissolved in the distilled water and citric acid was added to achieve 1:2 metal to citrate ions ratio. Thereafter, pH of resultant solution was maintained to 7 by liquor ammonia solution. Titanium isopropoxide was separately mixed with citric acid in 1:2 molar ratio, and pH was adjusted to 7 by same procedure. Both the solutions were mixed and stirred well and heated at 90°C till the gel formation. Then, the gel was decomposed at 250°C to get porous powder. The resulting powder was calcined at 700°C for 4 hours to get desired crystalline sample.

RESULT AND DISCUSSION

Fig. 1(a) shows raw X-ray powder diffraction pattern of BKT-BST sample. It is indexed with tetragonal structure

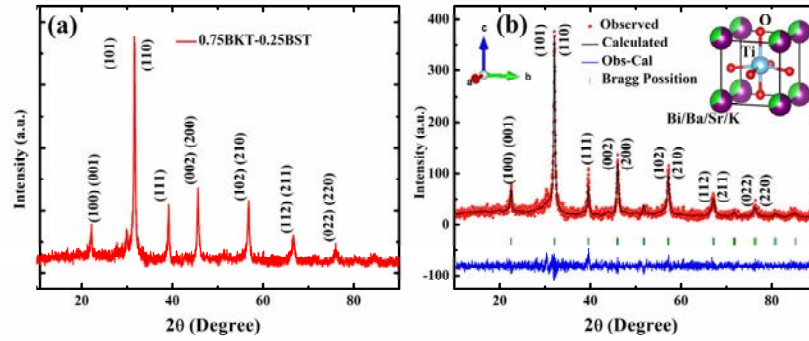


FIGURE 1. (a) XRD pattern of BKT-BST sample, (b) Rietveld refinement of raw XRD patterns of BKT-BST solution

(space group: $P4mm$) without any traces of impurity phases. Rietveld refinement (Fig.1b) of XRD data display a good agreement with tetragonal perovskite phase of $P4mm$ symmetry. The refined lattice parameters are obtained to be $a=b=3.93930 \text{ \AA}$ and $c=3.9510 \text{ \AA}$ and c/a ratio is observed to be 1.002 which are comparable with the earlier report[10]. It indicated a slight distortion in tetragonal unit cell. The 3D unit cell is visualized via VESTA software and presented in the inset of Fig. 1b. It shows the existence of distorted TiO_6 octahedra at the centre of unit cell.

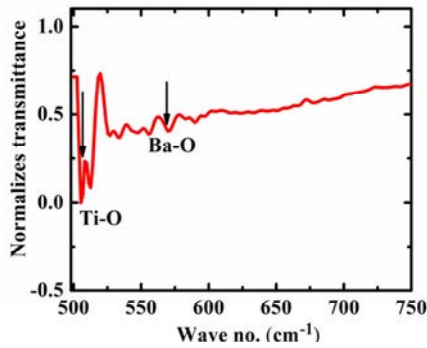


FIGURE 2. Room temperature FTIR spectrum of BKT-BST

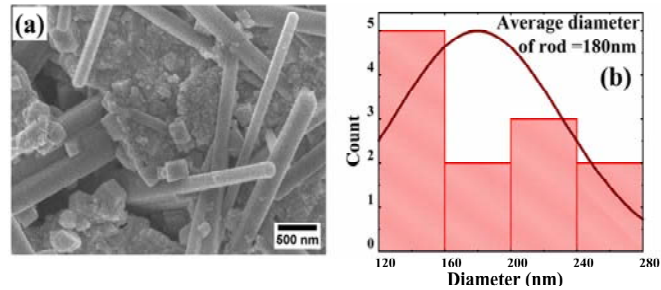


FIGURE 3. (a) FESEM image of BKT-BST with (b) size distribution plot of rods.

The FTIR spectra of BKT-BST sample exhibits strong transmission bands in the range of $500\text{--}750 \text{ cm}^{-1}$ as shown in Fig 2. The transmittance peak appeared at $500\text{--}520 \text{ cm}^{-1}$ is corresponding to stretching vibration of Ti-O bonds [11], The bands around 566 cm^{-1} are due to Ba-O bonding vibrations [12], Fig 3a indicates a surface morphology of BKT-BST solid solution was recorded using FESEM. It reveals a dense microstructure with rod-like morphology. The size distribution plot (Fig. 3b) yielded average diameter of 180 nm. Due to the Sr content, the structure becomes denser and the experimental density was found to be 3.5087 g/cm^3 .

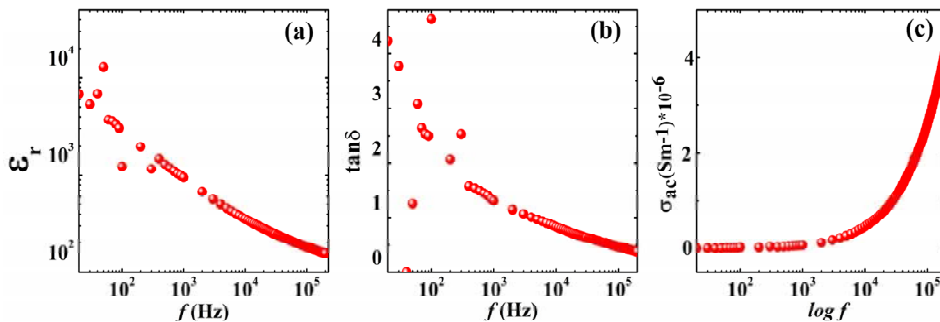


FIGURE 4. Frequency- dependent a) dielectric constant , b) $\tan\delta$ c) ac conductivity at room temperature

The room dielectric properties of BKT-BST solution were analyzed over a frequency range 20 Hz to 200 kHz as shown in Fig. 4a-c. Fig. 4 provides detailed insights into the dielectric constant (ϵ_r), loss tangent ($\tan\delta$), and Ac conductivity. Fig. 4a. shows the values of dielectric constant (ϵ_r) exhibits a decreasing trend with increasing frequency.

At low frequency high value (6872) of ϵ_r was observed that is due to interfacial and space charge polarization effect. The dissipation factor of BKT-BST system (Fig. 4b) at lower frequency was found to be relatively high due to conduction losses. As the frequency increases dielectric loss decreases reflecting reduced interfacial polarization. Above 1 kHz of frequency, the dissipation factor goes below 1. The AC conductivity (Fig. 4c) values were found to be of the order of 10^{-6} indicates resistive nature of sample. Moreover, the conductivity increases with frequency since charge carriers are responsive with respect to changing the frequency of electric field[13].

CONCLUSION

The lead-free BKT-BT submicrorods were successfully synthesized by sol-gel method. XRD result shows a single phase tetragonal perovskite structure with considerable unit cell distortion. FESEM result shows the dense microstructure of submicrorods with an average diameter of 180 nm. Room temperature frequency dependent dielectric spectra exhibited a high magnitude of dielectric constant of the order of 10^3 and low loss tangent. The overall results may facilitate for the utilization of BKT-BST submicrorods for advanced microelectronics application.

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Design of a High Performance Flexible Mechanical Energy Harvester Based on Graphene Doped Y_2O_3 -P(VDF-HFP) Nanocomposite

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Abstract. Flexible piezoelectric nanogenerator (PNG) fabricated by Yttrium oxide (Y_2O_3), and Graphene nanoplatelet doped composite film shows a maximum open circuit voltage output of 12 V. The capacitor-charging capability by the PNG indicates its suitability for effectively harvesting mechanical energy from finger impact (a pressure amplitude of ~ 11 kPa) and as an alternative in the area of self-powered energy harvesting devices.

INTRODUCTION

Nanoscale piezoelectricity is a recently developed field of study in academia shows enormous potential for powering tiny electronics and creating self-powering electronic systems.¹ Devices like flexible piezoelectric nanogenerators (PNGs) may offer a novel approach to battery-free gadget powering. The copolymer P(VDF-HFP) exhibits an unusual piezoelectric response, good alternative of similar kind of applications. Energy harvesting capability arises due to molecular dipoles (i.e., $-\text{CH}_2-/-\text{CF}_2-$) present in the P(VDF-HFP) copolymer matrix existing in the β - and γ -, and δ -phases.² So far, it has been established that the β -phase is fully electroactive due to its maximum dipole moment per unit cell. Among these, δ -phase is comparable to non-polar α -phase; nevertheless, it is a polarized, electroactive variant of α -phase, also referred to as α_p -phase. In this work, we have fabricated the polymeric PNG based on P(VDF-HFP) co-polymer. For this purpose, we have selected Y_2O_3 , and Graphene as fillers to investigate the cooperative effect within the composite $\text{hfp}^G\text{-y}(1)$ for efficiently reduce the dielectric heterogeneity of two different phases to induce electro-active phases to enhance the piezoelectric response. In contrast, electrical poling steps can be avoided as self-poled techniques are implemented and, thus, a cost-effective piezoelectric-based device becomes easier to fabricate.

EXPERIMENTAL SECTION

Simple solution casting method was used to prepare those films. First, 6 wt.% of P(VDF-HFP) pellets ($M_w \sim 275000$, SigmaAldrich, USA), was dissolved in 10 ml of DMF (Merk Chemical, India), via continuous stirring for 12 hours at 60°C and named 'hfp' solution. Then, the concentrations of 1 wt. % (Y_2O_3 , Alfa-Aesar) and 0.1 wt. % of (Graphene nanoplatelet, SRL India) fillers were added into the 'hfp' solution in different vial and vigorously stirred under constant magnetic stirring for 6 hours to ensure homogeneous dispersion. Afterward, the 'hfp' and the resulting solutions were dropped cast onto the clean glass slides, and dried at 60°C for 5 hours. Finally, the dried free-standing films were peeled off from the glass substrates for characterization and device fabrication and designated as 'hfp' film and $\text{hfp}^G\text{-y}(1)$ for the composite film. A thick film (thickness ~ 0.2 mm) of the composite was also prepared at 60°C for energy harvesting application purposes. FTIR (Bruker Tensor II) spectrometer with 4 cm^{-1} spectral resolution and XRD (Empyrean, D8 Advance) in the range ($2\theta = 0^\circ\text{--}100^\circ$) with $\text{CuK}\alpha$ radiation of $1.54\text{ \AA}$ wavelength was used to analyze the crystalline phases of the P(VDF-HFP) polymorph and its degree of crystallinity (χ_c). The surface morphology of the films was studied using (SEM) (JEOL, JSM – IT100) operated at an accelerating voltage of 20 kV. An elemental composition study was performed by XPS, (Thermo Fischer Scientific $\text{K}\alpha$) with a monochromatic source of Al $\text{K}\alpha$ (photon energy $\sim 1486.6\text{ eV}$). Piezoelectric output performances and capacitor charging voltage data by finger tapping from the PNG through a typical bridge circuit were taken using digital storage oscilloscope (DSO) and a normal digital multimeter. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

The FTIR spectra (Fig. 1(a)), shows the characteristic phonon modes of the well-known phases of the two films. After the Y_2O_3 , and Graphene fillers are introduced prominent characteristic peaks at 1277 and 1233 cm^{-1} appeared as the signature of β -phase and γ -phase respectively.³ The intense peak at 764 cm^{-1} of the hfp^G-y(1) composite signified as growth of the polarized α_P -phase i.e., the formation of δ -phase may occur during film preparation has analogous electroactive properties like the piezoelectric β -phase.⁴ The peak at 840 cm^{-1} also indicates the signature of both β - and γ -phases.³ Thus, the external fillers utilized in the P(VDF-HFP) solution, play an essential role in crystallographic phase transformation (i.e., $\alpha \rightarrow \gamma/\beta/\delta$ phases). The intensity of absorption at the 840 cm^{-1} band is selected to calculate the electroactive phases (F_{EA})% of the hfp^G-y(1) composite. The following equation can be used for the calculation of F_{EA} i.e.,

$$F_{EA} = \frac{A_{EA}}{\left(\frac{K_{840}}{K_{764}}\right) \times A_{NEA} + A_{EA}} \times 100\% \quad (1)$$

where A_{EA} is the intensity of absorbance at 840 cm^{-1} , A_{NEA} is the intensity absorbance at 764 cm^{-1} , K_{840} is the absorption coefficient at 840 cm^{-1} , and K_{764} is the coefficient of absorption at 764 cm^{-1} . The values are $K_{840} = 7.7 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$ and $K_{764} = 6.1 \times 10^4 \text{ cm}^2 \text{ mol}^{-1}$.⁵ Fillers Y_2O_3 , and Graphene interact with P(VDF-HFP) molecules and the formation of δ -phase contributes in dipole moment along with the β - and γ -phase shows higher piezo response for the hfp^G-y(1) composite containing lower β -phase.⁶

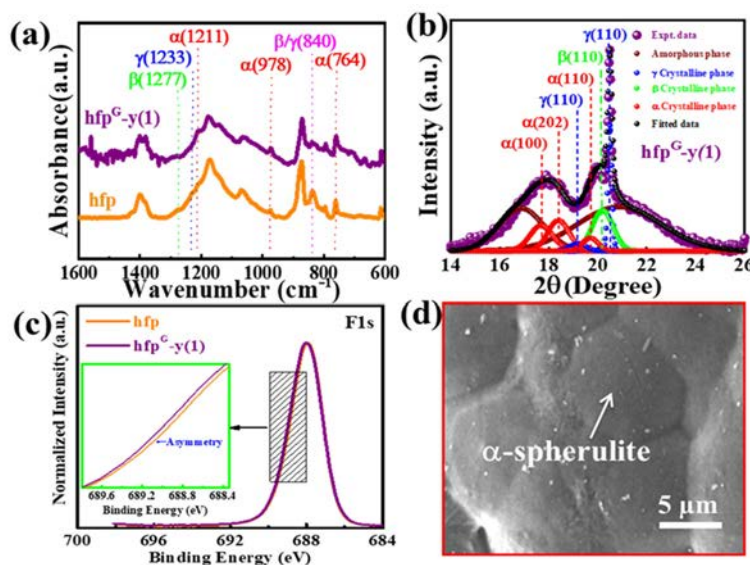


FIGURE 1. (a) FTIR spectra of the 'hfp' film and hfp^G-y(1) composite film, (b to d) The XRD and XPS spectra with SEM image of the composite. The inset of (c) shows the asymmetry that arises in the F1s spectra in the composite.

The estimated electroactive phases (F_{EA}) for hfp^G-y(1) composite is about 22% and the proportion of β -phase, i.e., $F(\beta)$ is 17%. The XRD pattern of the composite (Fig. 1(b)) represents the presence of β -phase at $2\theta \sim 20^\circ$ (110/220) along with α -, and γ -phases and the overall crystallinity in the composite is found to be ($\chi_c \sim 34\%$).⁵ It is a common characteristic of reinforced polymer composite film, which is well-suited for improving dielectric properties. Fig. 1(c) shows XPS spectra of the normalized F1s level originated from F atoms in P(VDF-HFP) copolymer matrix with an expected unique peak at a binding energy of 688 eV. The change of normalized peak area with an asymmetry at higher binding energy side (inset of Fig. 1(c)), justifying interfacial interactions.⁷ The SEM image (Fig. 1(d)) illustrates the surface morphology of the composite hfp^G-y(1) film showing typical spherulite platelet-like microstructure with an average diameter of around 9 nm respectively.⁶ It is identical for both α -, and δ -phases and is reasonable to assume the α_P -phase formation within the composite.^{6,7}

The flexible PNG-based piezoelectric harvester where the mechanical energy harvesting capability has been assessed by impacting repetitive stress amplitude of ~ 11 kPa by constant finger tapping on the surface of the PNG of the hfp^G-y(1) composi.⁵ It demonstrated a maximum open-circuit output voltage of about 12 V (Fig. 2(a)) and could

successfully charge the 1 and 2.2 μF capacitors independently using full-wave bridge circuit in a very short time, about 50 s (Fig. 2(b)) and the power stored in the capacitors as shown in Fig. 2(c) promising for the development of energy harvesting applications. So, together with the β - and γ -phases, the δ -phase may have contributed to the dipole moment in aligned molecular ($-\text{CH}_2-/-\text{CF}_2-$) dipoles of P(VDF-HFP) which is the reason the composite with smaller β -phase exhibits higher piezo voltage.⁴

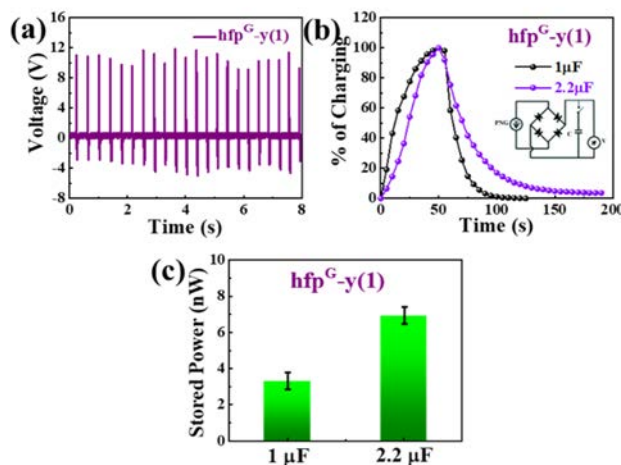


FIGURE 2. (a) PNG's open-circuit voltage caused by finger touch response, (b) Charging response of capacitor (1 and 2.2 μF) as a function of time and the inset displays the equivalent circuit schematic, (c) Power stored in the capacitors from the PNG.

CONCLUSIONS

In summary, we have fabricated the flexible (PNG) by hfp^G-y(1) composite film shows a maximum open circuit voltage output of 12 V. The capacitor charging ability of fabricated PNG under repeated finger-touch motion is very promising for several possible implementations and an interesting candidate for electromechanical systems like security monitoring, noise detection, and health care monitoring.

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Exploring the Influence of Lanthanum doping on Electrical Properties of $K_{0.5}Bi_{0.5}TiO_3$ Ceramics

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Abstract. Potassium bismuth titanate (KBT) of perovskite structure is among the lead-free piezoelectric and ferroelectric materials that shows number of applications in sensors, Micro-electro-mechanical systems and actuators. However, KBT with rare earth doping is still under discussion, although KBT in bulk ceramic form has been widely studied. In this article, we synthesized lanthanum doped $K_{0.5}(Bi_{1-x}La_x)_{0.5}TiO_3$ at $x = 0.0$ and 0.3 ceramic by sol-gel technique. An optimized concentration has been taken to study the electrical and ferroelectric properties of lanthanum doped KBT. Leakage current density with electric field was observed from 20-200 °C. According to current density electric field characteristics (J-E curve), ohmic conduction was determined to be the predominant conduction mechanism. The lanthanum doped ceramic exhibits low dielectric loss compared to the undoped KBT ceramic at room temperature. P-E loop traces demonstrated good saturation in the curves.

INTRODUCTION

Increasing demand of environment friendly materials has led the world's scientists to explore lead free piezoelectric materials to meet this demand. In search of promising alternatives for lead-based piezoelectric and ferroelectric materials, there has been numerous findings from all over the world. Promising lead-free piezoelectric materials are still under research as there has been no single composition which is comparable to that of $(Pb [Zr_xTi_{1-x}] O_3)$, PZT. In such findings, Potassium bismuth titanate (KBT) has found its place in number of applications like sensors, actuators, Micro-electro-mechanical systems (MEMS), and transducers [1, 2]. Smolenskii et al. reported KBT in the 1960s [3]. KBT is a piezoelectric material and has perovskite type (ABO_3) structure at room temperature (RT) [3]. Due to its high Curie temperature ($T_c = 380$ °C), KBT is a good candidate for high temperature applications [4]. However, KBT has been rarely reported due to the hygroscopic nature of potassium and bismuth which makes it difficult to sinter with high density. In order to overcome this, we doped KBT with lanthanum, a rare earth element which has been figured highly efficient for better electrical and ferroelectric properties. The incorporation of La^{3+} ions for K^+/Bi^{3+} ions could help stabilize the oxygen ions in the lattice and may even lower the dielectric loss and dc conductivity of KBT. Indeed, the incorporation of La^{3+} due to similar ionic radius as that of K^+ ions, increases the A-site disorder which leads to a local phase fluctuation with the random field distribution [5]. The structural and optical characteristics of $K_{0.5}(Bi_{1-x}La_x)_{0.5}TiO_3$ (at $x = 0.0, 0.1, 0.2$ and 0.3) has been studied in the previous article [6]. In order to study the electrical and ferroelectric properties, $K_{0.5}(Bi_{1-x}La_x)_{0.5}TiO_3$ at $x = 0$ and 0.3 was studied which gives a refined perovskite structure.

METHODOLOGY

Stoichiometric amount of potassium nitrate (purity-99.98%), lanthanum nitrate (purity-99.99%), tetra-n-butyl orthotitanate (purity-99.99%) and bismuth nitrate pentahydrate (purity-99.98%) were used as chemical precursors in the synthesis process. The synthesis process used was sol-gel technique. To prepare a dry gel, a prepared solution of precursors was heated at 80 °C for 12 h. The dried gel was grounded and calcined at 950 °C in alumina crucibles for 3 h in a hot furnace. The powder was taken for two lanthanum concentration named as KBT for $K_{0.5}(Bi_{1-x}La_x)_{0.5}TiO_3$ for $x = 0.0$ and KLBT-3 for $K_{0.5}(Bi_{1-x}La_x)_{0.5}TiO_3$ for $x = 0.3$. The powders were then calcined and pressed into pellets at 5 tons pressure. After that pellets were sintered at 1100 °C for 3 h. Silver paste was then applied to study the electrical properties of the ceramic.

RESULTS AND DISCUSSION

Phase Study

XRD study of the prepared samples were carried out which was calcined at 950 °C for 3 h as shown in Fig 1(a). JCPDS Card No. 36-0339 confirmed the perovskite phase having tetragonal symmetry [6]. The intensity of XRD peaks are stronger which shows high tetragonality of the ceramics increases with La^{3+} ion concentration. The ionic radius, La^{3+} ions can occupy the A-site of Bi^{3+} ions, but they are unable to reach the B-site due to the very short ionic radius of Ti^{4+} (0.0605 nm). The ionic radius of the substituted ion is comparable to that of the $\text{K}^+/\text{Bi}^{3+}$ ion, this suggests that lanthanum occupied the A-site. The sharp peak at about 32.05 degrees illustrates how the doping alters peak width and intensity. Nevertheless, the peak intensifies and the (101) peak shifts, indicating an increase in the degree of crystallinity. This suggests that the crystal structure's symmetry has increased.

Leakage Current Density

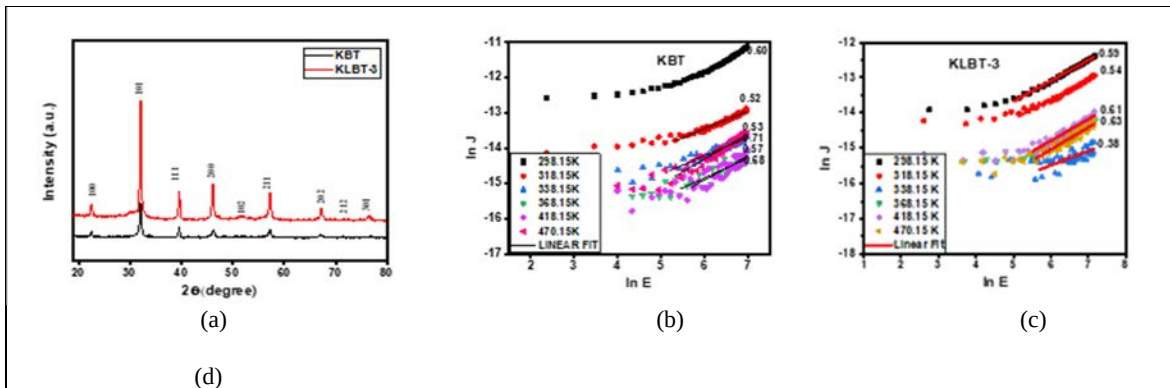
Leakage current density with electric field was studied. Fig.1 (b) and (c) shows the variations of $\ln J$ with $\ln E$. Leakage current density (J) increases with applied electric field due to cationic vacancies and defect states, particularly oxygen vacancies formed by cation evaporation. The leakage current density ranges from 10^{-9} to 10^{-4} A/cm² for KBT and 10^{-10} to 10^{-5} A/cm² for KLBT-3, with the lower values in the doped sample attributed to reduced oxygen vacancies upon lanthanum substitution. At higher applied fields, linear ohmic conduction dominates, as confirmed by slope values obtained from linear fitting.

Ferroelectric Study

Fig. 1(d) presents the P-E hysteresis loops for KBT and KLBT-3. The unsaturated loop in KBT is attributed to oxygen vacancies, which increase conductivity and leakage current density, resulting in a weakly developed ferroelectric response. With lanthanum substitution, the loop becomes saturated in KLBT-3, indicating improved ferroelectric behavior. As listed in Table 1, both remanent polarization (P_r) and coercive field (E_c) decrease with increasing lanthanum concentration, P_r from 18.64 to 18.17 $\mu\text{C}/\text{cm}^2$ and E_c from 4.32 to 3.16 kV/cm, consistent with the lower coercive field and reduced conductivity observed in the doped ceramic[6].

Table 1. Ferroelectric properties of $\text{K}_{0.5}(\text{Bi}_{1-x}\text{La}_x)_{0.5}\text{TiO}_3$ (at $x = 0.0$ and 0.3)

	E_c (kV/cm)	P_r ($\mu\text{C}/\text{cm}^2$)
KBT	4.32	18.64
KLBT-3	3.16	18.17



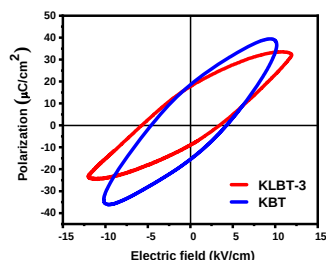


FIGURE 1.(a) XRD patterns revealing perovskite phase of KBT and KLT-3 (b) and (c) $\ln(J)$ vs $\ln(E)$ curves (d) P–E hysteresis loops of KBT and KLT-3

CONCLUSION

Electrical and ferroelectric properties of $K_{0.5}(Bi_{1-x}La_x)_{0.5}TiO_3$ (at $x = 0.0$ and 0.3) ceramics were studied by sol-gel technique. No impurities were detected in the phase structure by the XRD technique. Temperature dependent leakage current density analysis with electric field shows that ohmic conduction is the predominant mechanism. Leakage current density reveals low value for lanthanum doped ceramic when compared to KBT. P-E loop shows good saturation curve for lanthanum doped ceramic.

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Enhancing Dielectric and Energy Storage Properties of PVDF-HFP Electrospun Fibers through Variation in Drum Collector Rotation Speed

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Abstract. PVDF-HFP thick films have been prepared by electrospinning technique and the effect of rotation speed (200 rpm, 500 rpm, 500 rpm) of drum collector has been studied on the structural, dielectric and energy storage properties. A systematic enhancement in the dielectric, ferroelectric and energy storage properties has been observed with an increase in the rotation speed. The fiber films prepared at 500 rpm i.e. (HP-500) possesses the highest discharged energy density of 2.53 J/cm³ and the highest value of dielectric constant i.e., 13.7.

INTRODUCTION

The emerging era of modern technologies introduces a greater challenge with opportunities in the domain of energy storage devices [1]. The formation of chemically and thermally stable, flexible energy storage devices is critical. Polyvinylidene fluoride (PVDF) based dielectric polymers exhibit interesting properties, such as a high dielectric constant, breakdown strength, and energy densities, with chemically and thermally stable behavior, which makes them suitable candidates to be used as a capacitor in energy storage devices. PVDF-HFP, i.e., a co-polymer of PVDF, has drawn the attention of researchers due to its higher energy densities, low dielectric loss, and being more economical for preparing composites and pristine flexible films. Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) exhibits four different crystalline phases, i.e., α , β , γ , and δ . All these phases exist in a different chain conformation known as Trans (T) & Gauche (G) [2-3]. These different phases play a significant role in deciding the ferroelectric properties of the polymer according to their chain conformations. Different preparation methods, such as solvent casting, tape casting, electrospinning, and twin-screw extruder, have been adopted by various researchers to prepare composite films [4]. Electrospinning has become more appropriate in preparing flexible fiber films with a diameter ranging from several nanometers. The different reports suggested that PVDF fiber films prepared via electrospinning have a larger amount of β phase due to the effect of high voltage that helps in poling of the prepared fiber film [5-6]. In this study, we have prepared PVDF-HFP fiber films using the electrospinning technique at different rotation speeds of the drum collector and further hot-pressed at 150 °C to get defect-free, pore-free, high-quality films. The dielectric and ferroelectric properties of the prepared films have been studied.

EXPERIMENTAL

Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) solid pellets, density = 1.78 g/mL) was purchased from Sigma ALDRICH, N, N-dimethylformamide (DMF) and acetone solvents from LOBA CHEMIE, having a density of 0.948 g/mL.

First, PVDF-HFP pellets were dispersed in a mixed solvent of N, N-dimethylformamide/Acetone with a weight ratio of (7:3), followed by continuous stirring of the solution on a magnetic stirrer. This prepared solution was transferred to a 5 mL syringe and set in an electrospinning instrument. Afterwards, a high DC voltage of 15 kV was applied at a distance of 15 cm between the collector plate and syringe, which resulted in the formation of a Taylor cone, and fibers were obtained on the drum collector at different speeds of 200 rpm, 500 rpm, and 800 rpm. The prepared fibers were hot-pressed at 150 °C with an applied force of 150 kN for 10 minutes and then used for characterization. The obtained hot-pressed fiber mats have a thickness in the range of 50 - 70 μ m. Structural study of

the samples was done by PANALYTICAL diffractometer (with source beam of Cu K α having a wavelength of 0.154 nm) in a range of 10° - 50° with a slow scanning rate at room temperature. Room temperature dielectric properties were measured by Wayne Kerr 6500B impedance analyzer in the frequency range 100 Hz – 1 MHz. The ferroelectric polarization versus electric field (P-E) loop studies were done by employing a 10 Hz triangular wave in the Premier Radiant-II Multi ferroelectric tester in the room temperature.

RESULTS & DISCUSSION

The structural study of the prepared films has been done via XRD, as shown in Fig. 1. For the HP-200 film, various crystalline peaks correspond to the α phase are observed at 18.4 ° (020) and 26.76 ° (021), for β -phase at 20.02 ° and 36.6 ° (101), and at 38.7 ° for γ -phase. In the case of HP-500 film, the peaks located at 18.36 ° (020) and 26.38 ° (021) correspond to α phase, β -phase peaks are observed at 20.04 ° and 36 ° (101) and γ -phase peak at 39.4 ° (211). For HP-800 film, two peaks correspond to α and β -phase are observed at 18.4 ° (020) and 20.16 °. [7-11] From the XRD pattern, β -fraction (X_β) and crystallinity (X) of all the films have been evaluated using these expressions [10]:

$$X(\beta) = \frac{A(\beta)}{\sum A(\alpha, \beta, \gamma)} \quad (1)$$

$$X = \frac{X_C}{X_C + X_A} \times 100 \quad (2)$$

; $A(\beta)$ is the area under the peak of β phase, and $\sum A(\alpha, \beta, \gamma)$ is the sum of the total area under the corresponding peaks, X_C is defined as the area under the crystalline region, and X_A is the area under the amorphous region. The amount of β fraction is estimated using Eq. (1) and Eq. (2) is used for calculating crystallinity. In the case of HP-200 film, the calculated β -phase is 46.42 % with a crystallinity of 29.83 %. The β -fraction and crystallinity is found to increase up to 50.48 % along with an increase in crystallinity to 30.34 %. The Highest amount of β -phase has been obtained for the HP-800 film, i.e., 53.23% with crystallinity of 27.73 %.

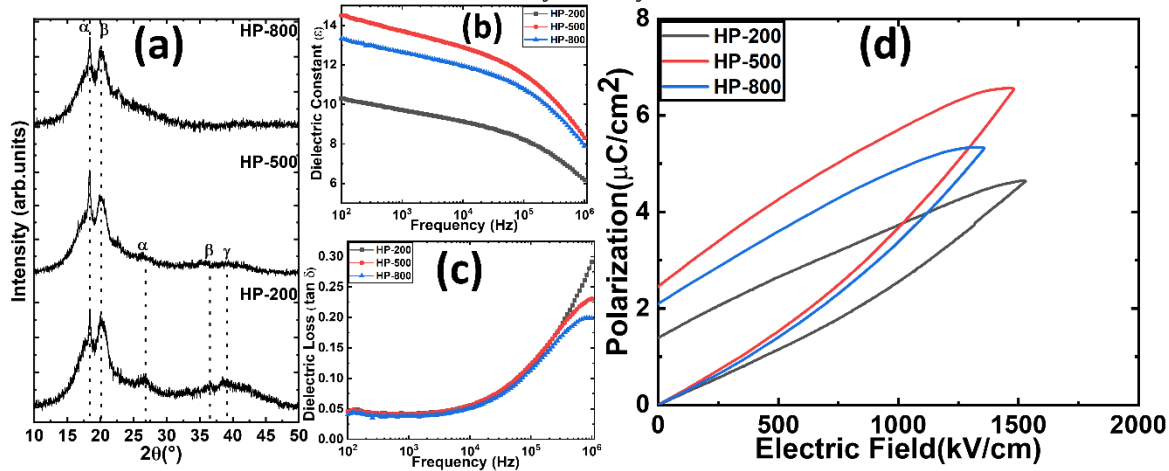


FIGURE 1. (a) X-ray diffraction patterns of HP-200, HP-500 & HP-800 films, (b) Dielectric constant (ϵ), (c) Loss ($\tan \delta$) and (d) Unipolar P-E loops of all samples

Dielectric and Energy Storage Properties

The dielectric study has been done for all samples in the 100 Hz - 10⁶ Hz frequency range, as shown in Fig. 1(b) & (c). A decrement in the dielectric constant while increase in dielectric loss with frequency was observed for all the films. This decrease in the dielectric constant is due to the inability of the dipoles to synchronize with the frequency [12]. For the HP-200 film, the dielectric constant of 9.72 is obtained with a dielectric loss of 0.042 @ 1 kHz of frequency. The dielectric constant increased to 13.7 with dielectric loss of 0.041 @ 1 kHz for HP-500 sample. For the HP-800 film, the dielectric constant decreased to 12.63 with a reduced dielectric loss of 0.037 @ 1 kHz of frequency. The increment in the dielectric constant of HP-500 rpm is attributed to the amount of the ferroelectric β & γ phases present in the system [13] and crystallinity of the system.

The P-E loop study of all the samples has been done to investigate the energy storage properties of the samples, as shown in Fig. 1(d). The various parameters, such as discharged energy density (U_d), charged energy density (U_e), and energy efficiency (η), have been calculated using the following expressions:

$$U_e = \int_0^{P_{\max}} E dP \quad (3)$$

$$U_d = \int_{P_r}^{P_{\max}} E dP \quad (4)$$

$$\eta = \frac{U_d}{U_e} \times 100 \quad (5)$$

here, $P_{\max}$, P_r , and η are the maximum polarization, remnant polarization, and discharge energy efficiency. For the HP-200 film, the value of maximum polarization ($P_{\max}$) is $4.64 \mu\text{C}/\text{cm}^2$ with remnant polarization (P_r) of $1.39 \mu\text{C}/\text{cm}^2$ at an electric field of $1529 \text{ kV}/\text{cm}$. Corresponding to these values, the discharged energy density (U_d) of $2.24 \text{ J}/\text{cm}^3$ with an energy efficiency of 55.6% was obtained for the HP-200 film. In contrast, the highest value of discharged energy density of $2.53 \text{ J}/\text{cm}^3$ with an energy efficiency of 44.91% at an electric field of $1481 \text{ kV}/\text{cm}$ has been observed for the HP-500 film. The highest value of maximum polarization ($P_{\max}$), i.e., $6.54 \mu\text{C}/\text{cm}^2$, with a remnant polarization (P_r) of $2.46 \mu\text{C}/\text{cm}^2$, was also observed for HP-500 film. For the HP-800 film, the value of maximum polarization ($P_{\max}$) and remnant polarization (P_r) was $5.32 \mu\text{C}/\text{cm}^2$ and $2.10 \mu\text{C}/\text{cm}^2$ at an applied field of $1358 \text{ kV}/\text{cm}$. The discharged energy density of $1.8 \text{ J}/\text{cm}^3$ with an energy efficiency of 43.92% has been obtained for this sample. This increment in the higher value of discharged energy density and efficiency is attributed to the higher crystallinity and the ferroelectric β & γ phases of the films that enhance the polarization in the prepared thick films.

CONCLUSION

The PVDF-HFP electrospun nanofiber hot-pressed films prepared at different drum collector speeds (200 rpm, 500 rpm, and 800 rpm), exhibits an enhancement in the dielectric and energy storage properties. The HP-500 film shows the highest value of discharged energy density of $2.53 \text{ J}/\text{cm}^3$ at an applied electric field of $1481 \text{ kV}/\text{cm}$ and highest value of dielectric constant i.e., 13.7 as compared to HP-200 (9.72) and HP-800 (12.63) films. The films prepared at 500 and 800 rpm (HP-500 and HP-800) possess a higher ferroelectric β phase and crystallinity value. Therefore, a variation in drum collector speed in preparing pristine fiber films will also be a favorable approach in improving the dielectric and energy storage properties of the thick films.

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Impact of annealing on the structural and dielectric properties of PVDF-5 KNN polymer –ceramic nanocomposite thick film

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Abstract. A poly (vinylidene fluoride) (PVDF) – Sodium potassium niobate (KNN) nanorods-based PVDF – 5 KNN nanocomposite films has been prepared using the solution casting method. The dispersion of KNN nanorods within the PVDF matrix leads to enhancing the electroactive phase (β -phase) with annealing temperature as estimated from X-ray diffraction. An increase in dielectric constant is observed for synthesized films and obtained maximum dielectric constant for film annealed at 80 °C.

INTRODUCTION

In recent years, polymer–ceramic based composites have become a research of interest because of their extensive applications in sensors, piezoactuators, multilayer capacitors [1 - 4], etc. By combining the merits of both polymers (flexibility, high breakdown field) and ceramics (high dielectric constant), the newly formed composites enhance overall properties in comparison to their separate parts. In polymer–ceramic composites, polymers act as a matrix in which ceramic nanoparticles are embedded as fillers. Among the polymers, poly (vinylidene fluoride) (PVDF) is widely studied due to its excellent dielectric performance, such as high dielectric constant ($\epsilon \sim 10 - 12$), breakdown strength and flexibility [4-6].

In ceramics, sodium potassium niobate (KNN) ceramic has been widely studied in the last few years due to its excellent dielectric and piezoelectric properties make it interesting to use it as filler in PVDF. In the PVDF – KNN nanocomposites, the physics at the interface of KNN and PVDF is unrevealed. The role of annealing temperature on interfacial interaction, structural, morphological, and dielectric properties still needs to be explored. In the present study, PVDF – 5 KNN nanocomposites were fabricated. The structural and dielectric properties of PVDF – 5 KNN nanocomposite thick films are examined. The effect of interfacial interaction and annealing conditions on structural and dielectric properties is studied.

EXPERIMENTAL DETAILS

Polyvinylidene fluoride (PVDF) film was synthesized by the solution casting method. PVDF pellets of amount 2 grams were mixed in 100 ml of dimethylformamide (DMF). The solution stirred continuously at 60 °C for 12 h. A viscous solution was obtained. The obtained solution was spread over a petri dish and placed at 60 °C for the evaporation of DMF solvent. A thick film was formed and peeled off from petri dish. Sodium potassium niobate (KNN) nanorods were synthesized by the hydrothermal method with reaction temperature of 160 °C for 6 h. The obtained powder was calcined at 500 °C for 2 h.

PVDF- 5 KNN nanocomposite was synthesized by adding 5 wt% of KNN nanorod powder into a solution of 2g PVDF in 100 ml DMF. After a continuous stirring for 12 h at 60 °C, the solution was gently spread over a petri dish and placed at 60 °C for solvent evaporation. Thick films of PVDF - 5 KNN were obtained. The films were annealed at 60 °C, 80 °C, and 100 °C temperatures named as PVDF-5KNN_AN_60, PVDF-5KNN_AN_80, and PVDF-5KNN_AN_100, respectively, throughout the manuscript. The structural properties of the sample were examined by X-ray diffraction (XRD PANalytical X'pert PRO MRD) using Cu - K α radiation of wavelength ($\lambda = 0.15406$ nm). The surface morphology examined by field emission scanning electron microscopy (FE-SEM) model Carl Zeiss Sigma 500. The dielectric data measurement was carried at room temperatures over frequency range 100 Hz - 1 MHz using a Wayne Kerr 6500B precision impedance analyzer.

RESULTS AND DISCUSSION

PVDF is a semi-crystalline polymer possesses crystalline phases α , β , γ , δ and ϵ , and the rest of the amorphous phase [4]. Among them three phases are stable in which α -PVDF is non-polar, whereas β -PVDF and γ -PVDF phases are polar [5]. The formation of these phases highly depends on synthesis conditions such as casting temperature and annealing conditions [5-7]. The formation of these phases can be confirmed from XRD.

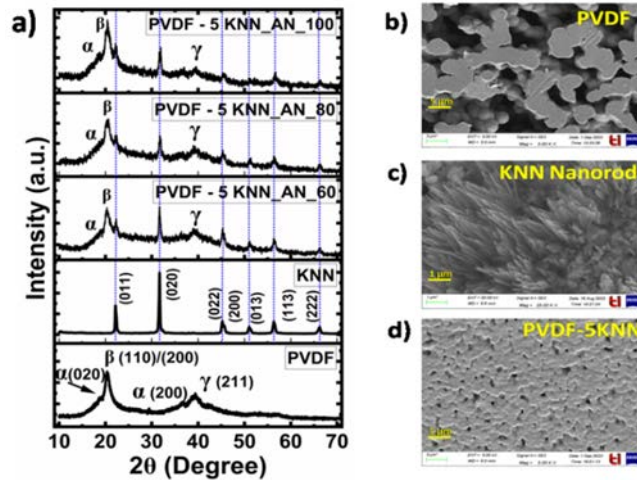


FIGURE 1: a) XRD pattern of PVDF, KNN nanorods, and PVDF-5KNN nanocomposites annealed at temperatures 60°C, 80°C, and 100°C, FE-SEM micrographs of b) PVDF, c) KNN nanorods, and d) PVDF – 5 KNN nanocomposite film.

Fig. 1a) represents the XRD pattern of synthesized PVDF film, KNN nanorods, and PVDF – 5 KNN nanocomposite films annealed at 60 °C, 80 °C, and 100 °C. The α -PVDF phase is identified by the peaks associated with 2θ values at 18.4° (020), 36.1° (200) [6-8]. The β -PVDF phase is identified by peaks within the range of 2θ values 20.2° to 20.8° and associated with (110/200) planes. The γ – phase is identified by peaks within the range of 2θ values 38° - 39° corresponding to the (211) plane. For the PVDF - 5 KNN film annealed at 60 °C, it is observed that the electroactive phase β -PVDF phase starts growing which is indicated by a peak around 20.3°.

Table 1: Semiquantitative values of β phase fraction $X(\beta)$ and degree of crystallinity calculated from XRD pattern.

Sample Name	$X(\beta)$ %	Degree of crystallinity (%)	Dielectric constant (ϵ) at 100Hz	Dielectric loss tangent ($\tan \delta$) at 100Hz
PVDF	35.66	31.04	9.57	0.28
PVDF-5 KNN_AN_60	39.31	32.06	13.72	0.26
PVDF-5 KNN_AN_80	52.87	32.14	19.54	0.68
PVDF-5 KNN_AN_100	52.20	34.36	15.01	0.35

As the annealing temperature increases, the β -PVDF phase starts dominating over the α -phase. The crystallinity also increases with increasing annealing temperature. The obtained values of degree of crystallinity and β - phase fraction are tabulated in Table 1. The surface morphology of pristine PVDF film, KNN nanorods, and PVDF – 5 KNN nanocomposite film is shown in Fig. 1b), 1c) and 1d), respectively. The enhancement of β - phase fraction in composite films may results in improving the dielectric properties.

Dielectric Properties: Frequency-dependent dielectric constant (ϵ) for PVDF and PVDF–5KNN nanocomposite films annealed at 60 °C, 80 °C, and 100 °C is shown in Fig. 2a) and corresponding dielectric loss tangent ($\tan \delta$) and ac conductivity (σ_{ac}) is shown in Fig. 2b) and Fig.2c), respectively. The obtained values of ϵ and $\tan \delta$ are given in Table 1. The values of dielectric constant increase with increasing annealing temperature up to 80 °C and then slightly decrease for film annealed at 100°C. This increment in dielectric constant is due to the conversion of PVDF phases from nonpolar α to polar β – phase. These results are consistent with XRD analysis, which depicts that with annealing temperature the electroactive β phase increases. At lower frequency the higher value of dielectric constant is observed which decreases with increasing frequency. This is due to space charge and interfacial polarization contribution in dielectric constant which eliminates at higher frequencies. From the dielectric loss ($\tan \delta$) profile, it is observed that $\tan \delta$ slightly increases for films annealed at 80 and 100 °C, which may attributed to the interface mismatch between

polymer and ceramic, and expansion of pores at higher temperature. The values of $\tan \delta$ with frequency are decreasing up to 100 kHz and then increases for higher frequencies. The enhancement in $\tan \delta$ for higher frequency is due to the α_a – relaxation process and micro-Brownian movement of chain segments of PVDF [5, 6]. From the ac conductivity (σ_{ac}) profile, the low values of σ_{ac} at lower frequency reinforce the dielectric behavior of the composite film. At higher frequencies the dispersive behavior in σ_{ac} is observed, as indicated in two different regions. In the first region, the linear response of σ_{ac} is due to frequency-independent conductivity and interfacial polarization. In the second region, the behavior of σ_{ac} can be related to the dipolar orientations at the interface of PVDF and KNN for high frequency field.

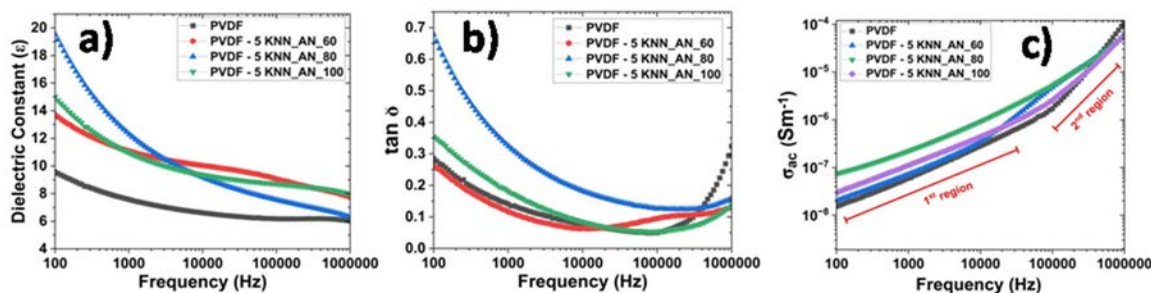


FIGURE 2: The frequency dependence of **a)** dielectric constant (ϵ'), **b)** loss tangent ($\tan \delta$), and **c)** ac conductivity (σ_{ac}) for PVDF-5 KNN films annealed at 60 °C, 80 °C, and 100 °C.

CONCLUSION

The structural and dielectric properties of PVDF -5KNN nanocomposite film annealed at 60 °C, 80 °C, and 100 °C are examined. Dielectric behavior reveals that the optimization of annealing conditions is necessary to get the transformation of more electroactive phase. This study concludes that the annealing temperature is the key parameter for obtaining a better dispersion of filler and matrix that enhance interfacial polarization, and improving dielectric response in polymer–ceramic nanocomposites.

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Enhanced Dielectric Response in PVDF-CoFe₂O₄ Nanocomposite Thick Films

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Abstract. The fabrication of polyvinylidene fluoride (PVDF)-based thick films embedded with cobalt ferrite (CoFe₂O₄) nanoparticles has been considered to achieve superior dielectric performance. CoFe₂O₄ nanoparticles are uniformly incorporated into the PVDF matrix using a solution casting technique at varying weight fractions 20%-100% in the step size of 20wt.% and denoted as PC20, PC40, PC60, PC80 and PC100 with the thickness 0.05mm. The resulting nanocomposites are extensively characterized using X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), and impedance spectroscopy. Structural analysis confirmed the development of the electroactive β -phase in PVDF. PC40 has achieved highest values for permittivity as $\epsilon_r \sim 54.5$ with real (ϵ') and imaginary (ϵ'') parts be ~ 54.3 and 5 respectively, along with low loss ~ 0.09 at 1kHz. These findings underscore the influence of nanoparticle loading on tuning the dielectric behavior of PVDF-CoFe₂O₄ nanocomposites, positioning them as promising materials for applications in capacitors, sensors, microwave and energy storage devices.

INTRODUCTION

The rapid growth of electronics, telecommunications, and energy storage technologies has increased the demand for dielectric materials with high permittivity, low loss, and good thermal/mechanical stability. Polymer-based composites are attractive candidates due to their flexibility, low weight, ease of processing, and tunable electrical properties via functional fillers. Poly (vinylidene fluoride) (PVDF), being a semi-crystalline polymer has excellent chemical resistance, mechanical flexibility, and electroactive properties such as ferroelectricity, piezoelectricity, and pyroelectricity, which are enhanced in its electroactive β -phase [1]. However, its low dielectric permittivity limits high-energy-density applications. Incorporating high-permittivity fillers can overcome this limitation. Cobalt ferrite (CoFe₂O₄) is a promising candidate due to its high dielectric constant, moderate conductivity, chemical stability, and magnetostrictive behavior. With a cubic spinel structure, CoFe₂O₄ can enhance PVDF's dielectric properties through Maxwell-Wagner-Sillars (MWS) interfacial polarization and by promoting β -phase formation [2].

SYNTHESIS AND CHARACTERIZATIONS

CoFe₂O₄ powder was synthesized via a hydrothermal route and weighed at 20, 40, 60, 80, and 100 wt.% loadings. Each batch was dispersed in 20 mL *N, N*-dimethylformamide (DMF) and ultrasonicated for 30 min. Separately, appropriate amount of PVDF was dissolved in required amount of DMF and mixed for ~ 30 min. The ferrite suspension was slowly added to the PVDF solution, ultrasonicated for 15 min, and magnetically stirred at 60–80 °C for 1–2 h. The slurry was cast onto petri dish, dried for ~ 6 h at 60 °C, and the resulting films (0.05 mm $\sim$ 50 μ m), denoted as PC20, PC40, PC60, PC80 and PC100 with respect to ferrite loading were peeled and stored for XRD, FTIR, FESEM, and dielectric characterization.

RESULTS AND DISCUSSION

Structural properties: Figure 1. (a) presents the X-ray diffraction study of synthesized nanocomposite films in which β phase of PVDF has been formed along with the presence of characteristic diffraction planes (220), (311), (400), (422), (511), and (440) of CoFe₂O₄ [3] suggesting the successful integration of filler into the matrix material. Similarly, FTIR spectra shown in Fig. 1(b) depicts the incorporation of ferrite into the polymer as the Fe-O bond attributing to CoFe₂O₄ is observed at 481 cm⁻¹. FTIR analysis exhibited a strong absorption band at 879 cm⁻¹, characteristic of CH₂

rocking vibrations in the β -phase, along with peaks at $1170\text{--}1173\text{ cm}^{-1}$ and $1405\text{--}1406\text{ cm}^{-1}$ corresponding to CF_2 stretching, confirming the β -crystalline phase of PVDF [2].

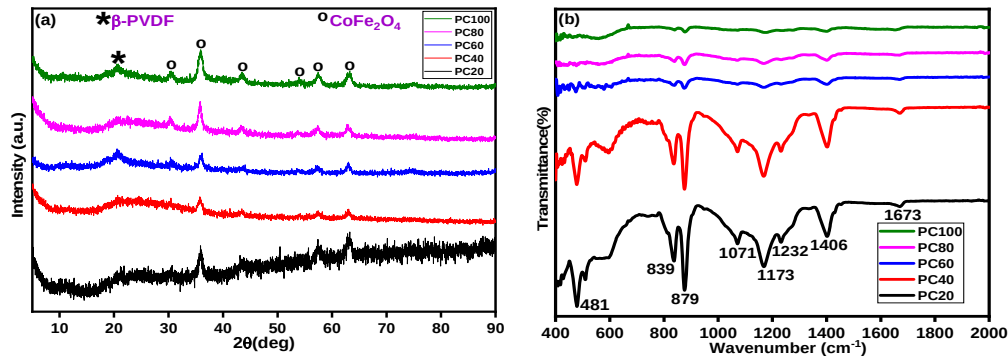


FIGURE 1. (a) XRD graph (b) FTIR spectra of PVDF- CoFe_2O_4 nanocomposite thick films

Morphological Studies:

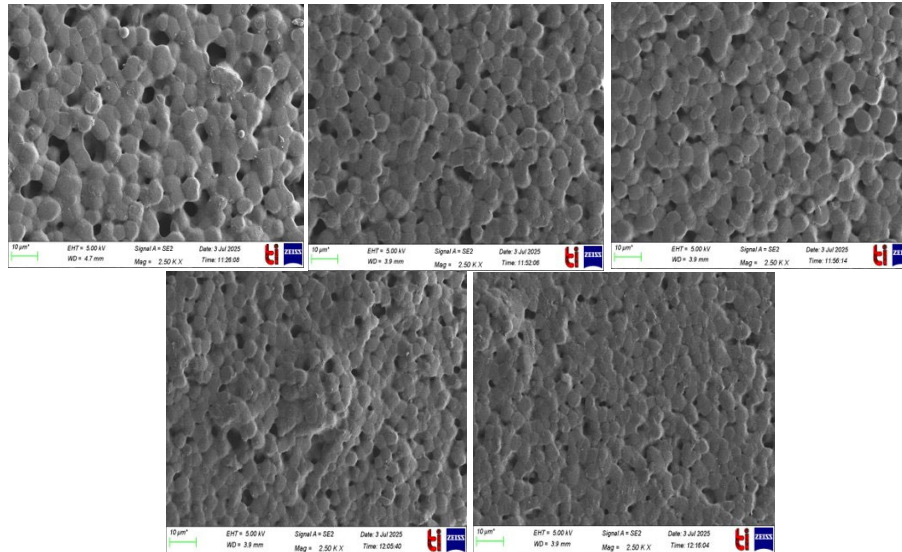


FIGURE 2. FESEM micrographs of PVDF- CoFe_2O_4 nanocomposite thick films

The FESEM images shown in Fig. 2 corresponds to microstructure evolution of PVDF based CoFe_2O_4 incorporated thick films. The increasing CoFe_2O_4 content transforms the PVDF film surface from porous (PC20) to dense and continuous (PC40-PC80), with PC100 exhibiting maximum compactness but slight nanoparticle agglomeration resulting into enhanced density and improved interfacial interactions among ferrite nanoparticles and PVDF matrix [4]. Figure 3. presents the dielectric response of the nanocomposites with respect to applied frequency which follows the Maxwell-Wagner-Sillars interfacial polarization characterized by a high dielectric constant (ϵ_r) at low frequencies due to space-charge accumulation at phase boundaries, followed by a gradual decline with increasing frequency [Fig. 3(a)]. Similar frequency-dependent trends are observed for dielectric loss ($\tan \delta$) [Fig. 3(b)], ϵ' [Fig. 3(c)], and ϵ'' [Fig. 3(d)], while AC conductivity (σ_{ac}) [Fig. 3(e)] increases with frequency, indicating hopping conduction of localized charge carriers [5]. PC40 with 40 wt.% of CoFe_2O_4 has achieved highest values for ϵ_r , $\tan \delta$, ϵ' , ϵ'' and σ_{ac} suggesting an optimal filler concentration for maximizing interfacial polarization and charge transport pathways without excessive particle agglomeration.

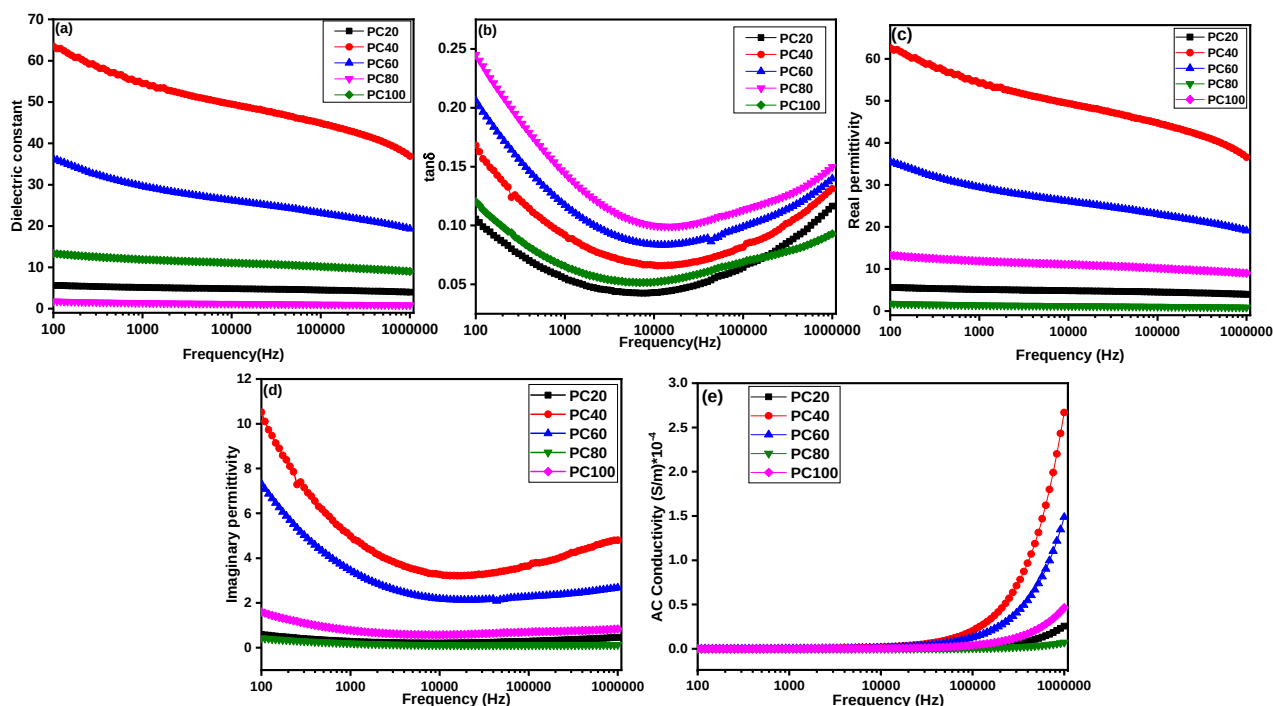
Dielectric properties:

FIGURE 3. (a) Dielectric constant (ϵ_r) (b) Tangent loss ($\tan\delta$) (c) Real permittivity (ϵ') (d) Imaginary permittivity (ϵ'') (e) AC conductivity (σ_{ac}) of PVDF- CoFe_2O_4 nanocomposite thick films

CONCLUSION

PVDF- CoFe_2O_4 nanocomposite thick films with varying filler loadings (20-100 wt.%) are successfully fabricated through solution casting process. XRD and FTIR analyses confirms the formation of the β -phase in PVDF upon incorporation of CoFe_2O_4 nanoparticles. Among the compositions, PC40 exhibited the most favorable dielectric performance, achieving a high permittivity ($\epsilon_r \sim 54.5$) with low dielectric loss (~ 0.09) at 1 kHz. The enhancement is attributed to synergistic effects of MWS interfacial polarization and filler-induced β -phase nucleation. These findings exhibit that optimal nanoparticle loading is critical for balancing permittivity enhancement and loss minimization, positioning PVDF- CoFe_2O_4 thick films as promising candidates for applications in high-performance capacitors, sensors, microwave devices, and energy storage systems.

ACKNOWLEDGMENTS

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Cu-Substituted YCrO₃: Structural and Electrical Modifications for High-Frequency Devices

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Abstract. The current study comprises the extensive investigations on the structural, morphological, and electrical properties of the copper (Cu) substituted yttrium chromite nanoparticles [YCr_{1-x}Cu_xO₃ (x = 0.00, 0.05, 0.10)] prepared via modified sol-gel auto combustion synthesis route. The obtained HRXRD patterns confirmed the formation of orthorhombic structure with Pnma space group. The average particle size of the prepared samples has been calculated using FESEM studies. Whereas, the EDX studies confirmed the existence of elements present in the sample along with their % composition. The performed dielectric studies displayed the existence of conventional Maxwell-Wagner Polarization in all samples. The presence of the grain boundary contribution to the sample's relaxation is evident from the complicated impedance plot. The composition, x = 0.05, depicted maximum dielectric permittivity with low tangent loss, and very least value of impedance. Hence, these obtained results declare that the 5% Cu doped YCrO₃ (x = 0.05) is well suited for its development in high frequency devices applications.

INTRODUCTION

Multiferroic materials have gained a significant attention due to its promising technological applications [1,2]. Currently, researchers are executing their prime focus on multiferroic materials as they have co-existing ferroelectric and ferromagnetic orderings which makes them a suitable candidate for spintronics applications. Rare earth chromites, or RCrO₃ (R = Yttrium or rare earth), are the most extensively used perovskite material which have been widely used for the magnetoelectric coupling parameter [3]. In YCrO₃, there is a strong interaction between R³⁺ and Cr³⁺ ions due to which they usually reveal the high magnetic characteristics. The rotation of the BO₆ octahedral about one or more crystal axes in ABO₃ perovskites results in unique phenomena. It has a centrosymmetric Pnma structure and an orthorhombic perovskite structure. Yttrium chromite (YCO) and other perovskite-type rare earth chromite, which are p-type semiconductors, have garnered a lot of interest in recent decades because of their potential use in magnetoelectric material [4], thermistor and various electrical devices [5], sensor [6], SOFC (solid oxide fuel cells) [7], and several other applications.

EXPERIMENTAL

The modified sol-gel auto combustion method was opted for preparing the Cu-doped YCrO₃ [x = 0.00, 0.05, 0.10] nanoparticles. In the first step, the precursors of metal salts [Y(NO₃)₃.6H₂O (99% pure, Sigma Aldrich), Cr(NO₃)₃.6H₂O (98.7% pure, Loba Chemie), Cu(NO₃)₃.3H₂O (98% pure, sigma Aldrich) were weighed as per the stoichiometry and dissolved in the deionized DI water. Each salt solution was left on stirring for 30 min to form the homogeneous mixture as shown in Fig 1 (a). Next, add copper nitrate solution into the chromium nitrate solution and left their entire mixing for 1 h. In the meanwhile, prepare the 1 M citric acid solution which will act as chelating agent. Then after 1 hr, add all as prepared salt solution into the CA solution and left on stirring for next 1 h. Now, 6 mL of ethylene glycol was added drop wise into the prepared homogenous mixture. Then, the NH₃ solution was further added drop wise to maintain the pH of the solution between 7-8. In the last step, turn on the heating of the solution to 80°C for 5 h to form gel. After the gel gets formed, the heating was increased up to 200°C until the dry powder gets formed. Then, the prepared dry ash was grounded into powder form using agar pestle mortar. Finally, the prepared dry black powder was then sintered at 800°C for 4 h to form the light greenish coloured powder. The whole schematic representation of the preparation of the Cu doped YCrO₃ nanoparticles represented in Fig 1 (a).

RESULTS AND DISCUSSION

The HRXRD pattern of the Cu-doped YCrO_3 [$x = 0.00, 0.05, 0.10$] nanoparticles have been shown in Fig 1 (b). The obtained XRD peaks are very well indexed using the available JCPDS card number: #00-034-0365 of YCrO_3 , confirming the orthorhombic phase of the samples along with its space group Pnma [8]. The Debye Scherrer equation has been used to calculate the average crystallite size of the samples using the equation given as; $D = \frac{k\lambda}{\beta \cos \theta}$, where D is the average crystallite size, λ is the wavelength of X-ray and β is the width of the diffraction peak at half height [9]. The average crystallite size is varying from 21 to 34 nm. FTIR studies confirmed the orthorhombic structure of the prepared samples along with the presence of tetrahedral and octahedral voids in the samples as shown in Fig 1 (d). The FESEM studies (as shown in Fig 1 (e)) was further done to explore the surface morphological and micro-structural properties of the Cu doped YCrO_3 . The average particle size of the prepared nanoparticles come around 40-50 nm for $x = 0.05$ which is calculated using Image J software. Fig 1 (f) shows the EDX pattern which further confirms the presence of elements and its atomic % and weight % in the prepared samples.

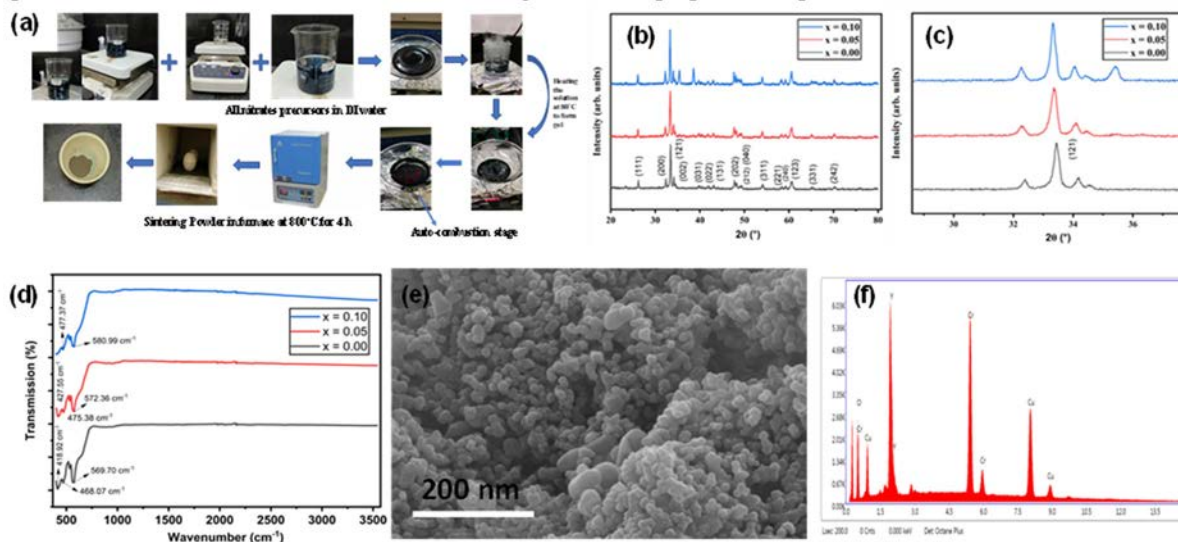


Figure 1. (a) Synthesis of Cu-doped YCrO_3 nanoparticles via sol gel auto combustion synthesis method, (b) High resolution X-ray diffraction (HRXRD) pattern of the prepared samples, (c) Highly intense peak shifting of XRD pattern, (d) FT-IR pattern of the samples, (e) FESEM image of the $x = 0.05$ or $\text{YCr}_{0.95}\text{Cu}_{0.05}\text{O}_3$, and (f) EDX spectra of the sample, $x = 0.05$

Figure 2 (a-f) exhibits the complete dielectric and impedance studies done for the prepared samples at room temperature. In the Fig 2 (a), the sharp step like reduction in the real value of permittivity (ϵ') with the successive rise in the frequency is shown for the samples ($x = 0.00, 0.10$) at room temperature. It has been noticed that the value of ϵ' is found to be maximum (near 1000) for the sample, $x = 0.05$ or 5% Cu-doped- YCrO_3 (as shown in Fig 2(b)). The other compositions showed very least value of ϵ' at the room temperature. Fig 2 (c) depicts the least value of tangent loss for the sample, $x = 0.05$ which is around, 0.035 at the frequency of 1 KHz. Fig 2 (d) shows the Cole-Cole plots of the prepared samples obtained at room temperature. It can be concluded that the sample $x = 0.05$ exhibited least value of impedance which would lead to higher conductivity and the same result is directly correlated with the Fig 2 (f). However, Fig 2 (e) justifies the plot of imaginary value of impedance against frequency and the obtained plot justifies the least resistance in the sample, $x = 0.05$ which is due to the reduction in the resistance of the grains and grain boundaries of the $x = 0.05$.

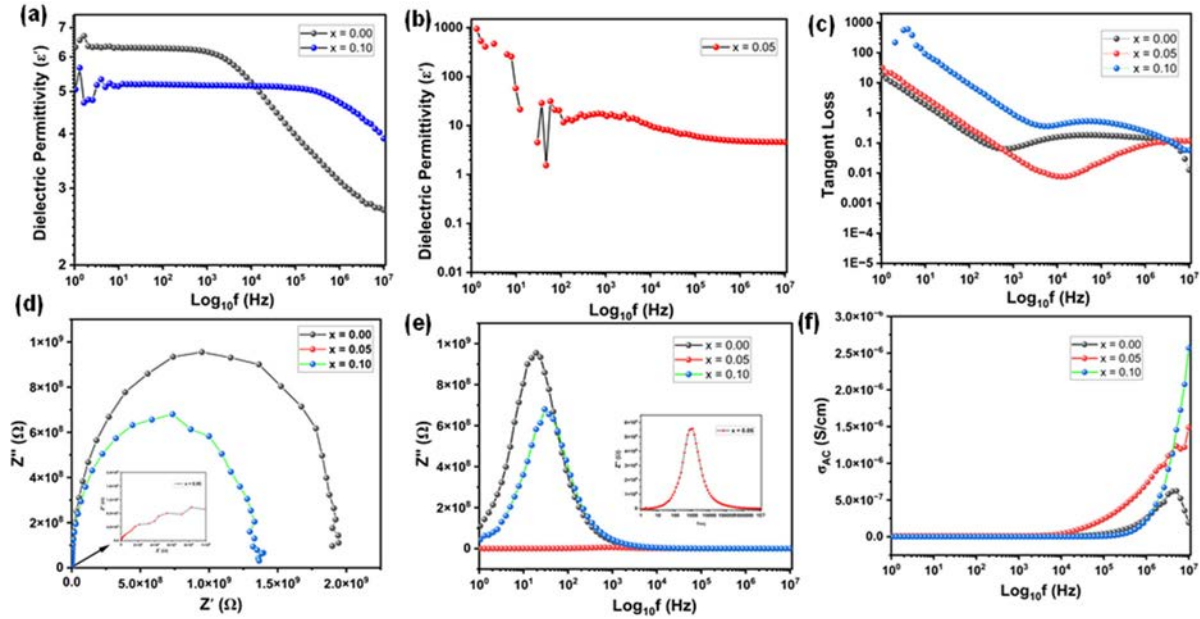


Figure 2. (a) Variation of ϵ' against frequency for pure and 10% Cu doped YCrO_3 , (b) Plot of ϵ' against frequency for $x = 0.05$, (c) Tangent loss against frequency, (d) Cole-Cole plots for the samples at RT, (e) variation of Z'' against Z' , (f) Plot of AC conductivity against frequency at RT.

CONCLUSION

The copper doped yttrium chromates nanoparticles have been prepared successfully using modified sol-gel auto combustion synthesis method. In this work, we have investigated the effect of Cu doping on the structural, morphological, and electrical properties of YCrO_3 perovskite nanoparticles. With the increase in doping % of Cu^{2+} ions, the lattice parameters reduced and would result in the decrease of the volume of the unit cell. The structural and morphological studies done using HRXRD and FESEM measurements confirmed the formation of Cu doped YCrO_3 nanoparticles. The impedance spectra of the prepared samples exhibit the non-Debye behavior and the dominance of grain boundary resistance over the grains. Additionally, the composition, $x = 0.05$, is found to be the most optimal one among all prepared compositions due to its higher ϵ' , lower tangent loss, lower impedance values, and higher AC conductivity values.

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Morphotropic Phase Boundary Assisted Energy Storage Response in BCST Ceramics for Next Generation Green Energy Solutions

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Abstract. The development of lead-free dielectric capacitors with high energy density is essential for next-generation energy storage devices. However, balancing the trade-off between energy density and efficiency is a long-standing challenge for the realization of miniaturized pulsed power technologies. In this context, we developed $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{0.93}\text{Sn}_{0.07})\text{O}_3$ (BCST) ceramics using the sol-gel chemical route. The morphotropic phase boundary (MPB) evolution is confirmed from Rietveld refinement of the XRD pattern. The presence of dielectric anomalies supports the tetragonal and orthorhombic phase assemblage in BCST ceramics. The BCST sample exhibits $W_{\text{rec}} \sim 155 \text{ mJ/cm}^3$ and $W_{\text{tot}} \sim 217 \text{ mJ/cm}^3$ with a corresponding efficiency of 72 % at a maximum applied electric field of 55 kV/cm with considerable frequency stability. These findings highlight Sn-induced MPB evolution and relaxor behavior as key factors that position BCST ceramics as a strong candidate for pulsed power and next-generation energy storage applications.

INTRODUCTION

Energy storage dielectric capacitors play an unprecedentedly crucial role in next-generation electronics and pulse power technologies. The high-power density and ultrafast charging-discharging rate ($\sim \text{ns}$), position them as a leading contender in high/pulsed power technologies such as hybrid electric vehicles, power electronics, hybrid energy storage devices, high power weapons [1]. However, a persistent challenge is their low energy storage density which significantly impedes their use in cost effective and miniaturized next generations technology. Therefore, growing emphasis is being placed on advancing dielectric capacitors that can simultaneously deliver high energy density and exceptional efficiency.

The energy density of dielectric capacitors is given by $W_{\text{rec}} = \int_{P_r}^{P_s} E dP$, where P_s and P_r represent the saturation and remnant polarization. Thus, High energy density requires high P_s , low P_r and strong breakdown strength (E_b) supported by a dense microstructure, strong polarizability and uniform fine grains with dynamic nano-polar regions are key to enhancing energy density in dielectric capacitors. Therefore, various strategies aim to promote P_s and suppress the P_r . For example, high saturation polarization ferroelectrics with MPB around room temperature favors the high saturation Polarization. Further, a slim hysteresis loop can be achieved by disrupting long-range ferroelectric order and lowering the polarization switching barrier which suppresses the P_r . In this context, the Ca^{2+} and Sn^{4+} are incorporated into the BaTiO_3 (BT) system occupying A and B sites respectively. The Sn^{4+} substitution can shift the rhombohedral to orthorhombic (T_{R-O}), orthorhombic to tetragonal phase transitions (T_{O-T}) and Curie Temperature (T_c) towards room temperature and lead to MPB evolution [2]. The Sn^{4+} substitution also induces relaxor characteristics to BT ceramics. Here, we have synthesized BCST ceramics by sol-gel chemical method and its energy storage performance is explored.

EXPERIMENTAL SECTION

The $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{0.93}\text{Sn}_{0.07})\text{O}_3$ ceramics were synthesized by sol-gel method. The $\text{Ba}(\text{CH}_3\text{COO})_2$ (Merck), $\text{Ca}(\text{CH}_3\text{COO})_2 \cdot x\text{H}_2\text{O}$ (Merck), $\text{Sn}(\text{CH}_3\text{COO})_2$ (Sigma Aldrich) and $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ (Merck) employed as starting precursors with 2-ethylhexanoic acid (Sigma Aldrich, $\geq 98\%$ purity) as a common solvent. Fig 1 illustrates the systematic sol-gel processing route to synthesize the BCST ceramic samples. The stoichiometric amount of all precursors was dissolved in the Solvent and the obtained gel was dried at 80°C . Finally, the dried powder was calcined at 1000°C for 4h, followed by sintering of the pellets at 1400°C for 5h. The detailed synthesis process is reported in the previous report in the literature [3].

RESULTS AND DISCUSSION

The XRD pattern of BCST ceramics is shown in the Fig. 1 (b). The XRD pattern shows pure Perovskite structure with no secondary phases, indicating successful substitution of Ca^{2+} and Sn^{4+} in BaTiO_3 ceramics at their respective A and B sites. Rietveld refinement of the XRD pattern was performed using FullProf software to confirm the dual-phase coexistence consisting of orthorhombic (Amm2) and tetragonal (P4mm) phase. The observed and theoretical patterns show close agreement, with fitting parameters of $\chi^2 \sim 1.34$, $R_{\text{wp}} \sim 6.91$, $R_{\text{exp}} \sim 5.97$ and $R_p \sim 5.47$. These results confirm the coexistence of orthorhombic (22.7 %) and tetragonal (77.3 %) phases, indicating MPB evolution near room temperature in the BCST sample.

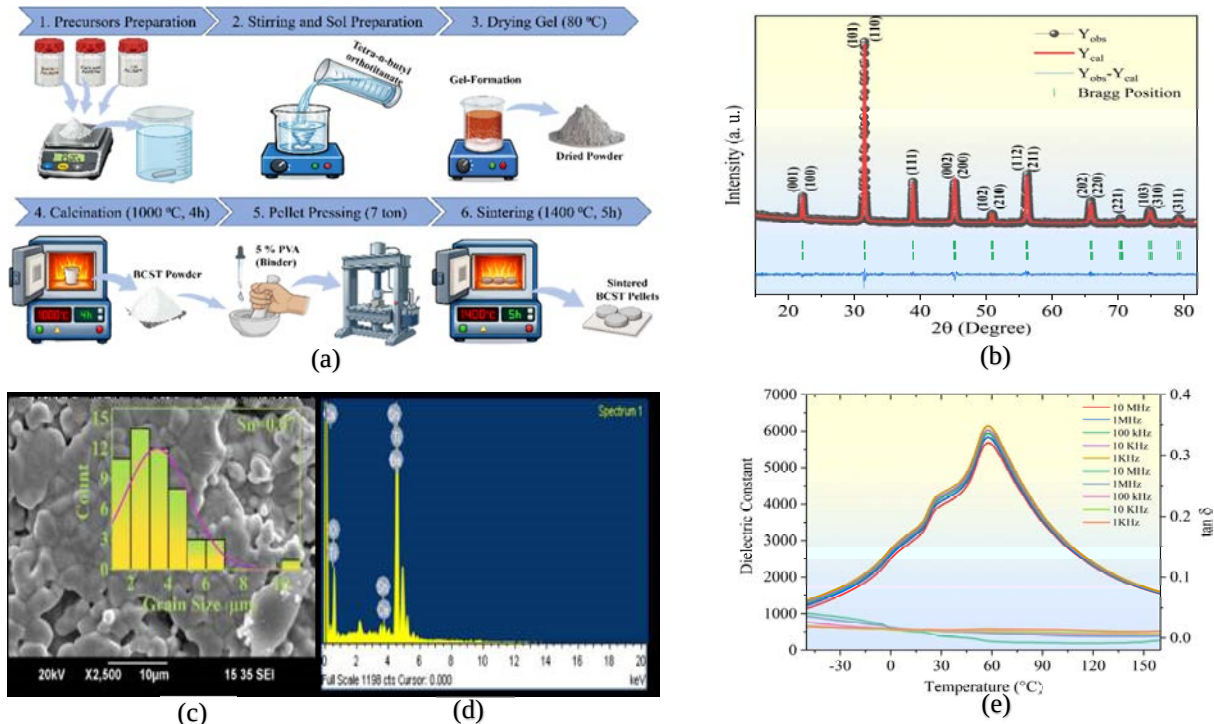


Figure 1. (a) flow chart of sol-gel synthesis route, (b) Rietveld refined XRD pattern at room temperature, (c)&(d) FESEM micrograph and EDS spectrum respectively and (e) Temperature dependent dielectric constant and $\tan\delta$ for BCST sample.

Figure 1 (c) & (d) shows FESEM micrographs and EDS spectrum for BCST sample. The micrograph reveals a nearly homogeneous, compact grain structure with some visible pores. The grain size distribution histogram is shown in the inset of the micrographs with average grain of 3.6 μm . Additionally, the elemental composition is determined from EDS spectrum confirms the presence of all expected elements. The observed elemental composition is Ba (18%), Sn (1.6%), Ti (16%), Ca (0.5%), and O (66%), which closely matches the theoretical values: Ba (19%), Sn (1.8%), Ti (18.2%), Ca (1%), and O (60%). Figure 1 (e) Shows the temperature dependent dielectric constant and $\tan\delta$ for BCST sample. The dielectric constant exhibits two minor anomalies arising from rhombohedral to octahedral ($T_{\text{R-O}}$) and orthorhombic to tetragonal ($T_{\text{O-T}}$) phase transitions respectively followed by Curie temperature (T_c). Thus, the MPB evolution involving the coexistence of R-O-T phase is confirmed from dielectric measurements. Additionally, the broad dielectric peak indicates a diffused phase transition or relaxor like behavior attributed to the formation of dynamic polar nano regions (PNRs) resulting from Ca^{2+} and Sn^{4+} substitution. Figure 2 (a) shows the room temperature PE loops for the BCST sample recorded at 20 Hz of frequency under varying electric fields. The loops are slim, with $P_s \sim 16.4 \mu\text{C}/\text{cm}^2$ and $P_r \sim 5.1 \mu\text{C}/\text{cm}^2$ at $E_b \sim 55 \text{ kV}/\text{cm}$. The Ca^{2+} and Sn^{4+} substitution induces the chemical heterogeneity and disrupts the long-range order, leading to formation of polar nano regions. The small PNRs usually

require low field to reorient compared to ferroelectric domains, resulting in slim hysteresis loops [4]. Such slim loops are the characteristics of relaxor ferroelectric, consistent with the dielectric measurement.

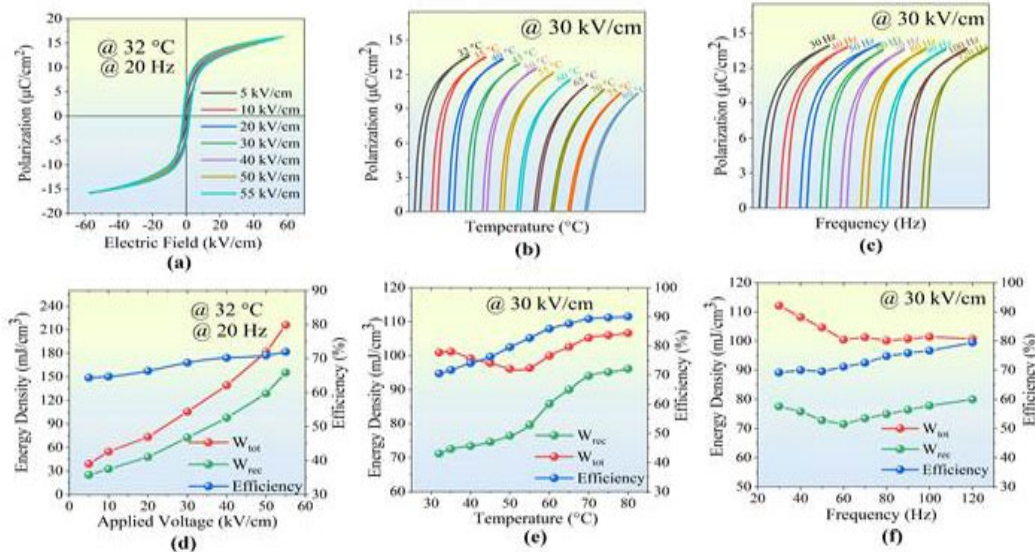


Figure 2 (a) Room temperature PE loops at different voltage (b) temperature dependent PE loops at 30 kV/cm (c) frequency dependent PE loops at 30 kV/cm (d)-(f) energy density and efficiency with voltage, temperature and frequency variations.

Figure 2(d) shows the energy density and efficiency of the BCST sample calculated at various applied electric fields using established formulas [5]. The BCST sample exhibits $W_{\text{rec}} \sim 155 \text{ mJ/cm}^3$ $W_{\text{tot}} \sim 217 \text{ mJ/cm}^3$ with corresponding efficiency of 72% at maximum applied electric field of 55 kV/cm. The temperature and frequency stability are crucial for practical dielectric capacitor applications. To assess these, P-E loops were recorded at a fixed field of 30 kV/cm over temperature (32 °C to 80 °C) and frequency (30 Hz to 120 Hz) ranges, as shown in Figures 2(b) & (c). The corresponding energy density and efficiency values are plotted in Figures 2(e) & (f), respectively. The BCST sample shows limited temperature stability in energy density, with efficiency remaining nearly stable between 60 to 80 °C. Conversely, energy density and efficiency are stable across the frequency range of 60 to 120 Hz.

CONCLUSION

In summary, the energy storage performance of sol-gel elaborated lead free $(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{0.93}\text{Sn}_{0.07})\text{O}_3$ ceramics, driven by MPB evolution and induced relaxor characteristics, was investigated. Rietveld refinement confirmed the O-T phases MPB evolution around room temperature. Dielectric measurement further supported the MPB evolution in BCST sample. The pristine BCST sample shows enhanced energy storage parameters with $W_{\text{rec}} \sim 155 \text{ mJ/cm}^3$, $W_{\text{tot}} \sim 217 \text{ mJ/cm}^3$ and an efficiency of 72% at maximum applied electric field of 55 kV/cm. These results demonstrate that BCST ceramics could be suitable contender for sustainable next generation pulse power technology.

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Filler Dependent Enhanced Dielectric Performance in PVDF/KNN Composites: Broadband Frequency Analysis in Relation to Microstructural Correlations

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Abstract. In this study, $K_{0.5}Na_{0.5}NbO_3$ (KNN) ceramic was synthesized through hydrothermal reaction method. The polymer composites comprising of polyvinylidene fluoride (PVDF)/crystalline KNN, prepared through the novel cold pressing method, where the varying wt% of KNN ceramic filler were incorporated into the PVDF matrix, systematically shows its direct effect on the energy storage behavior. The structural, microstructural and dielectric characterizations were done using XRD, FESEM and LCR meter. The formation of the KNN ceramic was confirmed through X-ray diffraction. The microstructure, homogeneity, and extent of agglomeration were found through the FESEM. The frequency-dependent dielectric behavior was investigated in the frequency range of 4Hz to 1MHz. The dielectric measurements showed a significant enhancement in the dielectric constant from PVDF ($\epsilon_r = 18$) to PVDF/KNN50% ($\epsilon_r = 78$). Moreover, the dielectric loss tangent suppressed from ~ 0.8 for pure KNN to ~ 0.3 for PVDF/KNN50%, showed improved energy storage capability. The improved dielectric performance of PVDF/KNN composites as compared to pristine PVDF makes them a promising candidate for high-performance flexible polymer/ceramic dielectrics for advanced electronic applications.

INTRODUCTION

Lead-free flexible polymer dielectrics combining dielectric ceramic phase and dielectric polymer phase are gaining popularity due to better electrical performance and design flexibility. They have numerous inherent benefits and are expected to be used in non-volatile memory, sensor, piezoelectric, dielectric, pyroelectric, and magneto-electric applications [1]. Conventionally used materials like PZT, $PbTiO_3$, $BaTiO_3$ and BNT have many applicability limitations such as brittleness and non-mouldable etc. Hence, to overcome these problems, PDs are undergoing development. KNN emerged as a very good alternative of conventionally used $BaTiO_3$ for energy storage applications as it provides temperature stability due to high $T_c \sim 420^\circ C$. Among the polymers PVDF shows very good electrical behavior [2]. Among the four phases of PVDF, β -phase of PVDF shows better ferroelectric response due to its high degree of polar nature. The limitation of adopting PVDF in conventional energy storage devices is that PVDF has inferior electrical performance relative to the conventionally used ceramics (e.g. KNN, BT, BCZT, BNT). To bridge this performance gap between ceramics and polymers the development of composite materials has become essential for practical device applications. The aim of this work is to develop high performance flexible polymer dielectrics by leveraging properties of both ceramic and polymer.

EXPERIMENTAL DETAILS

To synthesize KNN using hydrothermal reaction method, stoichiometric amounts of KOH and NaOH dissolve 50ml of DI water separately and stirred for 1 hr, then both solution mixed and Nb_2O_5 poured in the solution and stirred for 1hr to ensure homogeneity. The final solution then placed in the Teflon lined hydrothermal autoclave and heated inside a hot air oven at $200^\circ C$ for 24 hours to give high temperature and pressure environment. The obtained powder then filtered using filter paper and placed inside oven for drying. Dried powder was annealed at $600^\circ C$ for 6 hours in a muffle furnace to remove any impurity and to achieve highly crystalline KNN powder. A series of polymer composites $(1-x)$ PVDF- (x) KNN ($x = 0.2, 0.3$ and 0.5) were prepared using agate mortar and pestle incorporating varying weight fraction of KNN in PVDF matrix through mixing and grinding homogeneously for 4 to 5 hours at room temperature by mechanically using bare hands. Noval cold pressed method employed to prepare pellets of 1mm thickness and 13mm of PVDF/KNN composites using a die and hydraulic press with an applied pressure of 700MPa for 10 minutes.

RESULTS AND DISCUSSION

Fig.1a) represents the Rietveld-refined XRD spectra of KNN has ferroelectric monoclinic structure with P1m1 space group having lattice parameters: $a = 7.8848\text{\AA}$, $b = 7.7980\text{\AA}$, $c = 7.8483\text{\AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 90.52^\circ$, with lattice volume of $482.54\text{\AA}^3$, calculated crystallite size 133nm and reduced $\chi^2 = 3.52$. Figure 1 b), shows the XRD pattern of $(1-x)$ PVDF – x KNN ($x = 0.2, 0.3, 0.5$ and 1.0) polymer composites. The X-Ray diffraction peaks of PVDF came near $2\theta = 21^\circ$ confirms the presence of both α and β of PVDF. The formation of the β phase in PVDF is essential to improve the crystalline nature of PVDF present in the sample. All the crystalline peaks of KNN matched with JCPDS ref. no 96-210-4387, situated at 22.549° , 32.276° , 46.037° , 52.317° , 57.526° , 67.546° , 72.238° , and 77.233° corresponding to the planes (011), (020), (200), (040), (202), (222), (242), (420), and (161), respectively. Moreover, at low filler concentration ($x = 0.2$ and 0.3), a strong peak corresponding to PVDF is observed. However, as the filler concentration increases, the peaks of PVDF diminish, and the peaks associated with ceramic filler become more dominant [3].

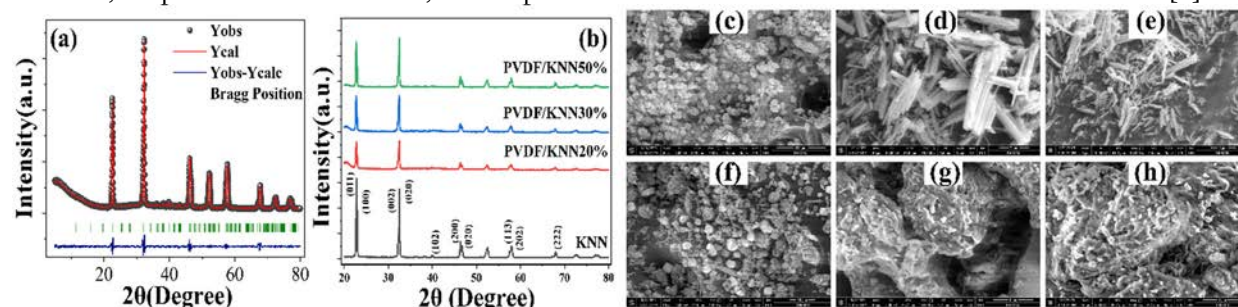


FIGURE 1. a) Rietveld-refined spectra of KNN. b) XRD spectra of $(1-x)$ PVDF- x KNN ($x=0.2, 0.3, 0.5$ and 1.0). (c) SEM Micrographs of KNN polygonal grains, (d), (e) KNN rods, (f) PVDF/KNN20%, (g) PVDF/KNN30% and (h) PVDF/KNN50%.

To understand the morphology PVDF/KNN composites, FESEM was used. As seen in figs. 1(c) and 1(d) and 1(e), respectively, KNN powder has mixed morphologies polygonal grains with a majority rod-like structure. Additionally, rods have an average length of $2\mu\text{m}$ and a width of 200 nm , whereas polygonal grains have an average size of about $1.5\mu\text{m}$. The microstructural arrangement of $(1-x)$ PVDF- x KNN ($x=0.2, 0.3$, and 0.5) was also studied. At lower filler concentration (0.2), Fig 1(f), clearly shows the even distribution of spherulites of PVDF and KNN particles, PVDF particles provide large surface area for electrical charge storage, filler particles are well isolated and well dispersed in the polymer matrix evenly. However, as the filler fraction increases to 0.3 and 0.5 , the filler particles become more agglomerated as shown in fig. 1(g), (h). Here, the polymer matrix works as a gluing agent and makes a dense ceramic network within the PVDF matrix, which leads to enhancement in the dielectric performance, but a relatively higher dielectric loss occurs as compared to lower filler fraction due to the formation of conductive pathways inside the sample which is also evident in the dielectric measurement.

Dielectric behavior was observed in the frequency range (4 Hz to 1 MHz) at room temperature, as shown in fig. 2(a). It can be observed that static frequency $\epsilon_r = 1620$ for KNN much higher than $\epsilon_r = 18$ for PVDF but the loss tangent at low frequency is very high due to MWS polarization as charge carriers have enough time to accumulate in the interfaces [4]. However, as frequency increases this effect vanishes. Figure 2(a) and 2(d) clearly shows that the incorporation of KNN enhances energy storage capacity of the polymer/ceramic composites. At lower filler fractions (0.2 and 0.3), effective permittivity remains relatively low ($\epsilon_{\text{eff}} \approx 20$ and 23 , respectively) due to the continuous insulating PVDF matrix. However, for filler fraction 0.5 , relative permittivity improved to ($\epsilon_{\text{eff}} \approx 78$). This enhancement caused due to increased connectivity between filler particles and stronger dipole-dipole interactions. Figure 2(b) shows the variation of $\tan\delta$ for all samples, it is observed that $\tan\delta$ decreases as frequency increases, due to MWS polarization vanishes at higher frequencies. Moreover, the dielectric loss is suppressed to ~ 0.3 , while maintaining high $\epsilon_{\text{eff}} = 78$ as compared to pure PVDF. This balance between high ϵ_{eff} and low $\tan\delta$ makes the PVDF/KNN50% composite an optimal choice for flexible energy storage devices. As shown in figure 2(c) and 2(f) σ_{ac} increases with both frequency and KNN content, from $\sim 10^{-8}\text{ S/m}$ (100 Hz) to $\sim 10^{-6}\text{ S/m}$ (1 MHz) for PVDF/KNN20% and reaching $\sim 10^{-5}$ – 10^{-4} S/m for PVDF/KNN50%. The initial decrease observed in σ_{ac} at lower filler fractions ($0.2, 0.3$) indicates insufficient conductive pathways. However, the sharp increase observed for PVDF/KNN50% suggests the formation of continuous conductive pathways and reaching the percolation threshold.

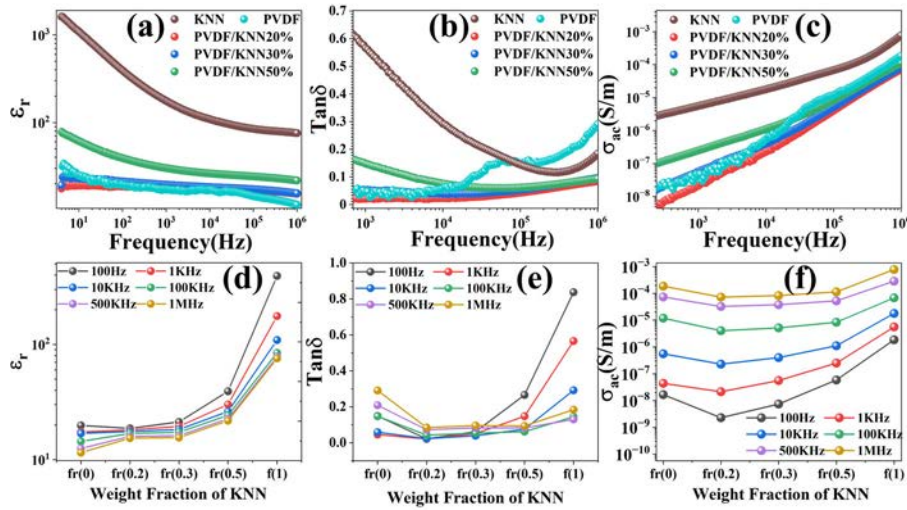


FIGURE 2.(a) ϵ_r , (b) $\tan\delta$, (c) σ_{ac} as function of frequency and (d) ϵ_r , (e) $\tan\delta$, (f) σ_{ac} as function of filler fraction.

CONCLUSIONS

PVDF/KNN50% composite shows a significant enhancement in $\epsilon_r \approx 78$ as compared to pure PVDF $\epsilon_r \approx 18$, while maintaining relatively low dielectric loss tangent ($\tan\delta < 0.3$) across the entire 4Hz–1 MHz range as compared to pure KNN ceramic. Uniform dispersion of KNN microrods and polygonal grains within the PVDF matrix, as evidenced by FESEM, ensures efficient interfacial polarization and enhanced dielectric response. Maxwell–Wagner relaxation dominant below 10 kHz and caused relatively high loss tangent. However, at higher frequencies above 100 kHz, MWS effect vanishes and dipolar relaxation becomes more dominant resulting in stable, frequency-independent dielectric behavior. These results show that the hydrothermally synthesized KNN ceramic filler significantly enhances PVDF permittivity without compromising loss or processability. In the whole series of composites, the PVDF/KNN50% composite is optimum ratio for flexible lead-free energy storage devices and ferroelectric devices.

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Comparative Study of Structural, Microstructural, Dielectric, and Energy Storage Properties of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ and SrTiO_3 -doped $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ Ceramic

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Abstract. In this study, we investigated the outcome of SrTiO_3 (ST) doping on the performance of energy storage of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT)-based ceramics. A 0.8BNT–0.2ST composition was synthesized via the conventional solid-state route and characterized for structural, microstructural, and dielectric properties. X-ray diffraction confirmed the formation of a single-phase P4bm perovskite structure, and FESEM analyses showed a noticeable reduction in grain size with 20wt% ST doping. A reduction in the dielectric constant was observed, along with a downward shift in the phase transition temperature. Consequently, an obvious improvement in recoverable energy density (W_{rec}) and efficiency (η) had been noticed from ferroelectric results, reflecting enhanced relaxor characteristics in the doped specimen. Overall, SrTiO_3 addition was found to be an effective strategy for boosting the energy storage capability of BNT ceramics.

INTRODUCTION

As the demand for efficient and reliable energy storage solutions grows, ferroelectric ceramics have gained attention because of their high energy density, fast charge and discharge capabilities, and eco-friendly characteristics [1]. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) is notable as a lead-free ferroelectric material with promising capabilities. However, its practical use is limited due to its large remanent polarization and comparatively low energy storage efficiency [2]. To overcome these issues, researchers have widely explored doping as a way to improve both the structure and electrical properties. Adding SrTiO_3 (ST), a paraelectric perovskite, into the BNT framework can disrupt the long-range ferroelectric ordering, promote relaxor-like characteristics, and enhance the material's energy storage performance [3]. In this work, BNT and 0.8BNT–0.2ST ceramics were prepared and thoroughly analyzed to investigate their structural, dielectric, and ferroelectric properties. Special attention was given to the impact of adding ST on phase composition, grain structure, dielectric behavior, and polarization–electric field (P–E) loops, which are important for improving capacitive energy storage performance.

MATERIALS AND EXPERIMENTAL METHODS

A conventional solid-state reaction method was used to synthesize $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) and 0.8 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ –0.2 SrTiO_3 (0.8BNT–0.2ST) ceramics. Highly pure precursors— Na_2CO_3 , Bi_2O_3 , SrCO_3 , and TiO_2 (all >99.9%, Hi-Media)—were weighed according to stoichiometry and ball-milled in ethanol for 24 hours. After drying and calcining the slurry at 100 °C and 850 °C, the powders were subsequently ball-milled for an additional 10 hours. Polyvinyl alcohol (PVA) served as the binder before uniaxial pressing into pellets (diameter of 12 mm, ~1 mm thickness), followed by sintering at 1100 °C. X-ray diffraction (XRD) pattern results were attained with the help of a Rigaku Smart Lab diffractometer with Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$), scanning from 20° to 80° (2 θ) at 0.02° step size and 2°/min. Microstructural studies were conducted utilizing field emission scanning electron microscopy (FESEM, Carl-Zeiss-Ultra Plus) on thermally etched surfaces. Grain size distributions were analyzed using ImageJ software. For electrical measurements, silver paste was applied to polished pellets and fired at 250 °C for 30 min. Temperature- and frequency-dependent dielectric properties were obtained utilizing an HIOKI 3532-50 LCR Hi-Tester. Ferroelectric

polarization-electric field (P-E) loops were recorded in silicone oil at 50 Hz using a ferroelectric loop tracer (Marine India). Energy storage parameters such as W_{rec} and η were derived from the P-E loops.

RESULTS AND DISCUSSIONS

Figure 1(a) displays the XRD pattern results of undoped BNT and 0.8BNT–0.2ST ceramics. Both samples exhibit characteristic peaks of the perovskite structure and match well with the standard JCPDS card #96-210-2069 (space group: P4bm), indicating phase purity. No secondary phases were observed within the detection limit. Notably, a slight shift in peak position upon ST doping suggests minor lattice distortion because of the incorporation of bigger Sr^{2+} ions in the A-site and Ti^{4+} in the B-site [4]. FESEM images in Fig. 1(b) and 1(c) reveal significant grain size refinement upon ST incorporation. The undoped BNT shows an average grain size of $\sim 3.6 \mu\text{m}$, while the doped 0.8BNT–0.2ST sample exhibits a much finer average grain size of $\sim 0.91 \mu\text{m}$. This grain size reduction is beneficial for enhancing breakdown strength and improving energy storage performance [5]. The relatively uniform grain distribution in the doped sample also suggests improved densification and grain growth control due to the presence of ST.

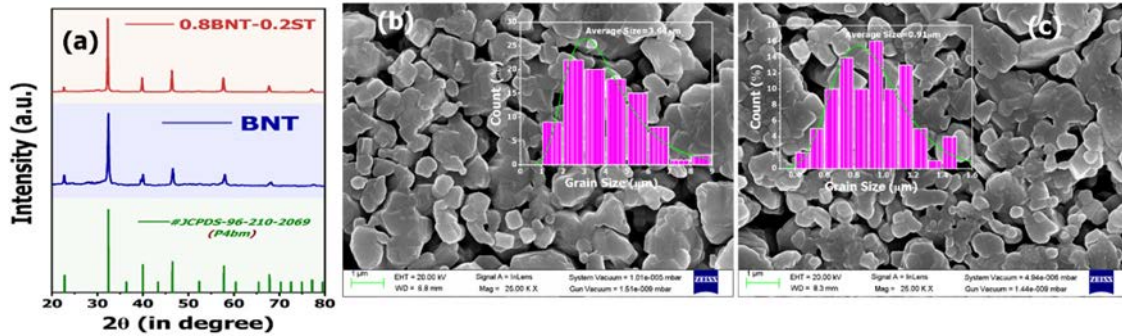


FIGURE 1. (a)XRD diffraction patterns and corresponding peak position; (b, c) FESEM micrographs and grain size distribution curves of BNT and 0.8BNT-0.2ST, respectively.

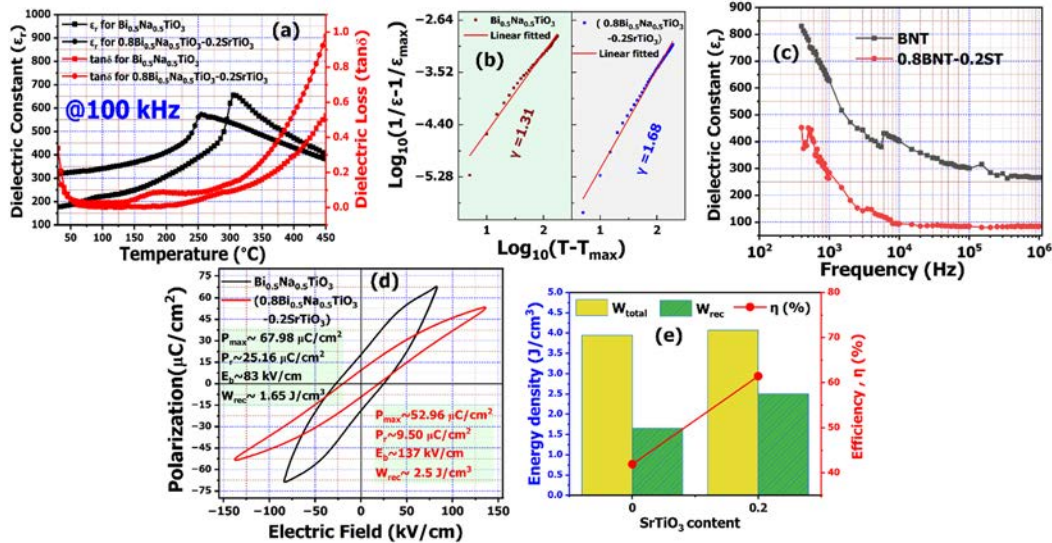


FIGURE 2. (a) Temperature-dependent ϵ_r and $\tan \delta$ at 100 kHz for both compositions; (b) Modified Curie–Weiss fit showing γ values indicating relaxor behavior; (c) Frequency-dependent ϵ_r showing reduced dielectric constant and dispersion in doped sample; (d) P–E loops showing enhanced energy storage properties in 0.8BNT–0.2ST; (e) Comparison of energy density and efficiency for BNT and 0.8BNT–0.2ST.

Temperature-dependent dielectric measurements at 100 kHz (Fig. 2(a)) show broad dielectric peaks after doping, corresponding to the maximum permittivity temperature (T_{max}), indicative of relaxor-type behavior. ST doping significantly reduces ϵ_r but broadens the permittivity peak, indicating enhanced relaxor behavior. The dielectric loss ($\tan \delta$) remains below 0.1 up to 300 °C for the doped sample, confirming good thermal stability. To quantitatively analyze relaxor behavior, the modified Curie–Weiss law was applied [6],[7]:

$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_{max}} = \frac{(T-T_{max})^\gamma}{C}$. The calculated γ values (Fig. 2(b)) are 1.31 for BNT and 1.68 for 0.8BNT–0.2ST, indicating a normal to strong relaxor ferroelectric transition behavior due to ST doping. Frequency-dependent dielectric measurements (Fig. 2(c)) show a decreasing trend in ϵ_r with frequency, more pronounced in doped samples, which is typical for relaxor ferroelectrics [8]. The lower dielectric constant at high frequencies for 0.8BNT–0.2ST can be attributed to suppressed domain wall contributions and enhanced polar nano-regions (PNRs) stability.

Figure 2(d) displays the P–E loops for both compositions. The undoped BNT exhibits a typical ferroelectric loop with high remnant polarization ($P_r \approx 25.16 \mu\text{C}/\text{cm}^2$) and maximum polarization ($P_{max} \approx 67.98 \mu\text{C}/\text{cm}^2$). In contrast, the 0.8BNT–0.2ST sample exhibits slimmer and more symmetric loops with significantly reduced P_r ($\approx 9.50 \mu\text{C}/\text{cm}^2$) and P_{max} ($\approx 52.96 \mu\text{C}/\text{cm}^2$), which is advantageous for applications in energy storage. The W_{rec} and η were derived using: $W_{tot} = \int_0^{P_{max}} E dP$; $W_{rec} = \int_{P_r}^{P_{max}} E dP$; and $\eta = \frac{W_{rec}}{W_{tot}}$. As shown in Fig. 2(e), W_{rec} increases from 1.65 to 2.51 J/cm³, while η improves from 41.5% to 57.6% upon ST doping. The enhancement in energy storage properties is primarily due to reduced P_r , improved breakdown strength ($E_b \approx 137 \text{ kV}/\text{cm}$), and induced relaxor behavior. These results demonstrate that ST doping effectively tunes the structure and polarization response of BNT ceramics, making 0.8BNT–0.2ST a promising candidate for energy storage capacitors.

CONCLUSION

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ and $0.8\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.2\text{SrTiO}_3$ dielectric ceramics were successfully synthesized using the solid-state method. ST doping led to refined microstructure, induced relaxor ferroelectric behavior, and enhanced dielectric stability. The doped sample exhibited a slimmer P–E loop with reduced remnant polarization and improved energy storage performance. The maximum recoverable W_{rec} of 2.51 J/cm³ and η of 61.42% were attained for 0.8BNT–0.2ST, compared to 1.65 J/cm³ and 41.88% for BNT. These enhancements are attributed to the suppressed long-range ferroelectric ordering and reduced grain size. Thus, SrTiO₃ doping offers a viable strategy to progress the capacitive performance in energy storage of BNT-based lead-free ceramic dielectrics.

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The Influence of La Doping on Ceria for the Enhancement of Dielectric Properties

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Abstract. Ceria (CeO_2) nanoparticles were prepared using sol-gel method. X-ray diffraction (XRD), scanning electron microscopy (SEM), and dielectric measurements were employed to characterize the samples. XRD analysis confirmed the formation of FCC structure corresponding to CeO_2 with space group $Fm\bar{3}m$. SEM investigations revealed that the CeO_2 nanoparticles with an average grain size of ~ 15.64 nm. Furthermore, the dielectric measurements performed as a function of frequency at room temperature showed an enhancement in dielectric constant with La doping.

INTRODUCTION

It has been realized that the high-dielectric constant materials like cerium oxide (CeO_2), aluminum oxide (Al_2O_3), lanthanum oxide (La_2O_3), zirconium dioxide (ZrO_2), and titanium dioxide (TiO_2) might be used as alternative gate dielectric material of SiO_2 [1, 2]. However, due to their exceptional properties, CeO_2 is considered as a suitable candidate for gate dielectric material in metal-oxide semiconductors as well as next generation memory devices [3, 4]. Most of the applications of CeO_2 are due to change in its valance state from Ce^{4+} to Ce^{3+} and due to the presence of large amount of oxygen vacancies [5, 6, 7, 8]. Various reports have shown tuning in structural, optical, and magnetic properties of La -doped cerium oxide nanoparticles [9-11]. Thus, present study focuses on enhanced dielectric performance of La -doped ceria nanoparticles.

EXPERIMENTAL SECTION

The $Ce_{1-x}La_xO_2$ ($x=0$, and 0.03) nanoparticles were synthesized via conventional sol-gel method. The structural characteristics of nanocrystalline samples were analyzed from X-ray diffraction (XRD) patterns using a Philips XPert/MPD diffraction system with $Cu K\alpha$ ($\lambda = 1.54$ Å) radiation ranging from $20-80^\circ$. The surface morphology of the samples is examined by Scanning Electron Microscopy (SEM) MIRA II LMH, TESCAN. The resistivity of the samples was examined by Keithley 6517-B Electrometer connected with Lakeshore 325 temperature controller in a temperature of 310 K- 400 K. Further, the dielectric measurements were performed as a function of frequency (5 kHz- 1 MHz) using Agilent E4980A LCR meter, interfaced via lab-view program.

RESULT AND DISCUSSION

X-ray Diffraction (XRD) Analysis

Figure. 1 shows the XRD patterns of pristine and 3% La -doped cerium oxide nanoparticles. All the diffraction peaks were well-indexed corresponding to the FCC structure of pure CeO_2 with space group of $Fm\bar{3}m$ (JCPDS card no. 75-0120). However, with the increased concentration of La , the peaks gradually broadened, which is attributed to the contraction of the crystallite sizes. In addition, the lattice parameter was found to slightly increased for 3 % La doped ceria as compared to pristine sample. The difference in ionic radii for La^{3+} ion (0.117 nm) compared with ionic radii of Ce^{4+} ion (0.097 nm) might be attributed to the variation in lattice parameter [11]. A slight variation is observed in

unit cell parameters with increase in dopant concentration, indicating substitution of doped atoms into the lattice sites of host atoms. **Table 1** summarized various structural parameters for pristine and *La*-doped ceria sample.

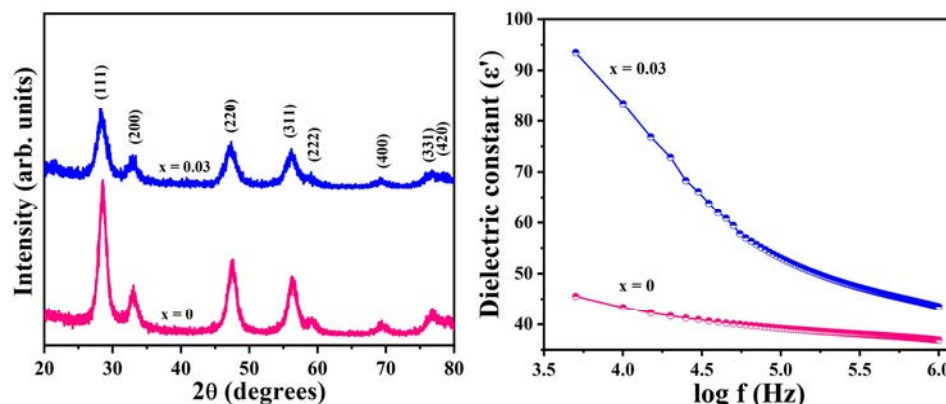


FIGURE. 1 X-ray diffraction patterns, and **FIGURE. 2** Variation of dielectric constant with frequency of $Ce_{1-x}La_xO_2$ samples.

Dielectric Analysis

The polarization of dielectric material describes energy storing ability of a material, which is an alignment of electric charges and electric field-induced separation [1]. **Figure. 2** displays variation of dielectric constant ϵ' with frequency (5 kHz-1MHz) of pristine and doped samples at room temperature. The ϵ' increases with *La* concentration into CeO_2 . The ϵ' is higher at lower frequencies and decreases sharply with increasing frequency and shows almost constant behavior at higher frequencies, governs normal behavior of ceramic materials [1]. The interfacial space charge polarization at the electrode-electrolyte interface attributed to the higher value of ϵ' at lower frequencies. The decrement in ϵ' with increasing frequency is attributed to rapid change in electric field signals at the interface, resulting reduction of charge carriers' contribution to the dielectric constant and finally saturates at higher frequencies owing constant value of dielectric constant. The value of ϵ' was found to increase from ~ 45.57 ($x = 0$) to ~ 93.45 ($x = 0.03$) at lowest frequency i.e. 5 kHz.

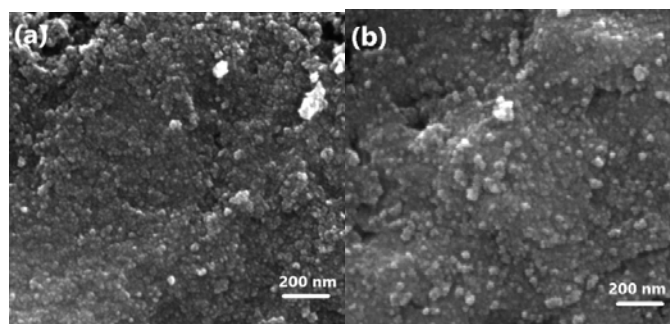


FIGURE. 3 SEM images of $Ce_{1-x}La_xO_2$ samples.

TABLE 1: Various calculated parameters of $Ce_{1-x}La_xO_2$ samples.

Composition	Lattice Parameter, a (Å)	Unit Cell volume, a^3 (Å ³)	Average Crystallite size, D (nm)	Average Grain Size (nm)	Dielectric constant (RT) ϵ' at 5 kHz	Resistivity (RT) ρ ($\Omega\cdot m$) $\times 10^{12}$
$x = 0$	5.413	158.60	6.10	15.64	45.57	0.15
$x = 0.03$	5.441	161.08	5.15	11.90	93.45	2.83

Scanning Electron Microscopy (SEM) Analysis

Figure. 3 displays the typical SEM micrographs of pristine and 3% *La*-doped samples and shows the formation of well-defined grains. The estimated average grain size of the pristine nanoparticles was found to be ~15.64 nm. Further, the average grain size was found to decrease to 11.90 nm (as per table) with *La*-doping. It can be clearly seen that the porosity decreases (i.e., increasing density) with *La* concentration in CeO_2 . The present decrement in average grain size and increase in density with *La* doping into CeO_2 is consistent with our earlier report [5]. However, the variation in average grain size is also consistent with our XRD outcomes.

CONCLUSION

The pure and *La* doped CeO_2 were synthesized via conventional sol-gel method. The prepared compositions of $Ce_{1-x}La_xO_2$ ($x = 0.0$ and 0.03) were investigated using XRD, SEM, RT and dielectric measurements. The XRD analysis confirmed distortion of ceria's crystal structure after *La*-doping results in decrement in crystallite size. The crystallite size estimated using XRD was found consistent with SEM results. Furthermore, the dielectric measurements were performed at room temperature with varying frequencies. It was found that the dielectric constant enhanced with *La* doping into CeO_2 . Thus, *La* doping makes ceria a suitable candidate for high frequency dielectric devices.

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Structural, Dielectric and Optical Properties of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ Perovskite Ceramic

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Abstract. In the present work, we have investigated the influence of Tb^{3+} ion on structural, dielectric and optical properties in $\text{Ba}_{1-x}\text{Tb}_x\text{TiO}_3$ (i.e. $x = 0.03$ mol) perovskite ceramic synthesized through the high-energy milling method. The XRD patterns reveal the tetragonal phase with P4mm space group. The average grain size of the $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ was calculated using an HR-SEM image and found to be $0.629 \mu\text{m}$. The temperature dependent dielectric study reveals the maximum relative dielectric permittivity (ϵ_r) ~4700 at 10 kHz with low loss less than 1. The diffuse reflectance spectra contain a broad band at 355 nm along with a peak at 681 nm due to 4f-4f transition of Tb^{3+} ions. The optical band gap of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ was calculated by using the diffuse reflectance spectra and found to be 3.28 eV. These characteristics of synthesized materials may be useful for potential application in capacitive energy storage and LEDs.

INTRODUCTION

In recent times, the rapid demand for energy utilization has led to the development of low-cost and environmentally friendly renewable energy sources. Currently, researchers are using traditional energy storage devices such as supercapacitors, batteries, Fuel cells, and dielectric capacitors. Among all, dielectric capacitors have become a focus of attention for high-pulsed-power systems due to their high-power density, large applied electric fields, fast charging/discharging rates and affordability [1-2]. Dielectric ceramics are considered to be the most appropriate materials for high-temperature applications due to their extraordinary thermostability, average breakdown field strength, minimal dielectric loss, and fatigue-resistant characteristics compared to other materials. The BaTiO_3 -based perovskite ferroelectrics have numerous applications, such as energy storage, memory devices, actuators and sensors. Substitution of impurities at crystallographic sites A or B can alter the properties, i.e. normal ferroelectric to relaxor ferroelectrics at higher concentrations also modify the Curie temperature along with a variation in the dielectric constant in dielectric study [3, 4]. However, there is a still need of improvement in obtaining high recoverable energy density along with better efficiency. Hence, the development of rare earth doped ferroelectric ceramics with high recoverable energy density is an emerging field of research in capacitive energy storage.

In this work, we have synthesized $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite ceramic for capacitive energy storage with the help of high-energy ball milling and examined its crystal structure analysis, dielectric and optical properties.

EXPERIMENTAL DETAILS

The $\text{Ba}_{1-x}\text{Tb}_x\text{TiO}_3$ (i.e. $x = 0.03$ mol) perovskite ceramic was prepared by the solid-state reaction method. The Tb_2O_3 (sigma-Aldrich, 99.99%), BaCO_3 (sigma-Aldrich, 98%) and TiO_2 (sigma-Aldrich, 99%) were used as a starting material. The ethanol was used as the grinding media. For the milling of raw powder, the zirconia balls and raw materials were taken in a 10:1 ratio under 300 rpm for 6 hours using a high-energy ball mill (PM400MA, RETSCH, GmbH, Germany). The slurry of the milled powder was kept in the oven for 24 hours to dry the raw powder and grind it. Further, the grounded powder was calcined at 1100°C for 8 hrs to get the pure phase. For sintering, the fine ground powder of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite ceramic was mixed into a 2wt% PVA binder to form a pellet. Furthermore, the sintering process was performed to densify the pallet at 1250°C for 6 hours in the muffle furnace for dielectric measurements. The room temperature XRD data were collected using RIGAKU X-ray diffractometer (MINIFLEX 600) through $\text{Cu-K}\alpha$ radiations. The average grain size of $\text{Ba}_{1-x}\text{Tb}_x\text{TiO}_3$ (i.e. $x = 0.03$ mol) perovskite ceramic was investigated using a high-resolution scanning electron microscope (Nova NanoSEM 450, FEI USA). A Keysight E4990A impedance analyzer was employed to measure the dielectric constant and dielectric loss

at varying temperatures. The diffuse reflectance spectroscopic spectra of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite ceramic was investigated using Spectrophotometer (Jasco- V-770) in the wavelength range of 200 - 800 nm. The optical band gap of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite ceramic was calculated using the Kubelka-Munk equation.

RESULTS AND DISCUSSION

To investigate the crystal structure of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite ceramic, we have recorded the X-ray diffraction (XRD) patterns of the synthesized powder samples in the 2θ range 20° - 90° . **Fig. 1(a)** shows room temperature XRD patterns of the samples of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite calcined at 1100°C for 8 hrs. All the peaks in the XRD patterns well matches with the standard pattern of the tetragonal structure corresponds to the PCPDF file 05-0626. The absence of an impurity peaks confirms the single pure phase of tetragonal structure. All the XRD patterns show crystalline nature of the samples and can be indexed using tetragonal crystal system with $P4mm$ space group.

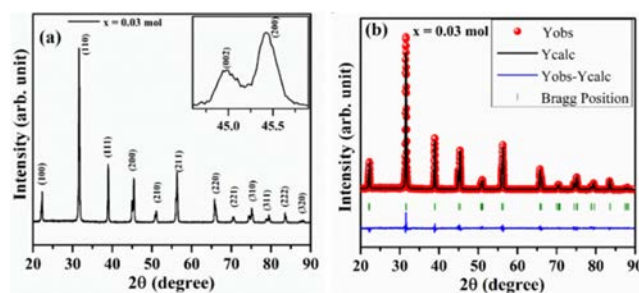


Figure 1. (a) X-ray diffraction patterns of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite Ceramic, at room temperature (b) Rietveld Refinement fitting.

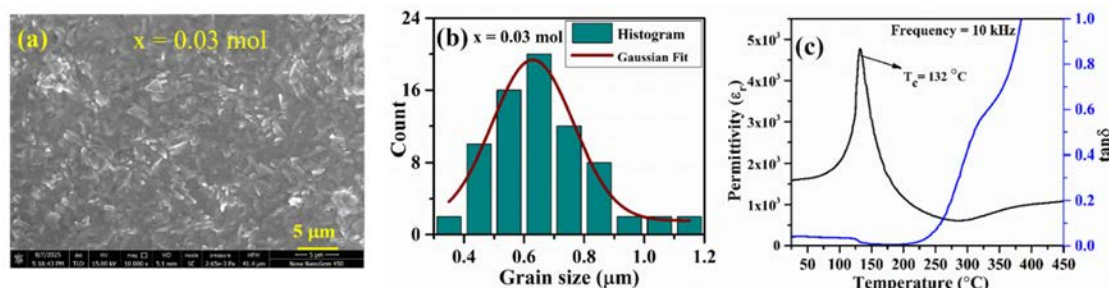


FIGURE 2. (a) FE-SEM image of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite Ceramic, (b) Histogram for distribution of grain size along with Gaussian fit and (c) represents the dielectric permittivity and dielectric loss as a function of temperature at fixed 10 kHz frequency, sintered at 1250°C

Rietveld fit for $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite Ceramic calcined at 1100°C is shown in **Fig. 1(b)**. Rietveld Refinement of the XRD pattern illustrate the lattice parameters $a = b = 3.9950$ and $c = 4.0350$ for $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite ceramic. The crystallite size has been calculated using Debye-Scherrer formula [5] and it is found to be 64 nm.

Figures 2(a, b) exhibit the HR-SEM micrograph and histogram image for the estimation of the average grain size of sintered perovskite ceramic, respectively. Fig.2(a) exhibits that the grains are in irregular shape. However, it contains dense microstructure with less porosity. Further, the average grain size was estimated from the HR-SEM micrograph using ImageJ software, as shown in Fig. 2(b). The estimated average grain size is found to be $0.629 \pm 0.01 \mu\text{m}$. Figure 2(c) shows the temperature dependence of dielectric permittivity of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite Ceramic at a frequency of 10 kHz. The dielectric behaviour of the sample, illustrating the phase transition near the Curie temperature (T_c) at 132°C . The highest value of permittivity is found to be 4700 along with minimal dielectric loss ~ 1 at 10 kHz.

Figure 3(a, b) exhibits the diffuse reflectance spectroscopic (DRS) spectra and corresponding band gap estimation using the Kubelka-Munk model. Figure 3(a) reveals the absorption bands at 210, 355 and 681 nm wavelengths, which occur due to charge transfer state (CTS) and f-f transitions of Tb^{3+} ions, respectively. The optical band gap has been

estimated through the Kubelka-Munk relation [6], as displayed in Figure 3(b). The band gap of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite Ceramic is found to be 3.28 eV.

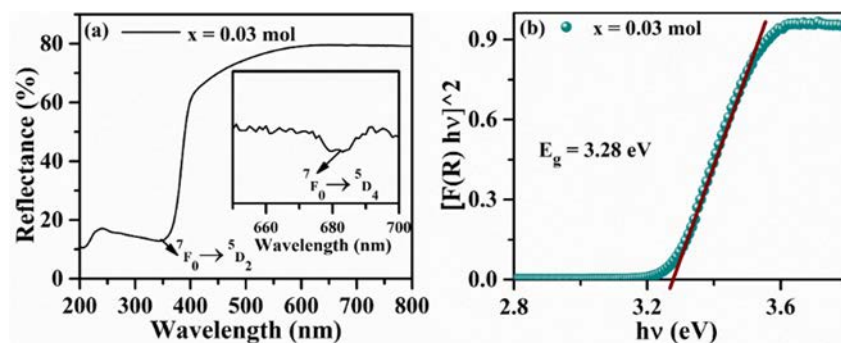


FIGURE 3. (a) The DRS spectra of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite Ceramic, (b) The optical band gap of $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite Ceramic calcined at 1100 °C

CONCLUSIONS

In summary, the bulk $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite ceramic was successfully prepared via high energy ball milling process. The structural analysis confirmed that the tetragonal structure crystallizes into P4mm space group. The FE-SEM images showed the irregular shape of grains. The optical band gap found to be 3.28 eV for $\text{Ba}_{0.97}\text{Tb}_{0.03}\text{TiO}_3$ perovskite ceramic. The dielectric study reveals the high permittivity and loss dielectric loss at transition temperature, which is suitable for capacitive energy storage and LEDs devices.

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Dielectric Loss Of Gd^{2+} Doped Lead Titanate Fabricated By High Energy Ball Milling Method

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Abstract. Our presumption is that this modification will be more dependent on the ionic radii difference. Such type of studies has hardly been reported as such lead titanate having perovskite structure (ABO_3) has been selected as host lattice gadolinium as the source of guest ions. Ceramic powder has been fabricated by using High Energy Ball Milling (HEBM) method, keeping these things in mind, fabrication has been done in a systematic way. Dielectric constant is minimum for undoped lead titanate sample and increases by about five percent (5%) for gadolinium doped samples. It also observed that for five percent (5%) gadolinium samples T_c shift to higher temperature side.

INTRODUCTION

On the basis of literature survey made to the extent possible studies of structural, microstructural, electrical and electromechanical properties of lead titanate ceramics doped with rare earth metal gadolinium. This work presents results of such studies with a little discussion in the case of gadolinium doped in the host lattice of lead titanate ceramics. It is expected that gadolinium being trivalent compared to lead i.e., host lattice ion may produce enhancement in the electrical properties.



High Energy Ball Miller

During a systematic study of generation of electrical charge on the application of pressure on crystals like quartz, zinc blende and tourmaline **Pierre Curie and Jacques** discovered piezoelectricity in 1880. W. Hanckle suggested the name piezoelectricity [1-3]. Electric polarization produced by mechanical strength in some crystals is called piezoelectricity. Here the polarization is proportional to the strain and changes sign with it. Piezoelectricity is of two types. When electrical charge is generated from mechanical stress, this is called direct effect. Similarly, application of an electric field produces mechanical movement in a crystal. This is called converse effect piezoelectricity[4-9]. Both the electricity is useful for device application.

The crystallite is made up of ions occupying specific position in a specific way which gets repeated. In other words, we can say that building wall is made up of bricks in same way as crystallite is formed. Thus, the unit cell of the crystallite represents the bricks and wall of the building in the piezoelectric ceramic materials. The unit cell in the crystallite decides whether or not the piezoelectricity will exist[11-13]. The external properties of the crystallite repeat the symmetry of internal structure. a) a center of symmetry b) axis of rotation c) mirror plane d) combination of these three.

According to symmetry elements all crystallites (crystal) are divided into 32 classes or point groups. Cubic, (rhombohedral), tetragonal orthorhombic, hexagonal, monoclinic and triclinic - in descending order of symmetry. Out of the thirty-two-point groups, twenty-one groups are non-centrosymmetric. For the existence of piezoelectricity, a

group must be non-centrosymmetric. Thus, twenty-one groups should be piezoelectric but one group although being non-centrosymmetric does not show piezoelectricity perhaps because of other combined symmetry elements[14-16]. When homogeneous stress is applied, the stress being also centrosymmetric is unable to produce an unsymmetrical result unless a material lacks a center of symmetry. Thus, homogeneous stress applied on the crystallite or crystal will reverse the charges i.e., an electric dipole moment is produced or polarization appears[17-19].

Thus, the polar piezoelectric ceramic is electrically isotropic but after polling the randomly oriented dipoles of the isotropic ceramics are switched to the crystallographically permitted directions almost in the direction of the field and remain so even after removal of the field. In other words, it can be said that piezoelectric crystallites have been converted to ferroelectric crystallites merely by polling[20-22].

The shift in Curie temperature towards lower side indicates that for samarium phase transition from ferroelectric to piezoelectric starts taking place earlier i.e., at a lower temperature because of larger distortion produced by samarium ion which is having an ionic radii difference from that of lead by about 0.24 Å i.e., 24 nm. and for Gadolinium it is 0.38 Å. This study has been made with a view that trivalent ion of larger ionic radius in comparison to lead ions and having more charge on it may distort the lattice of lead titanate in a larger way compared to isovalent impurities like calcium and magnesium doped in lead titanate ceramics[23-28]. As such our expectation is truly reflected by these results, incorporation of Gd^{+2} , based on the stoichiometric formula. Dielectric constant was found as 2453 at Curie temperature of 480°C in the case of 5 wt.% of Gd in ceramics. Piezoelectric Coefficient was obtained as 243×10^{-12} C/N at 38 Kv/cm of poling. The results found were comparatively better than in similar kind of materials reported as so far by various researchers.

Variation of dielectric constant (ϵ) and dielectric loss ($\tan\delta$) measured at 1 kHz to 20 kHz for 1 wt.%, 3 wt.% and 5 wt.% gadolinium doped lead titanate ceramics as a function of temperature have been placed at Figure.1 -2., show that dielectric constant and dielectric loss increases by very little amount from room temperature to 2000C except that in case of 5wt% Gd doped ceramics where increase in dielectric constant starts after 1000 C. On the other hand, dielectric loss ($\tan\delta$) starts increasing significantly only after 2000C. Dielectric vs. temperature curve has two peaks around 2000C and 5000C, the second peak being more pronounced. This curve has been placed in Figure.1 for clarity. It shows that dielectric constant increases with increase in dopant concentration. The Figure:3 shows that dielectric maxima shift to lower temperature side. For all concentration of the dopants the shift being maximum for 5 wt% concentration of gadolinium doped ceramics and it also shows a hump around 3750 C.

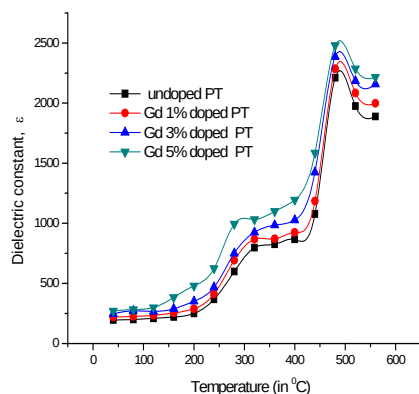


Fig: 1. Dielectric constant as a function of temperature of Gadolinium doped lead titanate ceramics

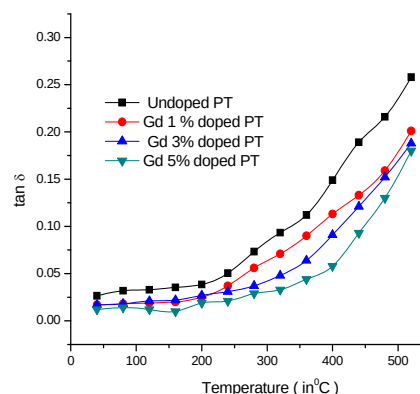


Fig:2. Dielectric loss as a function of temperature of Gadolinium doped lead titanate ceramics

Piezoelectric coefficient d_{33} i.e. charge produced per unit force because of application of a DC field called polling field on the undoped and 1wt%, 3wt% and 5wt% gadolinium doped lead titanate ceramics has been placed at Figure no.4. Value of coefficient seems to remain constant from 23 kV/cm to 27 kV/cm. for all concentration of the dopants, the constant value being different for different concentration. The d_{33} coefficient starts increasing for all the concentration of dopant from 27 kV/cm field to 38 kV/cm. A linear variation of the d_{33} values has been also observed.

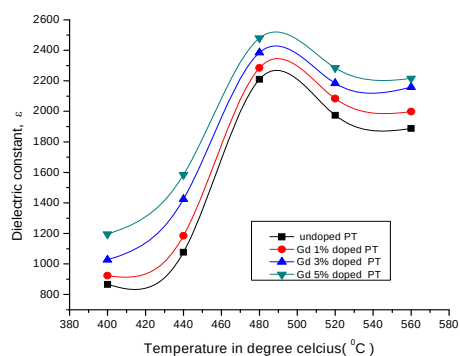


Fig. 3. Variation of dielectric constant maxima as a function of temperature of Gadolinium doped lead titanate ceramics

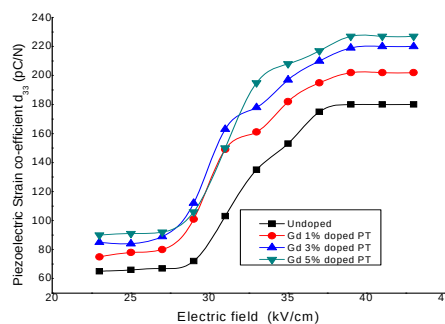


Fig. 4. Variation of piezoelectric strain as a function of electric field of Gadolinium doped lead titanate ceramics

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Mechanical Energy Harvesting by Quantum Rod Incorporated With Poly (Vinylidene Fluoride) Nanogenerators

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Abstract. In this work, cadmium selenide (CdSe) core quantum rods (QRs) induced electroactive phase nucleation in poly (vinylidene fluoride) (PVDF) free standing films has been investigated. The prepared QR-PVDF composite (PQRF) films show higher electroactive content ($F_{EA} \sim 75\%$) than that of pure PVDF films, resulting in a better voltage output ($V_{OC} \sim 18V$) coming from nanogenerator (NG) fabricated from PQRF films than that of NG made with PVDF film, under similar pressure application. The flexibility of PQRF nanogenerator makes it suitable for wearable sensors for physiological motion detection. As CdSe QRs have unique optical properties like highly polar photoluminescent emission at tunable wavelength, the PQRF composites could pave their way into the field of optoelectronic flexible nanogenerators.

INTRODUCTION

The fabrication of flexible self-powered electronics by utilizing green energy, such as solar, geothermal, wind, tidal and so on, have come to the research forefront and the most common method of harvesting green energy has become mechanical energy harvesting because of its ease of use in low-power electronics.¹ To achieve the goal of mechanical energy harvesting, piezoelectric polymer poly(vinylidene difluoride) PVDF and its copolymers are highly suitable because of their unique properties as flexibility, chemical and thermal resistivity and easy surface tunability.² PVDF is a semi-crystalline polymer exhibiting many distinct crystalline polymorphs, amongst which α -phase is the non-polar phase and needs to be converted to β - or γ -phases owing to their electroactive (TTT or T₃G-T₃G') configurations.³ One way of achieving these electroactive phases is by introduction of fillers with high surface area to volume ratio, as nanoparticles. In this work, we have used cadmium selenide (CdSe) quantum rods (QRs) in drop-casted PVDF films and nanogenerators (NGs) were fabricated from those films to study the enhanced piezoresponse achieved due to the enhancement of relative electroactive phase as compared to PVDF. Therefore, the reported NG can be used in wearable electronic gadgets in future.

EXPERIMENTAL SECTION

Materials. Poly (vinylidene fluoride) (PVDF) pellets ($M_w \approx 275000$, Sigma -Aldrich), N,N-dimethylformamide (DMF) (Emplura, Merck Life Science, purity > 99%), cadmium oxide (CdO) (Loba Chemie), trioctylphosphine oxide (TOPO) (Sigma-Aldrich), trioctylphosphine (TOP) (Sigma-Aldrich), tetradecylphosphonic acid (TDPA) (Sigma-Aldrich), selenium powder (Se) (Loba Chemie).

Fabrication of PQRF and PVDF NGs. The CdSe QRs were synthesized using the hot injection method. The cadmium (Cd) precursor was prepared by mixing 0.89 mM CdO and 0.155 mM TDPA and dissolving the mixture into 3.5 g of TOPO at 90 °C. The dissolved mixture was gradually heated to 320 °C under reflux in an inert atmosphere to form a transparent solution, proving the successful formation of Cd precursor. Meanwhile the selenium (Se) precursor was formed by dispersing 1 mM Se powder in 2.5 ml TOP and maintaining it at a temperature of 120 °C. The Se precursor was injected in batches into the Cd precursor for the seeding process of CdSe QRs. To prepare PVDF solution, PVDF pellets were dissolved in DMF to form a 6 wt% PVDF-DMF solution. This was named as PVDF solution. In order to prepare PQRF composite solution, QRs ($\sim 0.002:1$ v/v ratio of QR/polymer concentration) was mixed with the PVDF solution. The PVDF and PQRF solutions were drop-casted on clean glass slides at a temperature of 120 °C to form free-standing films. The films were sandwiched between aluminium electrodes connected to connecting wires, as shown in Fig. 1a, to form nanogenerators with the names PVNG and PQRNG.

Characterizations. Field Emission Scanning Electron Microscopy (FESEM) (FEI INSPECT F-50) was operated at an acceleration voltage of 10 kV. The fourier transform infrared spectroscopy (FTIR) (Bruker VERTEX70) was performed with 1 cm^{-1} spectral resolution and 40 number of scans. The X-ray diffraction (XRD) pattern was taken by X-ray diffractometer (Bruker D-8) with Cu-K α radiation ($\lambda = 1.5418\text{ \AA}$) operated at 35 kV voltage and 35 mA current. Open circuit output voltage (V_{OC}) measurements were observed using a digital storage oscilloscope (Keysight EDUX 1052A).

RESULTS AND DISCUSSIONS

The crystallographic phase study of the PVDF and PQDF films (Fig. 1c) was studied from the XRD spectrum. The XRD pattern for PVDF film showed prominent peaks at 17.7° , 18.3° , 19.8° and 26.5° of 2θ values which are relative to the diffraction planes (100), (020), (110) and (021), respectively, clearly representing the non-polar α -phase. The falling of diffraction peaks and existence of one single peak in XRD spectrum of PQRF film indicates the induction of relative electroactive phase into the polymer by losing its intrinsic semi-crystalline nature to a more crystalline nature.

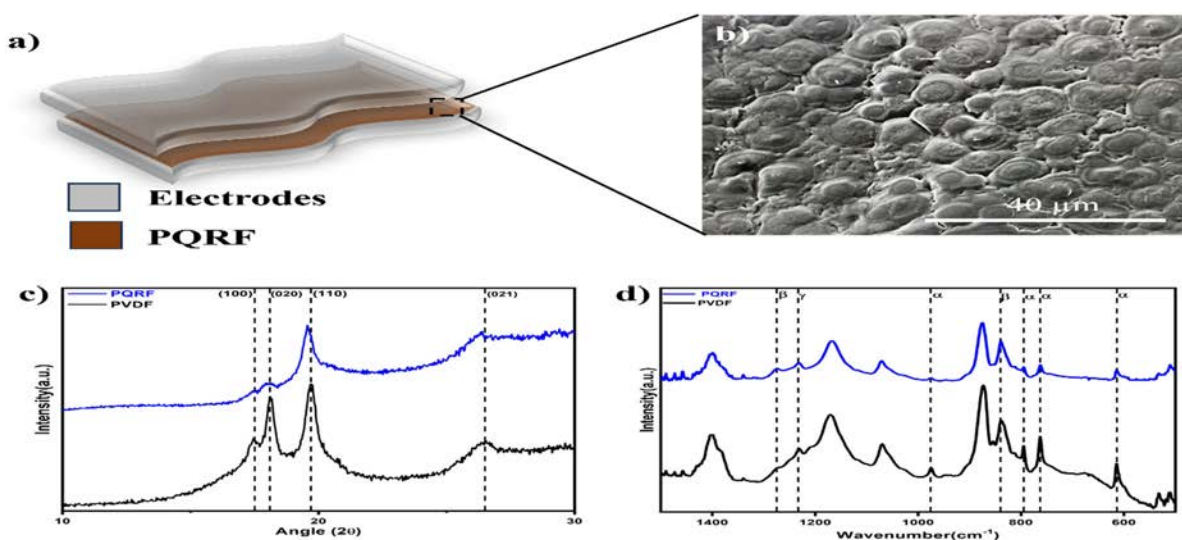


FIGURE 1. (a) Schematic diagram showing PQRNG device, (b) FESEM image of PQRF, (c) XRD Spectrum for PVDF (black) and PQRF (blue), (d) FTIR spectrum for PVDF (black) and PQRF (blue).

The electroactive phase study of PVDF and PQRF films were analyzed from the FTIR spectrum given in Fig. 1d. The presence of peaks at 614 cm^{-1} , 763 cm^{-1} , 795 cm^{-1} and 976 cm^{-1} in PVDF film indicated the preexistence of α -phase. These peaks were seen to fall in PQRF film, with the rise of the β -(1275 cm^{-1}) phase, revealing the conversion of non-polar configuration into a polar conversion. The relative electroactive phase content was quantified using the Beer-Lambert law, as,

$$F_{EA} = \frac{A_{\beta}}{1.3A_{\alpha} + A_{\beta}}$$

where, A_{β} and A_{α} represent the absorbances at 763 cm^{-1} and 840 cm^{-1} . The estimated F_{EA} for PVDF was about 40 %. On the other hand, for the PQRF, F_{EA} was about 67 %. Figure 1b shows the FESEM image of PQRF. From the Fig. 1b, the formation of circular domains with adequate pore formation further emphasizes on the enhancement of relative electroactive phase formation in the presence of CdSe QRs in PVDF. The interfacial interactions between dangling bonds of CdSe QRs with $-\text{CF}_2$ dipoles stretches the $-\text{CH}_2$ backbone of the PVDF chain, which in turn, aligns the $-\text{CH}_2/-\text{CF}_2$ dipoles and electroactive phase was established in PQRF.

The mechanical energy harvesting ability of the films based piezoelectric nanogenerators (PENG) has been studied by impacting consecutive compressions with the help of a soft hammer. A well-defined periodic alteration of positive and negative peaks corresponding to press and release of mechanical stress has been observed (Fig. 2a). It was fascinating to observe that PQRNG showed higher and sharper output voltage response than the PVNG. As observed, V_{OC} for PQRNG was about 18V which is higher than that of PVNG ($V_{OC} \sim 4\text{V}$). During the compressing mechanical stress application, the piezoelectric bound charges form a built-in potential generating the positive peak of output

voltage. When mechanical stress is removed, the reverse phenomenon occurs, giving rise to a negative peak of output voltage.

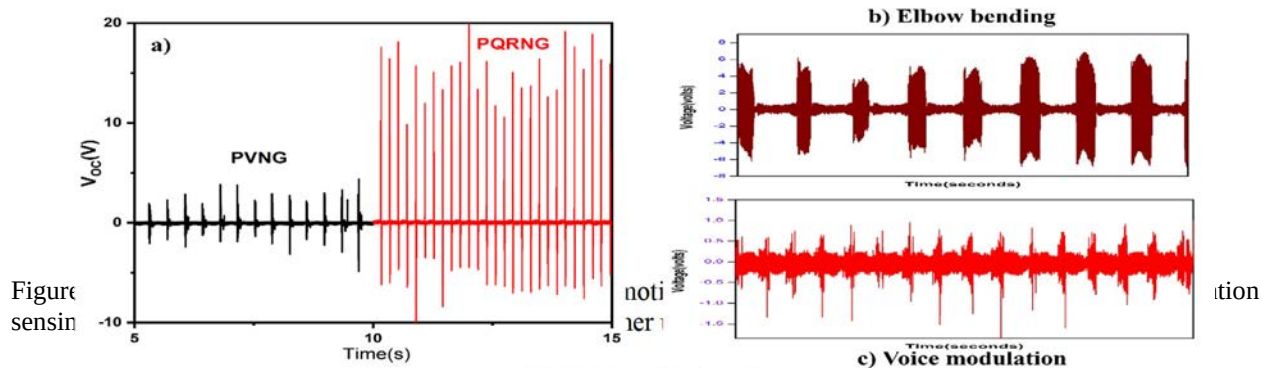


FIGURE 2. (a) Open circuit voltage of the NGs, Physiological motion sensing using PQRNG for (b) Elbow bending and (c) Voice modulation.

In comparative electroactive phase content compared to pure PVDF film. The then prepared NG with PQRNG provided better voltage output than that of PVDF and also showed sensitivity in physiological motion sensing. Therefore, PQRNG may be used in a wide range of applications including biomedical healthcare monitoring to flexible optoelectronic self-charging devices.

ACKNOWLEDGEMENT

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Structural, Morphological and Dielectric Characteristics of Gamma-Irradiated CeO₂-TiO₂ Nanocomposite

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Abstract. This study explores the effect of gamma irradiation on the structural, morphological, and dielectric properties of CeO₂-TiO₂ nanocomposites. The XRD spectra showed that gamma irradiation causes intensity reduction and peak broadening, which are signs of irradiation induced structural alterations without phase change. FE-SEM imaging revealed increased particle aggregation, and the development of defect-rich linked networks post-irradiation. Furthermore, the dielectric measurements were performed as a function of frequency at room temperature which shows an enhancement in dielectric constant with irradiation. The overall improvement in dielectric performance signifies that CeO₂-TiO₂ nanocomposite may be effectively tailored using gamma irradiation for advanced high-k dielectric and capacitor applications.

INTRODUCTION

The nanostructured metal oxides and their composites gained significant prominence in technological advancement due to their ability to alter the physicochemical features of compounds. Among various metal oxides, cerium dioxide (CeO₂) and titanium dioxide (TiO₂) have emerged as potential material for various applications due to their unique characteristics. CeO₂ has exceptional characteristics like wide bandgap, high dielectric constant, and high transparency in VIS-NIR region [1, 2]. In addition, Titanium (IV) oxide (TiO₂) has wide range of applications in various fields due to its strong chemical stability, biocompatibility, low cost and non-toxicity. Integrating CeO₂ and TiO₂ into composite materials offers synergistic advantages over individual components due to their enhanced photocatalytic effectiveness and sensing ability [3, 4, 5]. In the present work, the Gamma-irradiated nanocomposite will be studied for structural, morphological, and dielectric performance.

EXPERIMENTAL SECTION

The CeO₂-TiO₂ nanocomposite was synthesized by conventional solid state reaction method. The nanocomposite have been irradiated to Gamma-rays of a Co-60 gamma source with a dosage of 150 kGy at an effective dose rate of 1.14 kGy per hour from IUAC, New Delhi in the presence of air at room temperature. As-synthesized pristine CeO₂-TiO₂ nanocomposite is referred to as CT₁, and the 150 kGy gamma irradiated CeO₂-TiO₂ nanocomposite is referred to as CT₂. Structural and morphological characterization of pre and post gamma irradiated CeO₂-TiO₂ nanocomposite have been performed utilizing Bruker D8 advance X-ray diffractometer in 2θ range of 20°-90° with step size 0.05° and Field Emission-Scanning Electron Microscopy (FESEM) - FEI made by NOVA NANOSEM 450 respectively at UGC-DAE CSR, Indore. Further, the dielectric measurements were performed as a function of frequency (50 kHz-1MHz) using Agilent E4980A LCR meter, interfaced via lab-view program at IUAC, New Delhi.

RESULT AND DISCUSSION

X-ray Diffraction (XRD) Analysis

Figure. 1 showed the XRD patterns of CT₁ and CT₂ and confirmed the coexistence of cubic CeO₂ (Fm-3m) and rutile tetragonal TiO₂ (P42/mnm). However, the irradiated sample exhibits reduced peak intensities and broader reflections suggesting irradiation-induced structural disorder. In the CeO₂ phase, increased crystallite size and decreased microstrain (ϵ) indicates radiation enhanced grain growth accompanied by partial strain relaxation [6]. In the TiO₂ phase, decreased crystallite size and increased microstrain indicate that TiO₂ rutile structure is more radiation sensitive. The significant a-axis expansion with minimal c-axis variation indicate anisotropic lattice distortion caused by oxygen vacancies [7].

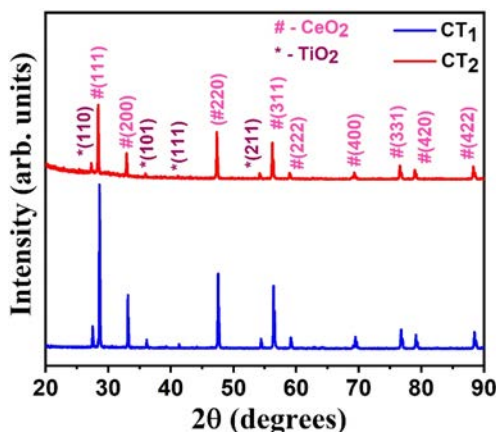


FIGURE. 1 X-ray diffraction patterns of CT₁ and CT₂ samples.

Field Emission Scanning Electron Microscopy (FE-SEM) Analysis

Field Emission scanning electron microscopy (FE-SEM) micrographs (**Figure. 2**) reveals well defined rod-shaped particles with uniform size distribution in CT₁. Upon gamma irradiation, CT₂ exhibits compact particles with poorly defined boundaries and increased aggregation, consistent with the irradiation induced grain growth observed in CeO₂ phase as per XRD outcomes. These defect rich grain fused clusters enhance Maxwell-Wagner interfacial polarization, responsible for enhanced dielectric constant of CT₂. Furthermore, lower $\tan \delta$ values of CT₂ is supported by compact grain network which restricts charge carrier movement.

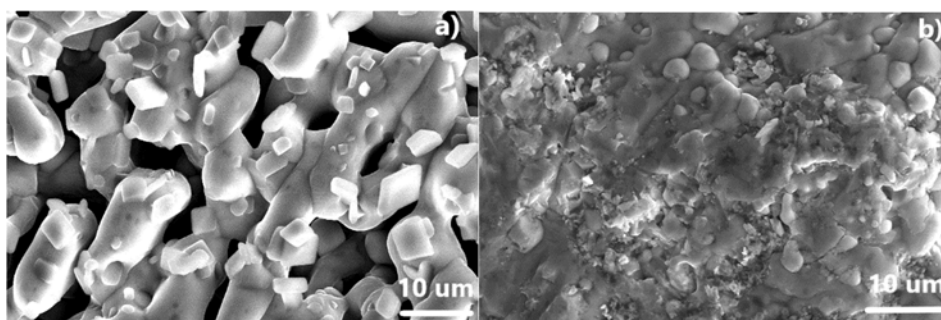


FIGURE. 2 FE-SEM images of a) CT₁ and b) CT₂.

Dielectric Analysis

Figure. 3 displays the dielectric constant (ϵ') and dielectric loss ($\tan \delta$) as a function of frequency in the range of 20Hz–2 MHz at room temperature. **Figure. 3(a)** exhibits that for both samples the dielectric constant is progressively decreasing with increasing frequency which is typical of interfacial polarization behavior where the dipoles and interfacial charges cannot keep pace with rapidly changing field at higher frequencies. However, a noticeable enhancement i.e., nearly double dielectric constant in CT₂ is attributed to the enhanced space charge polarization driven on by the intensified grain boundary interactions within the microstructure.

Figure. 3(b) shows that $\tan \delta$ initially decreases with increasing frequency for both the samples, as the polarization mechanism becomes less responsive to the rapidly changing alternating field reducing energy dissipation. However,

beyond $\sim 10^5$ Hz, both samples show increased dielectric loss which is explained by dominance of conduction losses and increased energy dissipation at higher frequencies. CT₂ maintains significantly lower $\tan \delta$ values throughout compared to CT₁ confirming that gamma exposure probably inhibits conduction losses and suppresses charge carrier mobility, either by repairing traps or reducing defect-related pathways that assist in energy dissipation.

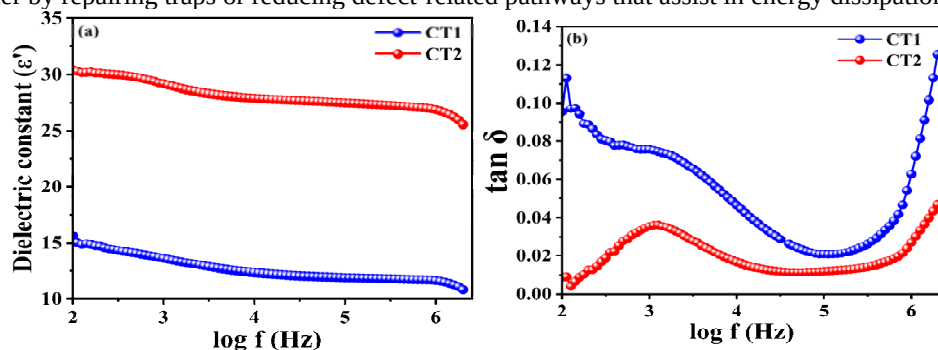


FIGURE. 3 (a) Variation of dielectric constant with frequency, **3 (b)** Variation of dielectric loss with frequency for CT₁ and CT₂ sample at room temperature.

CONCLUSION

Present study investigated the structural, morphological and dielectric properties of CeO₂-TiO₂ nanocomposite. The XRD analysis confirmed formation of phase of both CeO₂ and TiO₂. The gamma irradiated samples shows decreased intensity associated with structural modifications induced by gamma irradiation. FE-SEM analysis reveals noticeable agglomeration of irradiated nanocomposite which implies defect formation. Furthermore, the dielectric measurements carried out at room temperature with varying frequency reveals improved dielectric behavior of gamma irradiated samples by dramatically raising the dielectric constant and decreasing dielectric loss.

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Polar Resistors

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Abstract. It is seen that semiconductor INI structures give polar resistance when the thicknesses of the I (intrinsic) layers are properly tuned. A polar resistor (or, a directional resistor) is a resistor that has two values of resistance – each for a direction of current. When the current direction through the resistor changes the resistance value also changes. In this work, simulations are done for 3 semiconductor INI structures (Si, Ge and GaAs) and it is seen that all 3 show polar resistance between -1 V and +1 V (for I layer thicknesses varied between 100 μm and 500 μm for Si, 5 μm and 20 μm for Ge, and 3000 μm and 10,000 μm for GaAs). The N layer doping density is kept at 10^{15} /cc. N-type, 10^{18} /cc doped CdS (electron affinity = 4.5 eV) for Si, CdTe (electron affinity = 4.3 eV) for Ge, and SnO_2 (electron affinity = 4.7 eV) for GaAs can act as ohmic contacts giving the semiconductor structures a NININ configuration. Polar resistors can be used to add amplitude asymmetry to electrical waveforms in signal processing and music technology.

INTRODUCTION

Ohm's Law was discovered by Georg Simon Ohm in 1827. All resistors obey Ohm's Law. But, till date, a polar resistor has not been found. Polar resistors, or directional resistors, are defined to be resistors which have two values of resistance – one for each current direction. In other words, when the current through the polar resistor changes direction, the value of the resistance also changes. In the extreme regime, where there is a wide difference between the two resistance values, the device's behavior reminds us of diodes.

It is seen that polar resistance can be found in a semiconductor INI structure, where an N-type semiconductor is sandwiched between two intrinsic (I-type) semiconductors (Fig. 1).

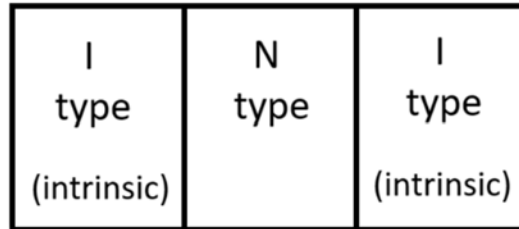


FIGURE 1. The schematic of a INI semiconductor structure. Simulations are carried out for such structures of Si, Ge and GaAs.

SIMULATIONS

The doping density of the middle N-type semiconductor is kept at 10^{15} /cc in all cases. The thickness of the middle N-type layer is 100 μm for Si, 5 μm for Ge and 3000 μm for GaAs. On varying the thicknesses of the 2 intrinsic layers polar resistance is established. Values of semiconductor properties (like band gap, electron affinity, etc) are retrieved from the Ioffe website [1]. Such values are put in ADEPT 2.1, the software used for simulations [2]. For simulations the thickness of 1 I-layer is kept at 100 μm and the thickness of the other I layer is varied between 100 μm to 500 μm . This is for silicon. For germanium, the thickness of 1 I-layer is kept at 5 μm and that of the other I-layer is varied from 5 μm to 20 μm . For gallium arsenide, 1 I-layer's thickness is 3000 μm and the other's thickness is varied between 3000 μm and 10,000 μm . Table 1 shows all the semiconductor parameter values that are used for the simulation in ADEPT.

TABLE 1. Semiconductor parameter values used for simulations in ADEPT 2.1.

Semiconductor Properties	Si	Ge	GaAs
Band Gap	1.1 eV	0.66 eV	1.4 eV
Electron Affinity	4.05 eV	4 eV	4.07 eV
Dielectric Constant	11.7	16.2	12.9
Electron Mobility	1000 cm ² /Vs	4000 cm ² /Vs	8000 cm ² /Vs
Hole Mobility	500 cm ² /Vs	2000 cm ² /Vs	400 cm ² /Vs
Conduction Band effective DOS	3.2 x 10 ¹⁹ /cc	1 x 10 ¹⁹ /cc	4.7 x 10 ¹⁷ /cc
Valence Band effective DOS	1.8 x 10 ¹⁹ /cc	5 x 10 ¹⁸ /cc	9 x 10 ¹⁸ /cc
SRH Electron Lifetime	1 s	1 s	1 s
SRH Hole Lifetime	1 s	1 s	1 s

The simulation results (current density - voltage characteristics) are shown in Fig. 2 and 3. It is seen that all 3 – Si, Ge and GaAs – give polar resistance. No charge recombination was assumed in the simulations. It is also to be remembered that a truly intrinsic nature in semiconductors is never found, and that all intrinsic semiconductors have a background doping density. Simulations were done with minimal background doping (not shown in this paper) and were seen to work. Occasionally, ADEPT generates distorted output plots due to numerical issues. In such cases, the underlying data was carefully reviewed and corrected to ensure accurate representation of the current-voltage characteristics.

Ohmic contacts for intrinsic semiconductors are notoriously difficult to make. To circumvent this problem 10¹⁸ /cc doped N-type CdS (with an electron affinity of 4.5 eV [3]) can be used as an ohmic contact to I-type Si. N-type CdTe (with an electron affinity of 4.3 eV [4]) can be used for Ge. And, N-type SnO₂ (with an electron affinity of 4.7 eV [5]) can be used for GaAs. Such use of ohmic contacts gives our device a NININ configuration.

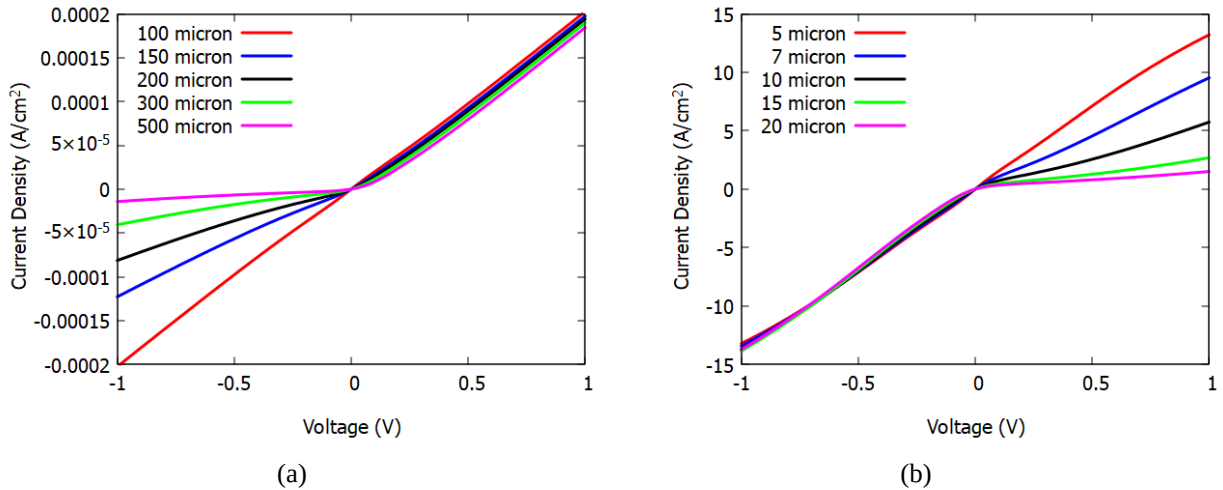


FIGURE 2. Current density - voltage characteristics of the two polar resistors (Si INI structure (a) and Ge INI structure (b)) are shown. The curves are linear between - 1 V and + 1 V.

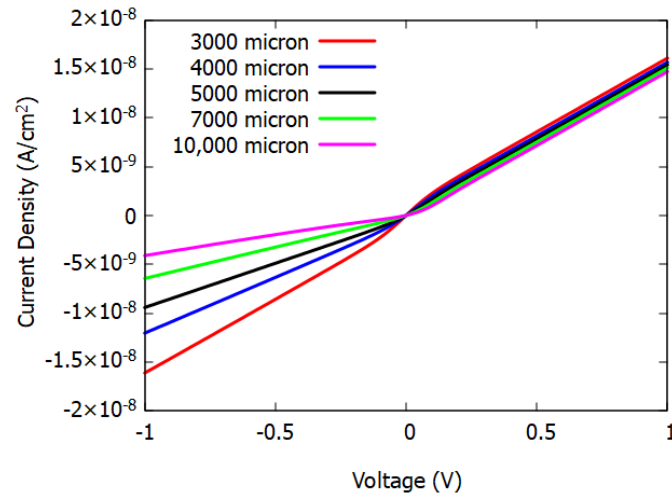


FIGURE 3. Current density - voltage curves of the GaAs INI polar resistor. All curves are linear between - 1 V and + 1 V.

CONCLUSION

3 polar resistors are simulated between - 1 V and + 1 V, – Si, Ge and GaAs INI structures. Ohmic contacts can be added to these INI structures, making the configuration NININ, by CdS, CdTe and SnO₂. All 3 polar resistors are seen to show linear current (density) – voltage relationships.

Asymmetric polar resistors fill the long-lasting gap between (symmetric) resistors and diodes (that conduct only in one direction). They also challenge the traditional (symmetric) interpretation of Ohm's Law by exhibiting two different resistances for the two voltage polarities.

Polar resistors can be used to add asymmetry in electrical circuits. For example, amplitude asymmetry can be added to waveforms in the field of signal processing. Also, complex waveforms used in music (audio) technology can be made asymmetric by the use of polar resistors.

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Fabrication and Characterization of Reactively rf Sputtered Titanium Oxide-Based metal-Oxide-Semiconductor Devices

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Abstract. This work investigates the resistive switching and dielectric properties of Ag/TiO_x/n-Si metal-oxide-semiconductor devices for potential applications in non-volatile memory and neuromorphic computing where TiO_x film was deposited on Si substrates using reactive rf sputtering. X-ray photoelectron spectroscopy study indicates presence of Ti⁴⁺ states and oxygen vacancies. Bipolar resistive switching behavior is observed in the I-V characteristics with distinct set and reset voltages indicating reliable memory operation. Further, a non-volatile nature in the I-V data is also distinctly visible. C-V measurements reveal stable dielectric performance with minimal/no hysteresis suggesting low interface trap density. The combined results demonstrate that TiO_x-based devices offer promising performance for both memory and synaptic applications. Further, the suitability of Ag/TiO_x/n-Si structures is also evidenced for future memory device applications.

INTRODUCTION

There is a growing demand for emerging non-volatile memory (NVM) solutions as the conventional silicon-based memory technologies approach their scaling limits due to increasing requirement of higher density, faster switching and lower power consumption. Among the promising candidates, resistive random-access memory (ReRAM) stands out due to its simple metal-oxide-semiconductor and metal-insulator-metal (MIM) architecture, compatibility with CMOS technology, and potential for multilevel data storage [1, 2]. Intense research to use various transition metal oxides have been going on and titanium oxide (TiO_x), a widely studied switching material has consolidated its position in the field of ReRAM devices because of its ability to support stable resistive switching and sensitivity to oxygen vacancy modulation. The resistive switching behaviour in TiO_x-based structures is often attributed to the formation and disruption of conductive filaments which are primarily governed by the movement of oxygen vacancies or localized redox reactions within the oxide layer [3]. These mechanisms can be influenced by the choice of electrodes, interface quality and film deposition conditions. These properties also make TiO_x suitable for applications beyond conventional memory particularly in neuromorphic computing where memristive behaviour mimics biological synapses [4, 5]. In this study, we explore the resistive switching performance of Ag/TiO_x/n-Si MOS structures where TiO_x was deposited using rf sputtering technique and top Ag electrode was deposited using electron beam deposition system. The electrical properties were measured using current-voltage (I-V) and capacitance-voltage (C-V) techniques. The TiO_x film was also studied using x-ray photoelectron spectroscopy (XPS). The results are presented and discussed here.

EXPERIMENTAL DETAILS

n-type Si (100) wafer was used as substrates to deposit titanium oxide (TiO_x) thin-films onto it by reactive RF magnetron sputtering at room temperature where the resistivity of Si wafer varies from 0.01 – 0.05 Ω·cm and area of the substrates is of 1 cm². A 99.9% pure titanium metal target was used in an argon-oxygen plasma. The substrates were cleaned using RCA technique before deposition and then submerged in 1% HF solution for 1 min for removal of stray oxide. Dry N₂ was used to dry the substrate surface and quickly placed into deposition chamber to avoid any further surface oxidation. Once the base pressure of 9×10^{-6} Torr is achieved, the deposition was carried out at 5 mTorr for 30 minutes with an RF power of 70 W. The gas flow was maintained at 20 SCCM for argon and 5 SCCM for oxygen. The deposition pressure was fixed using a programmable throttle valve. Substrate rotation at 30 rpm was set

to ensure film uniformity. XPS technique was utilized to know about the elemental composition and oxidation states of titanium and oxygen with a non-monochromatic Al K α source (1486.7 eV) and pressure of 4.5×10^{-9} mB. A hemispherical electron analyzer with a 150 mm radius and 20 eV pass energy was used for photoelectron detection. Metal contacts on the oxide films were made by depositing metal using electron beam evaporation and patterned to form gate electrodes. Current–voltage technique were utilized using a Keithley 2450 source meter and a Signatone S1160 probe station equipped with micropositioners to get their I – V data. A voltage sweep of $0 \rightarrow 3 \text{ V} \rightarrow -3 \text{ V} \rightarrow 0$ was applied to the gate electrode. C–V measurements were carried out at 1 MHz using an Agilent E4980A LCR meter. All electrical characterizations were performed at 27 °C under light tight and electromagnetically shielded conditions.

RESULTS AND DISCUSSIONS

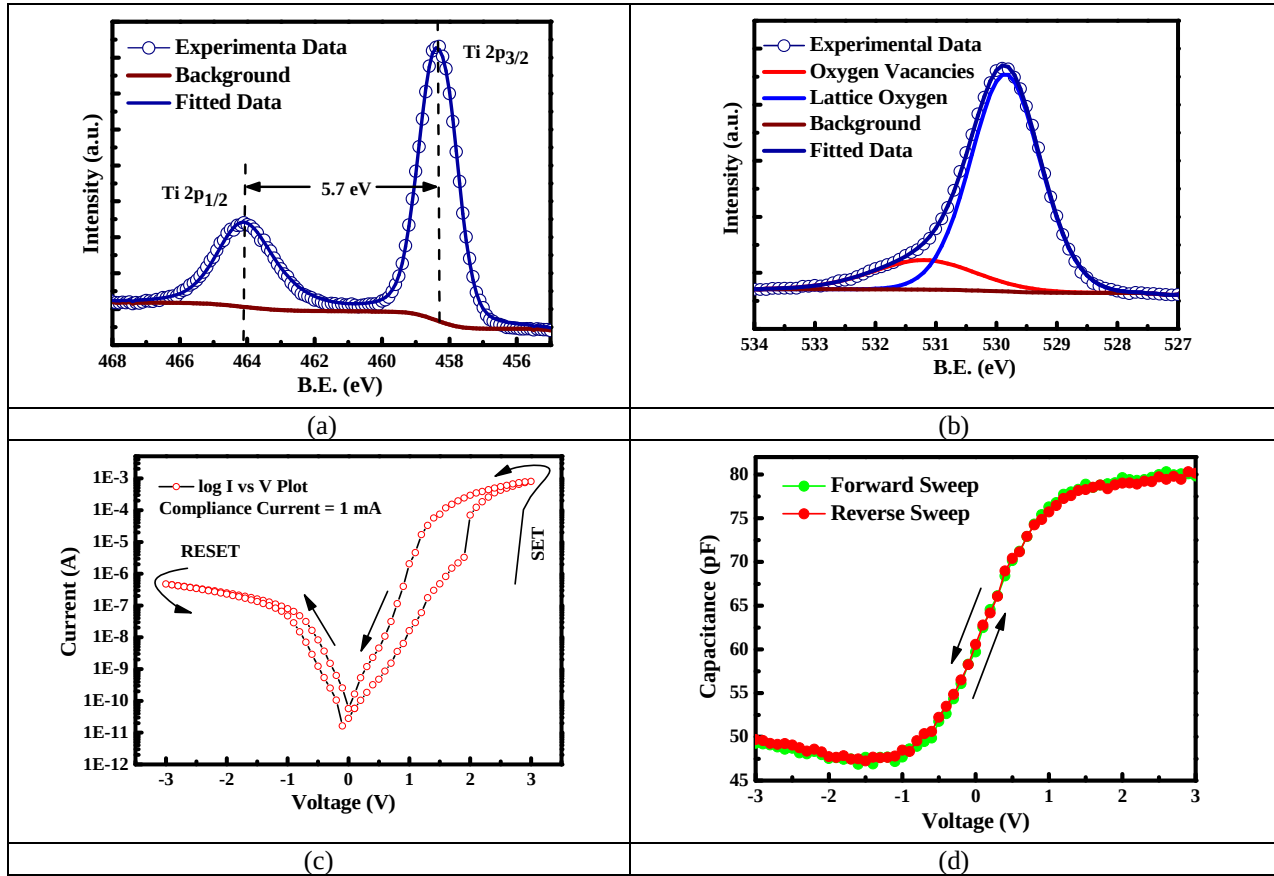


FIGURE 1. Deconvoluted x-ray photoelectron spectroscopy data of (a) Ti 2p, (b) O 1s, (c) I-V and (d) C-V plots of MOS device.

XPS technique was used to find the chemical states and surface composition of TiO $_x$ thin film. Figure 1 shows the deconvoluted XPS spectra of the TiO $_x$ thin film. Figure 1(a) represents the Ti 2p core-level spectrum. All XPS spectra was calibrated using the C 1s reference peak at 284.6 eV to ensure accurate alignment of binding energies. The spectral deconvolution was carried out using CasaXPS software using a GL(30) line shape with Shirley background correction. The spin-orbit splitting between Ti 2p $_{3/2}$ and Ti 2p $_{1/2}$ was fixed at 5.7 eV and their area ratio was constrained to 2:1. The Ti 2p $_{3/2}$ and Ti 2p $_{1/2}$ peaks were observed at 458.35 and 464.11 eV, respectively indicating that titanium predominantly exists in its Ti $^{4+}$ oxidation state within the film. No significant Ti $^{3+}$ signal was detected suggesting its concentration is below the detection limit.

Figure 1(b) shows the deconvoluted O 1s spectrum fitted with two components located at ~ 529.87 and 531.2 eV. The lower binding energy peak at ~ 529.8 eV corresponds to lattice oxygen in Ti–O bonds whereas the higher energy peak at ~ 531.2 eV is attributed to non-lattice oxygen species such as oxygen vacancies or surface hydroxyl groups,

consistent with previous reports [6]. Figure 1(c) illustrates the current–voltage (I–V) characteristics of the Ag/TiO_x/n-Si device. During the forward voltage sweep from 0 V to +3 V, a sudden increase in current was observed around +1.5 V indicating the transition of the device from a high-resistance state (HRS) to a low-resistance state (LRS), commonly referred to as the set process. The device remained in the LRS until a sufficient reverse voltage was applied. As shown in the negative sweep i.e. –3 to 0 V, a significant drop in current occurred near –0.9 V signifying a transition back from LRS to HRS, known as the reset process. These results confirm that the device exhibits bipolar resistive switching behavior. The switching window and transition between HRS and LRS suggest the formation and rupture of conductive filaments likely driven by the migration of oxygen vacancies or redox processes within the TiO_x layer [3]. Further, a non-volatile memory property is also observed in this case where a finite current is present at zero bias voltage. Figure 1(d) illustrates capacitance–voltage (C–V) characteristics of the Ag/TiO_x/n-Si device measured with voltage sweeps at a frequency of 1 MHz from accumulation to depletion and depletion to accumulation. The C–V curves are nearly identical in both directions with no significant hysteresis. This behaviour indicates stable dielectric properties and minimal charge trapping/de trapping effects within the TiO_x layer or at the TiO_x/n-Si interface. The observed capacitance variation with applied voltage reflects the expected behaviour of a MOS device on *n*-type Si where the application of positive bias induces accumulation and negative bias results in depletion. The absence of inversion suggests that minority carrier response is negligible under the measurement conditions indicating a non-inverting surface. Overall, C–V responses support formation of matched TiO_x/Si interface with a low density of interface states. Further, the resistive switching behaviour observed in I–V measurements is governed primarily by bulk or filamentary mechanisms rather than interface-related capacitive effects.

CONCLUSION

In summary, the Ag/TiO_x/n-Si MOS device exhibits bipolar resistive switching with well-defined set and reset voltages by exhibiting non-volatile memory property. Capacitance–voltage analysis further reveals a stable dielectric response. These results highlight the suitability of TiO_x-based structures not only for resistive memory but also for emerging applications in neuromorphic computing and synaptic devices.

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Optical and Capacitive Properties of Fe₂O₃-Sb₂O₃ Composites for Multifunctional Sensing Applications

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Abstract. The Fe₂O₃-Sb₂O₃ composite pellets were synthesized with varying Sb₂O₃ content to explore their multifunctional potential in sensing and electronic applications. The room temperature (RT) X-ray diffraction results confirmed pure and composite phases. UV-Vis DRS spectroscopy revealed tunable band gaps, influenced by particle size and electronic structure modifications. Capacitance measurements across different frequencies showed enhanced dielectric response, particularly at 3 wt.% of Sb₂O₃. The frequency-dependent electrical behavior was strongly correlated with optimum concentration and defect-mediated charge dynamics. These composites exhibit promising properties for optical and capacitive sensing, enabling their potential use in multifunctional devices such as humidity and gas sensors. The study highlights their versatility as a platform for multifunctional device applications.

INTRODUCTION

Iron oxide a widely studied *n*-type semiconductor, has garnered significant attention for its stability, non-toxicity, and rich defect chemistry, making it attractive for a wide range of applications like humidity sensors, gas sensors, photocatalysts, and energy devices [1]. However, the limitations of Fe₂O₃, such as low electrical conductivity and moderate photocatalytic efficiency, often restrict its practical utility in advanced functional devices. To overcome these issues, doping with metal oxides has proven to be a viable route to enhance the material's performance by modifying its structural, optical, and electronic properties [2]. Antimony trioxide (Sb₂O₃) is a wide band gap semiconductor that, when composited with Fe₂O₃, can influence grain boundaries, introduce beneficial defect states, and modulate charge transport mechanisms. The Fe₂O₃-Sb₂O₃ composites thus offer tunable optical band gaps, enhanced dielectric response, and improved sensitivity, making them potential candidates for optoelectronic and capacitive sensing devices. Additionally, such composites can serve as a platform for multifunctional device integration in areas like humidity/gas sensing, sustainable pollutant management, and flexible electronics. Recent studies show that controlled Sb₂O₃ incorporation can effectively tailor the band structure and electrical polarization behavior of Fe-based systems, paving the way for next-generation functional materials [3].

EXPERIMENTAL DETAILS

The composite samples of Fe₂O₃-Sb₂O₃ were prepared by the conventional solid-state reaction route and were labeled R0, R3, R5, and R7, corresponding to pure Fe₂O₃ (R0) and Fe₂O₃ doped with 3, 5, and 7 wt.% Sb₂O₃, respectively. Commercial grade Fe₂O₃ and Sb₂O₃ powders were taken in stoichiometric amounts, weighed, and ground by using an agate mortar and pestle for 2 hr. The homogeneous fine powder was calcinated at 550°C for 6 hr. The pellets of 10 mm diameter and thickness around 3 mm were made using a hydraulic press and sintered at 650°C for 5 hr. The phase purity of synthesized samples was analyzed by X-ray Diffraction (XRD) using a Panalytical diffractometer with Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$) at RT. The particle size was calculated from FESEM images. The absorbance of the composites was recorded using UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS), and Capacitance as a function of frequency (1 kHz, 10 kHz, 100 kHz) was obtained using an LCR meter (Wayne Kerr 6500) at room temperature.

RESULTS AND DISCUSSION

Figure 1 (a) shows the XRD data of Sb_2O_3 , R0, R3, R5, and R7 samples. The structural analysis shows that the R0 sample exhibits sharp diffraction peaks indexed to the hexagonal hematite phase of Fe_2O_3 (space group: $R\text{-}3c$, JCPDS: 01-072-0469), with the (104) plane being the most prominent [4]. In the doped composite R3, R5, and R7, additional weak peaks emerge, corresponding to the orthorhombic phase of Sb_2O_3 (space group: $Pccn$, JCPDS: 11-689), particularly evident with the (111) and (112) reflections [5]. This confirms successful incorporation of Sb_2O_3 into the Fe_2O_3 matrix.

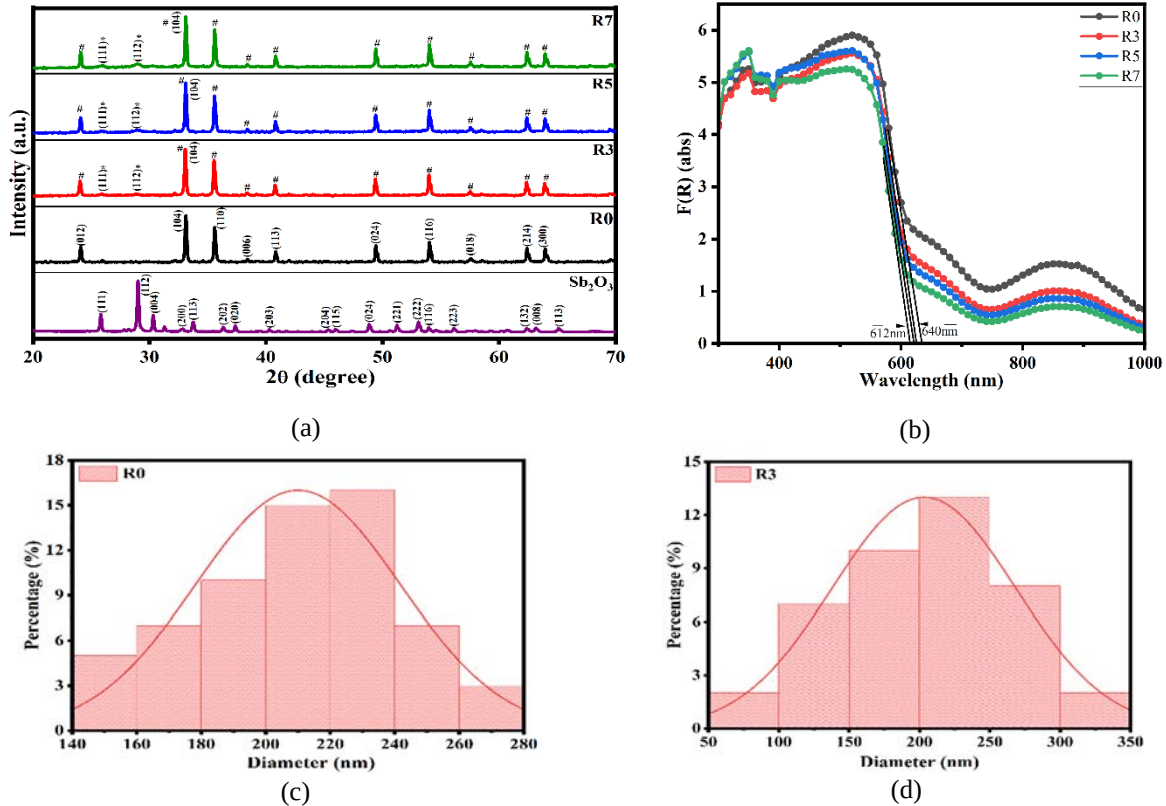


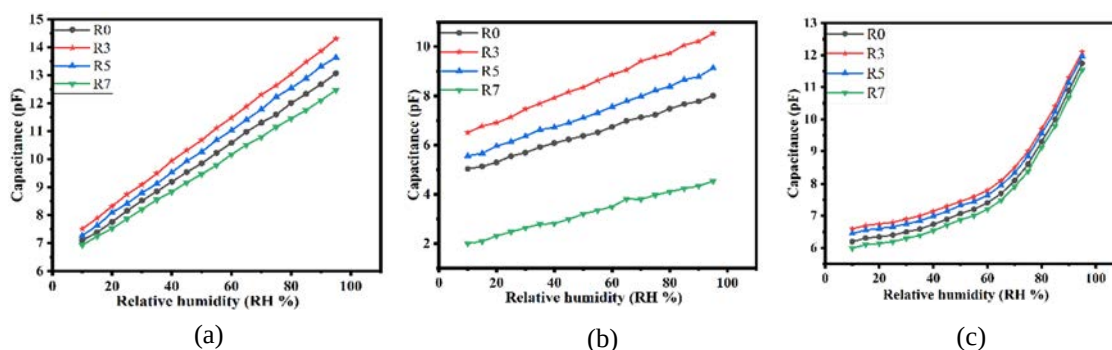
FIGURE 1. (a) The XRD patterns of Sb_2O_3 , R0, R3, R5, and R7 composites, (b) absorbance spectra of Fe_2O_3 - Sb_2O_3 composites, (c) particle size distribution histogram of the R0 sample, (d) particle size distribution histogram of the R3 sample.

The UV-Vis DRS spectra of the composites with varying Sb_2O_3 content (R0, R3, R5, and R7) are presented in Fig. 1 (b). All samples exhibit strong absorption in the visible region (400-700 nm), characteristic of Fe_2O_3 , with a pronounced absorption edge between 600-650 nm. An increase in the optical band gap is implied by the continuous blue shift in the absorption edge that is seen with increasing Sb_2O_3 concentration. In particular, the edge shifts from 640-612 nm, indicating altered electronic interactions and smaller particles, as shown in Fig. 1 (c), where the particle size of R0 is found to be 210 nm, Fig. 1 (d) shows the particle size of R3, which is about 200 nm. Lattice strain and defect formation brought on by Sb inclusion are probably the causes of this change in absorbance spectra. These results demonstrate that moderate Sb_2O_3 doping effectively tunes the optical band structure [6]. Table 1 presents the optical absorption edge and the band gaps estimated from the Tauc plot for the composite samples. Figure 2 (a-c) shows the frequency-dependent capacitance behavior of composites evaluated at 1 kHz, 10 kHz, and 100 kHz under varying relative humidity (RH %) conditions at RT [7]. At all three frequencies, the capacitance increased steadily with RH, confirming the humidity sensitive nature of the material. The R3 consistently exhibited the highest capacitance across all frequencies, indicating superior dielectric response and enhanced water molecule adsorption. This improvement is attributed to the optimized defect density and increased surface polarity introduced by moderate Sb content, which facilitates dipole formation and charge mobility.

TABLE 1. Optical absorption edge and estimated band gap for composite samples from UV-Vis DRS.

Sample	Adsorption Edge (nm)	Estimated band Gap (eV)
R0	640	1.94
R3	625	1.98
R5	618	2.00
R7	612	2.02

At lower frequencies (1 kHz), capacitive values were higher due to enhanced interfacial polarization and full dipole alignment. As frequency increased (10 kHz and 100 kHz), the capacitance values decreased slightly, reflecting the reduced response time of dipoles to rapidly alternating fields. Overall, R3 demonstrated the most efficient frequency tunable performance, making it a promising candidate for capacitive type sensing devices.

**FIGURE 2.** Capacitance variation R0, R3, R5 and R7 with Relative humidity (RH %) measured at three different frequencies at room temperature: (a) 1 kHz, (b) 10 kHz, and (c) 100 kHz

CONCLUSION

Composites with varying Sb_2O_3 content were successfully synthesized and characterized for multifunctional applications. XRD confirmed a composite phase with reduced particle size upon doping, particularly at 3 wt.%. According to UV-Vis DRS spectroscopy, the absorption edge showed a blue shift that is indicating band gap tuning via defect engineering. Capacitance studies revealed frequency dependent dielectric behavior, with R3 exhibiting the most response. These findings demonstrate the potential of $\text{Fe}_2\text{O}_3\text{-Sb}_2\text{O}_3$ composites for dual mode sensing and optoelectronic applications.

ACKNOWLEDGMENTS

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Development and Characterization of *p*-Type Transparent Conducting Oxides: A Study on Pure CuGaO₂ and Ga₂O₃-Modified Cu₂O Compounds for Transparent Electronics

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Abstract. Transparent conducting oxides (TCOs) are critical for optoelectronic devices because of their unique combination of optical transparency and electrical conductivity. While *n*-type TCOs are well developed, efficient *p*-type TCOs remain a challenge. This study explores pure CuGaO₂ and Ga₂O₃ modified Cu₂O (5 wt.% and 7 wt.%) as a potential *p*-type TCO material. Samples were synthesized via the conventional solid-state reaction route and characterized for their structural, optical, and electronic properties using X-Ray Diffraction, UV-Visible spectroscopy, and Hall transport measurements. Structural analysis confirmed phase formation and crystallinity, while optical studies revealed direct band gaps and good transparency in the visible range. Hall measurements verified *p*-type conductivity, with Ga₂O₃ doping influencing carrier concentration and mobility. The findings suggest that both CuGaO₂ and Ga₂O₃:Cu₂O systems are promising candidates for future *p*-type transparent electronics.

INTRODUCTION

Transparent Conducting Oxides (TCOs) have applications in optoelectronic devices such as solar cells, LEDs, and thin film transistors due to their combination of high optical transparency and electrical conductivity [1]. These are wide band gap materials having an optical band gap greater than 3 eV, which ensures optical transparency. While *n*-type TCOs, such as ITO and ZnO, are widely used and well-developed, the development of efficient and stable *p*-type TCOs remains a significant challenge due to limitations in achieving high hole mobility and carrier concentration [2]. Copper-based materials such as Aluminium-doped Copper oxide and Gallium-doped Copper oxide, were found to be promising *p*-type TCOs due to their delafossite structure, and intrinsic *p*-type conductivity arising from Cu⁺ 3d and O 2p orbital hybridization [3]. This work focuses on the synthesis and characterization of pure CuGaO₂ and Ga₂O₃-modified Cu₂O compounds (with 5 wt.% and 7 wt.% Ga₂O₃) as a potential *p*-type TCO. Ga³⁺ is chosen as a dopant due to its chemical stability and smaller ionic size compared to Cu⁺. The structural, optical, and electronic properties of the material were investigated to evaluate its suitability for *p*-type transparent electronics.

EXPERIMENTAL METHODS

The samples were prepared using the conventional solid-state method. Commercial grade Copper (I) oxide (Cu₂O) and Gallium (III) oxide (Ga₂O₃) powders were taken in appropriate stoichiometric amounts, weighed, and mixed thoroughly using an agate mortar and pestle for 2 hours to ensure homogeneity. The fine powder was then calcinated at 1000°C in a muffle furnace for 24 hrs. under controlled conditions to promote phase transition.

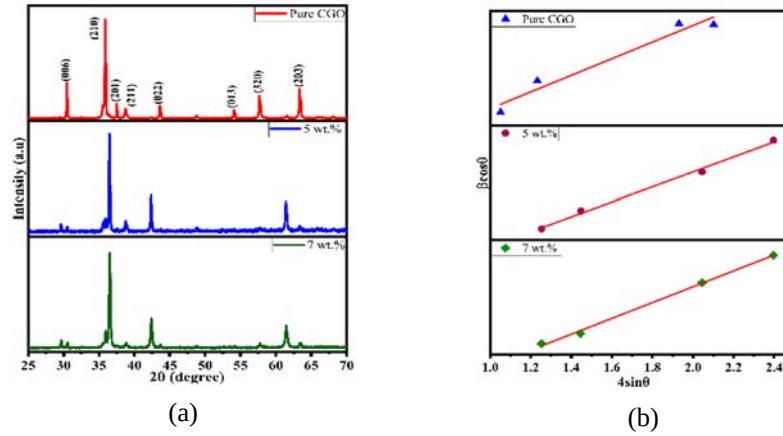


FIGURE 1. (a) The XRD pattern and (b) Williamson-Hall (W-H) plots for pure, 5 wt.%, and 7 wt.% Ga₂O₃-modified Cu₂O samples.

TABLE 1. Crystallite size and lattice strain for pure, 5 wt.% and 7 wt.% Ga₂O₃-modified Cu₂O samples.

Sample	Crystallite size (nm)	Lattice strain(ε)
Pure	45.76	1.11×10^{-1}
5 wt.%	40.07	1.43×10^{-1}
7 wt.%	22.67	1.37×10^{-1}

X-Ray diffraction (XRD) patterns were recorded using a PANalytical diffractometer with Cu-K_α radiation ($\lambda=1.5406$ Å) in the 2θ range of 20° to 80° to analyze structural properties. Optical absorption studies were performed using a UV-Visible spectrophotometer in the range 200 to 800 nm, and band gaps were estimated using Tauc plots. Hall transport measurements were conducted at room temperature using the Van der Pauw method under a magnetic field of 5148 Gauss to determine the type of conductivity, carrier concentration, and mobility of these samples.

RESULTS AND DISCUSSION

The XRD plots of the samples are given in Fig. 1 (a). The XRD patterns of the synthesized samples confirmed the formation of the expected crystalline phases. Pure CuGaO₂ exhibited peaks corresponding to a delafossite structure matching well with the standard JCPDS file No. 41-0255 [4], indicating successful phase formation. In Ga₂O₃-modified samples, characteristic peaks were observed along with a slight shift in peaks towards higher θ due to the lattice contraction caused by the substitution of smaller Ga³⁺ ions (0.62Å) in place of larger Cu⁺ ions (0.77Å). If the dopant ion has a smaller ionic radius than the ion that it replaces, it causes the crystal to shrink, hence shifting peaks to higher θ . The crystallite sizes were found using the Williamson-Hall (W-H) equation, which is given by [5]:

$$\beta \cos \theta = \frac{k\lambda}{D} + 4\epsilon \sin \theta \quad (1)$$

where D is the crystallite size, β is full width half maxima (FWHM), ϵ is lattice strain, k is shape factor, θ is Bragg angle, and λ is X-ray wavelength. Figure. 1 (b) shows the W-H linear fit plots of different samples, and Table. 1 shows the crystallite sizes of different synthesized materials. The crystallite size decreased with increasing doping. The optical absorption spectra showed a sharp absorption edge for all samples. The band gap energy was calculated using the Tauc plot method for direct allowed transitions, which is given by [5]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

where $h\nu$ is photon energy, A is a constant, and E_g is the optical band gap. Figure. 2 (a) and (b) show the Tauc plots and estimated band gaps for various samples. The estimated optical band gap of pure CuGaO₂ was found to be 3.35 eV and 7 wt.% sample had a band gap of 3.2 eV, indicating that our material is optically transparent, as TCOs typically have a wide energy band gap greater than 3 eV. The observed transport properties are presented in Table. 2. The Hall effect measurements confirmed p -type conductivity for all samples. Pure CuGaO₂ exhibited moderate carrier concentration and mobility. The Hall coefficient increased for higher wt.% sample. It is evident from the result that

doping of Ga_2O_3 in Cu_2O decreases the charge concentration as compared to the pure sample. The mobility of these samples decreased after doping.

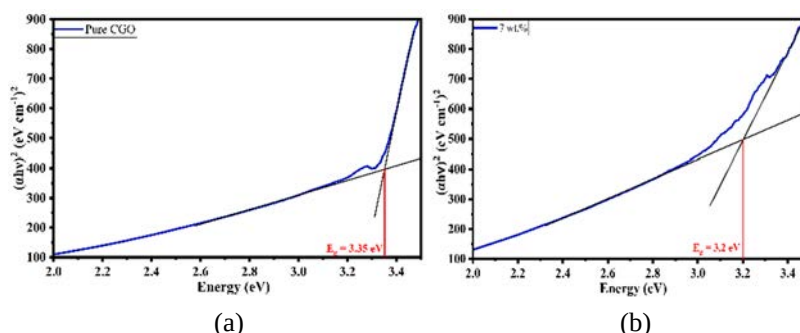


FIGURE 2. (a) The Tauc plot of pure CuGaO_2 . (b) The Tauc plot of 7 wt.% Ga_2O_3 -modified Cu_2O sample for the estimation of band gaps.

TABLE 2. Transport properties of pure, 5 wt.%, and 7 wt.% Ga_2O_3 -modified Cu_2O samples.

Sample	Resistivity ($\Omega\cdot\text{cm}$)	Carrier Concentration (cm^{-3})	Hall Coefficient (cm^3/C)	Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)	Carrier type
Pure	2.39	1.33×10^{17}	46.7	1.95×10^2	<i>p</i> -type
5 wt.%	2.85	6.20×10^{16}	60.5	18.3	<i>p</i> -type
7 wt.%	3.44	8.07×10^{15}	77.3	2.24	<i>p</i> -type

CONCLUSION

This study examined the structural, optical, and electronic properties of pure CuGaO_2 and Ga_2O_3 -modified Cu_2O compounds to evaluate their potential as a *p*-type TCO. XRD analysis confirmed the formation of well-crystallized phases, indicating successful incorporation of Ga^{3+} into the lattice. UV-Visible spectroscopy revealed direct optical band gaps in the range 3-3.6 eV and good transparency in the visible region for all samples. Hall effect measurements confirmed *p*-type conductivity in all samples. The 5 wt.% and 7 wt.% samples showed improved Hall coefficient and a decrease in carrier concentration due to doping. These findings suggest that both pure and modified samples are promising candidates for use as *p*-type transparent conductors in optoelectronic applications. Its wide band gap, good optical transparency, and moderate conductivity make it a strong candidate for use in optoelectronic devices. However, there are challenges in optimizing its electrical performance and ensuring it can be efficiently produced and integrated into devices on a large scale.

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Symmetry Analysis of Axion Insulating Phase in Magnetic Topological Heterostructures

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Abstract. We investigate axion-insulating phases in magnetic topological heterostructures using slab models of Bi_2Se_3 and MnBi_2Te_4 . In ferromagnet–topological insulator–ferromagnet (FM/TI/FM) trilayers, parallel spin alignment leads to quantized Hall conductivity due to broken time reversal symmetry (TRS), while antiparallel alignment yields a zero Hall plateau via effective TRS. MnBi_2Te_4 exhibits similar behavior: odd layers behave as Chern insulators and even layers as axion insulators. Our first-principles calculations confirm quantization of magnetoelectric coupling coefficient ($\theta \approx \pi$) for Bi_2Se_3 . We highlight inversion symmetry and effective TRS as an essential ingredient for realizing axion phases.

INTRODUCTION

The search for new quantum phases of matter has brought increased attention to topological magnetic insulators, particularly Axion insulators (AIs), which are defined by a quantized magnetoelectric coupling characterized by the axion angle $\theta = \pi$. In contrast to conventional topological insulators (TIs), whose topological invariants derive from unbroken TRS, axion insulators necessitate magnetic order that explicitly breaks TRS yet preserves spatial inversion (P) or effective TRS via specific spin configurations [1,2]. Several material systems have been proposed as potential candidates for realizing the axion insulating phase. Even-layer MnBi_2Te_4 thin films, which preserve effective time-reversal symmetry through antiferromagnetic ordering, show zero Hall conductivity and a quantized axion field, $\theta = \pi$ [1]. These theoretical predictions have been supported by recent experimental studies [2]. Another promising system is the FM/TI/FM trilayer heterostructure. In this case, antiparallel spin alignment preserves effective time-reversal symmetry, leading to $\theta = \pi$ and zero Hall response, while parallel spin alignment breaks time-reversal symmetry but retains inversion symmetry, resulting in a quantized anomalous Hall effect [3-6]. In the next section of this paper, we will discuss the symmetry properties and experimental signatures of these systems in more detail, aiming to clarify the necessary conditions for realizing the axion insulating state.

MODEL AND METHOD

We model a trilayer heterostructure based on the topological insulator Bi_2Se_3 using a slab Hamiltonian approach [7,8]. Magnetic proximity is introduced by applying a Zeeman term to the topmost and bottommost layers, simulating two distinct magnetic configurations: (I) parallel and (II) antiparallel spin alignment. The resulting electronic band structures are computed to investigate the effects of broken time-reversal symmetry (TRS) and preserved effective TRS, respectively. The Hall conductivity is calculated using the linear response Kubo formalism given by:

$$\sigma_{xy} = \left(\frac{e^2}{h}\right) \int \left(\frac{d^2\mathbf{k}}{(2\pi)^2}\right) \sum_{\{m \neq n\}} \frac{\langle u_n(\mathbf{k}) | v_x | u_m(\mathbf{k}) \rangle \langle u_m(\mathbf{k}) | v_y | u_n(\mathbf{k}) \rangle}{(\varepsilon_n - \varepsilon_m)^2} \cdot f(\varepsilon_n) \quad (1)$$

Here, $v_{x,y} = \partial H / \partial k_{x,y}$, $u_n(k)$ and ε_n are eigenstate and eigenvalues corresponding to the n^{th} band. $f(\varepsilon)$ is the Fermi Dirac distribution. Additionally, a slab model for MnBi_2Te_4 is constructed to analyze the dependence of Hall response on the number of septuple layers (unit cell for MnBi_2Te_4 comprise of seven atomic layers stacked along the z-direction known as a septuple layer), capturing the transition between Chern and axion insulating phases.

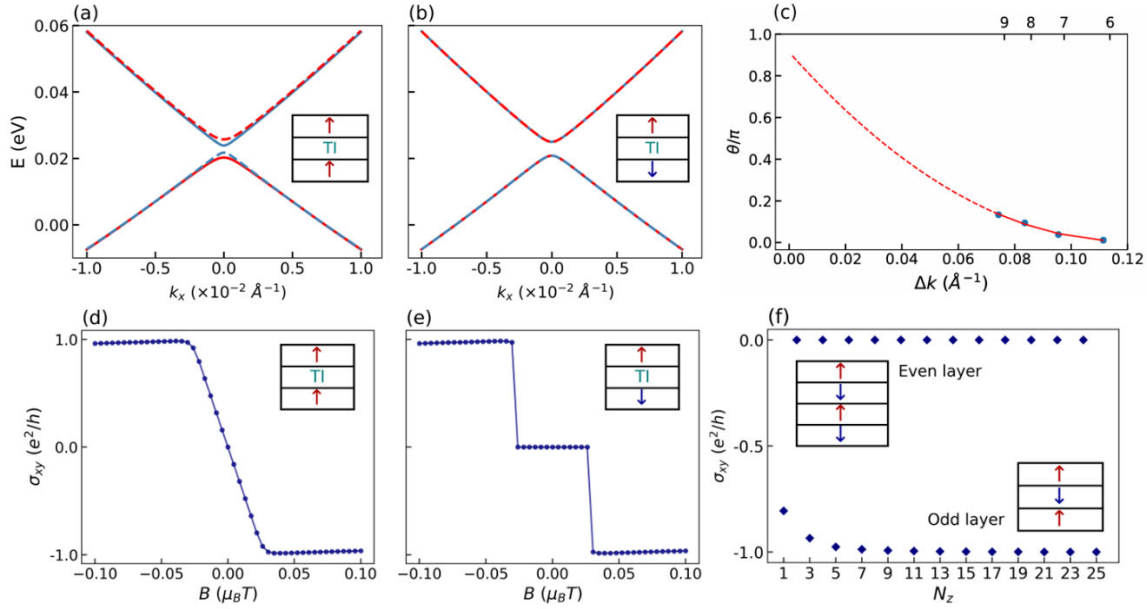


FIGURE 1. (a)-(b) Band structure of the trilayer heterostructure for (a) parallel and (b) antiparallel spin configurations, showing effects of TRS breaking and effective TRS preservation. (c) Axion angle θ computed from first-principles calculations for TRS-preserving Bi_2Se_3 . (d)-(e) Hall conductivity in the trilayer for broken and effective TRS. (f) Hall conductivity calculations in MnBi_2Te_4 versus layer number, zero for even layers and quantized for odd layers.

RESULTS AND DISCUSSION

Figures 1(a) and 1(b) illustrate the band structures of the trilayer system under parallel and antiparallel magnetic configurations. Parallel alignment breaks TRS, lifting Dirac band degeneracy near the Γ point and opening a gap. In contrast, antiparallel alignment preserves effective TRS via magnetic compensation, retaining the Dirac band degeneracy while also opening a gap. The corresponding Hall conductivities in Figs. 1(d) and 1(e) exhibit a quantized response and a zero Hall plateau, indicating Chern and axion insulating phases, respectively. For MnBi_2Te_4 , Hall conductivity exhibits a layer-number dependence: odd-layer systems show quantized values (Chern insulator), and even-layer systems show zero conductivity (axion insulator), as in Fig. 1(f). These findings align with theoretical predictions of Chern number, implying that the axion angle θ is quantized to $\pm\pi$ in systems preserving TRS or effective TRS. To validate this, we perform first-principles calculations to obtain θ in Bi_2Se_3 , a known TRS-preserving topological insulator [9-12]. The computed value, $\theta \approx 0.93\pi$, supports the expected quantization depicted in Fig. 1(c). In contrast, breaking TRS in the same model results in a non-quantized θ , further reinforcing the role of symmetry in axion electrodynamics. Inversion-symmetric systems are characterized by the $\mathbb{Z}_4$ invariant, computable via first-principles methods. Combined evaluation of the Chern number, $\mathbb{Z}_4$ invariant, and axion angle θ can offer deeper insight into axion insulating phases.

First principle calculations

The axion field as a Brillouin zone integral proposed by Xiao *et al.* 2008 [9], requires Berry connection matrix elements. The Berry connection is gauge-dependent, making its computation nontrivial. We employ a Wannier-based method to ensure smooth gauge selection and accurate calculation of the axion angle θ on dense k -meshes [10]. Using first-principles calculations within a non-collinear spin-polarized framework (USPP and PBE functional), we compute the band structure of Bi_2Se_3 followed by NSCF calculations on $6 \times 6 \times 6$ to $9 \times 9 \times 9$ grids. The position matrix elements $\langle \mathbf{0}m | r_j | \mathbf{R}n \rangle$ are obtained via Wannier90. θ values from each mesh are extrapolated using a quadratic fit. All calculations were performed using Quantum ESPRESSO and Wannier90 [11,12].

TABLE 1. Candidate systems and preserved symmetries that can support the axion insulating phase.

Symmetry	Chern number	$\mathbb{Z}_4$ invariant	θ	Example
TRS (T) Inversion (P)	$C = 0$	$\mathbb{Z}_4 = 2$	$\theta = \pi$	$\text{Bi}_2(\text{Se, Te})_3$
Effective TRS ($\mathbf{S} = \mathbf{T} \cdot \boldsymbol{\tau}_{1/2}$)	$C = 0$	$\mathbb{Z}_4 = 1,3$	$\theta = \pi$	Even layer MnBi_2Te_4
Inversion (P)	$C = \pm 1$	$\mathbb{Z}_4 = 2$	$\theta = \pi$	$\text{MnBi}_2\text{Te}_4(\uparrow) - \text{Bi}_2(\text{Se, Te})_3 - \text{MnBi}_2\text{Te}_4(\uparrow)$
Effective TRS and Inversion (T · P)	$C = 0$	$\mathbb{Z}_4 = 2$	$\theta = \pi$	$\text{MnBi}_2\text{Te}_4(\uparrow) - \text{Bi}_2(\text{Se, Te})_3 - \text{MnBi}_2\text{Te}_4(\downarrow)$

CONCLUSION

Our study provides a symmetry-based approach to identifying axion-insulating phases in magnetic topological heterostructures. We propose that both parallel (inversion symmetric) and antiparallel (effective TRS) spin configurations in a trilayer heterostructure can lead to a quantized axion response. Given the experimental difficulty in verifying antiparallel spin alignment, the use of inversion symmetry offers a practical route towards realizing axion insulators. A classification of symmetry-protected candidate systems is summarized in Table 1. These results offer guidance for the experimental exploration and realization of axion insulating phases in quantum materials.

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Effect of Site-Specific Substitution on Thermoelectric Properties of NiTiSn Based Half Heusler Alloys

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Abstract. Site-specific substitution in NiTiSn based Half-Heusler alloys ($\text{NiTi}_{0.95}\text{V}_{0.05}\text{Sn}$, $\text{NiTiSn}_{0.95}\text{Sb}_{0.05}$, $\text{Ni}_{0.95}\text{Cu}_{0.05}\text{TiSn}$) was examined using XRD, confirming the cubic C1b structure with near-stoichiometric compositions. Measurements of electrical resistivity, Seebeck coefficient, and power factor between 100–400 K showed that V-substitution at the Ti site achieved the highest PF ($\sim 25 \text{ mW m}^{-1} \text{ K}^{-2}$ at 400 K). In comparison, Sb and Cu substitutions led to marginal improvements, indicating Ti-site substitution as the effective strategy for enhancing thermoelectric performance.

INTRODUCTION

Among thermoelectric material families, Half Heusler (HH) alloys with the general formula XYZ (X and Y are transition metals, Z is a main group element) have emerged as promising candidates due to their thermal stability, mechanical strength, non-toxicity, and moderate band gaps suitable for thermoelectric transport [1, 2]. One of the most extensively studied HH systems is NiTiSn, an n-type semiconductor with a band gap of approximately 0.5 eV, offering high electrical conductivity and mechanical stability [3]. However, its relatively high lattice thermal conductivity ($\sim 8\text{--}10 \text{ W/m}\cdot\text{K}$) suppresses the overall ZT to below 0.5 in the undoped state [4]. To enhance the thermoelectric performance of NiTiSn, various strategies have been proposed, including nanostructuring, carrier concentration tuning, and alloying to enhance phonon scattering [5]. Among these, chemical substitution at different crystallographic sites has proven particularly effective. Substitution at the Ti site with transition metals like V, Zr, or Hf can modify the electronic density of states and increase the Seebeck coefficient through band structure modification [6]. Sb or Bi doping at the Sn site introduces extra electrons, shifting the Fermi level and enhancing carrier concentration [7]. Substitution at the Ni site with Cu or Pd has been shown to influence the carrier mobility and introduce point defects that scatter phonons, thereby reducing lattice thermal conductivity [8].

In the present study, we investigate the effect of partial substitution at three different sites in the NiTiSn system: V at the Ti site, Sb at the Sn site, and Cu at the Ni site. These specific dopants were chosen due to their electronic configurations and atomic radii, which are expected to influence both the electronic band structure and phonon transport. A systematic comparison of the structural, electrical, and thermoelectric properties of these substituted samples is carried out to understand how site-specific doping influences the power factor and overall thermoelectric behaviour.

EXPERIMENTAL

Polycrystalline NiTiSn, $\text{NiTi}_{0.95}\text{V}_{0.05}\text{Sn}$, $\text{NiTiSn}_{0.95}\text{Sb}_{0.05}$, and $\text{Ni}_{0.95}\text{Cu}_{0.05}\text{TiSn}$ samples were prepared by arc melting stoichiometric amounts of high-purity elements ($\geq 99.99\%$) in argon atmosphere. The ingots were flipped and remelted 3–4 times for homogeneity. The melted samples were vacuum-sealed in quartz ampoules and annealed at 800°C for 72 hours. Samples were characterized using XRD (Cu K α , $\lambda = 1.5406 \text{ \AA}$) for phase analysis, while electrical resistivity and Seebeck coefficient were measured using standard four-probe and differential methods respectively. Power factor ($\text{PF} = S^2/\rho$) was calculated from the measured values.

RESULTS AND DISCUSSION

Powder XRD patterns as shown in Fig. 1(a) confirmed a predominant cubic C1b-type structure (space group $F\bar{4}3m$) for all samples, with minor Ni_2TiSn and Sn_5Ti_6 impurities consistent with previous reports. The temperature dependence of electrical resistivity $\rho(T)$ is shown in Fig. 1(b). The parent $NiTiSn$ sample exhibited semiconducting behaviour, with ρ decreasing sharply above ~ 250 K. V-substitution at the Ti site reduced the temperature dependence and stabilized a lower resistivity (~ 0.07 m Ω -cm at 400 K) by increasing carrier concentration through donor levels. Sb-substitution led to the lowest resistivity (~ 0.04 m Ω -cm at 400 K), indicative of its strong electron-doping effect. Cu-doping at the Ni site slightly reduced the resistivity compared to the parent sample but did not achieve as low a value as Sb-doping.

The Seebeck coefficient $S(T)$ (Fig. 2a) of all samples was negative, confirming n-type conduction. The parent $NiTiSn$ sample showed the largest $|S|$ values (up to -300 μ V/K at 400 K), consistent with low carrier concentration. V-substitution enhanced $|S|$ across the entire temperature range (-150 μ V/K at 400 K), attributed to the modification of the electronic density of states near the Fermi level. In contrast, Sb-substitution significantly reduced $|S|$ (~ -50 μ V/K at 400 K) due to the increase in carrier concentration, while Cu-doping yielded intermediate values.

The power factor, $PF = S^2/\rho$ is plotted in Fig. 2 (b). V-substitution showed the most significant enhancement, reaching ~ 25 mW $m^{-1} K^{-2}$ at 400 K, more than an order of magnitude higher than the parent compound. Sb-doping also improved the PF (~ 12 mW $m^{-1} K^{-2}$ at 400 K) but less effectively than V-doping because of the reduced S . Cu-doping provided only a modest PF improvement. Among the doped samples, V substitution at Ti-site exhibited the highest power factor (PF) because it optimally modifies the electronic band structure and carrier concentration. V introduces donor levels near the conduction band edge, shifting the Fermi level upward and increasing electron concentration without heavily saturating it [6,7].

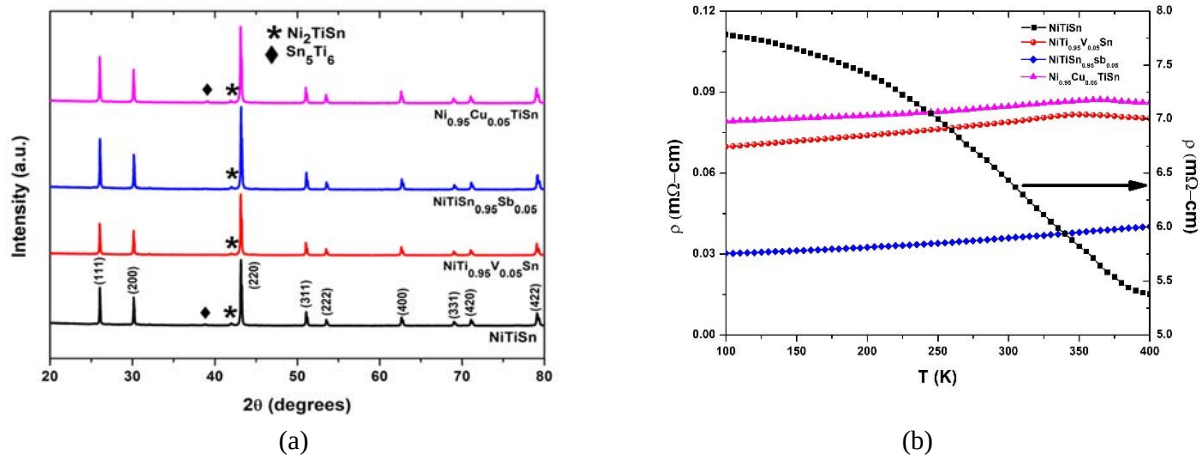


FIGURE 1. (a) XRD patterns and (b) Resistivity v/s temperature plots of $NiTiSn$, $NiTi_{0.95}V_{0.05}Sn$, $NiTiSn_{0.95}Sb_{0.05}$, and $Ni_{0.95}Cu_{0.05}TiSn$ alloys

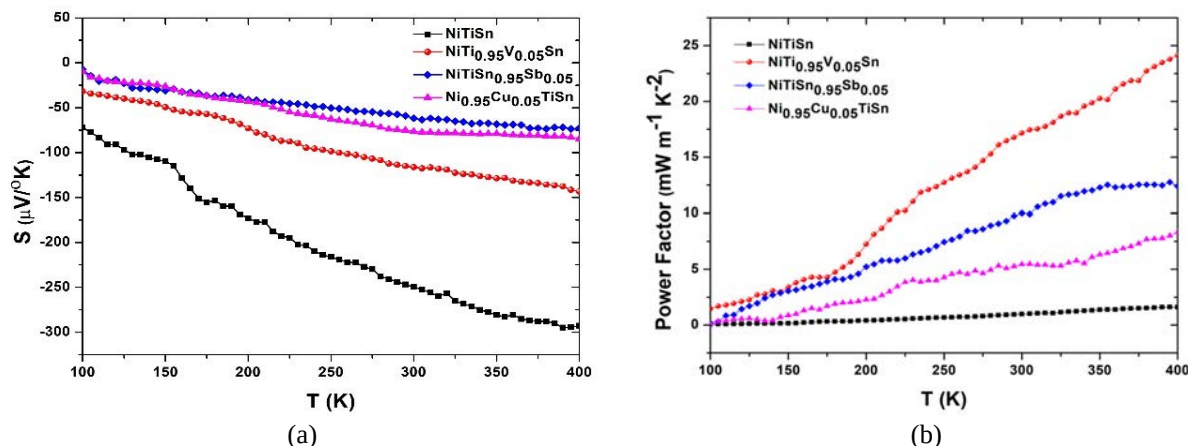


FIGURE 2. Temperature dependence of (a) Thermopower and (b) Power factor of NiTiSn, NiTi_{0.95}V_{0.05}Sn, NiTiSn_{0.95}Sb_{0.05}, and Ni_{0.95}Cu_{0.05}TiSn alloys

This moderate doping lowers the electrical resistivity while preserving a relatively high Seebeck coefficient by enhancing the density of states (DOS) slope near the Fermi level [6]. The simultaneous reduction in ρ and retention of S leads to the maximum PF among all substitutions. Thus, these results highlight the critical role of site-specific substitution in optimizing the balance between S and ρ .

CONCLUSIONS

We have studied the effect of site-specific substitution (V, Sb, Cu) on the structural and thermoelectric properties of NiTiSn-based Half Heusler alloys. XRD confirmed that all samples crystallized in the C1b cubic phase with minor secondary phases. Electrical transport measurements revealed that V substitution at Ti-site is the most effective strategy for enhancing thermoelectric performance, primarily due to the simultaneous enhancement of the Seebeck coefficient and reduction of resistivity, leading to a maximum power factor of $\sim 25 \text{ mW m}^{-1} \text{ K}^{-2}$ at 400 K. Sb substitution at the Sn site improved electrical conductivity but reduced the Seebeck coefficient, while Cu substitution at the Ni site showed marginal improvement. These findings provide useful insights into the role of site-specific chemical substitution in tailoring the thermoelectric properties of Half Heusler alloys.

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Synthesis and Study of Optical and Electrical Properties of Pure and Doped Graphene Quantum Dot Thin Films

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Abstract. This study focuses on the synthesis and characterization of the optical and electrical properties of pure and doped graphene quantum dot (GQD) thin films deposited on a quartz substrate. The films were prepared using hydrothermal synthesis followed by spin-coating techniques. UV-Visible spectroscopic analysis reveals a strong absorption peak in the ultraviolet region, and the direct optical band gap was determined to be 4.51 eV using Tauc's plot. The fabricated thin films exhibit high optical transparency, with a transmittance of approximately 83% at 500 nm in the visible region. Furthermore, the high-temperature current-voltage (I-V) characteristics of the samples were investigated over the temperature range of 393 K to 513 K to understand their electrical conduction behaviour. The calculated value of activation energy depicts the semiconducting behavior of the prepared graphene quantum dot thin films. It was found that the high optical transmittance and semiconducting nature of graphene quantum dot thin films show their applicability as a transparent conducting material in optoelectronic devices.

INTRODUCTION

In the present scenario, the development of new types of quantum dots (QDs) has attracted much attention. The graphene quantum dots (GQDs) are one of the most efficient nanomaterials of graphene for the photo-luminescent (PL) and optoelectronic applications [1]. GQDs can be utilized to fabricate new structures and devices with remarkable features, replacing frequently used semiconductor nanocrystals that are expensive and may contain toxic heavy metal elements. The zero-dimensional GQDs with the wide band gap of 4.5 eV exhibit remarkable optically transparent properties in the visible region that are directly related to quantum confinement and edge effects [1]. Further, the semiconducting nature of GQDs is useful for their usage in optoelectronics. It is reported in the literature that GQDs are highly efficient nanomaterials for increasing PL emission intensity and enhancing visible region absorption. In addition, most of the work in this field has been reported on aqueous solutions and powders, and very few studies have been found in thin film form. Therefore, in this study, we have prepared GQD thin films using the hydrothermal and spin-coating methods [2].

EXPERIMENTAL SECTION

In this study, the GQD thin films were prepared using hydrothermal synthesis and spin-coating methods. In the first step, the GQDs solution was prepared by the hydrothermal method using a 0.3 M solution of citric acid ($C_6H_8O_7$) as precursor was dissolved in 50 mL of deionized water, followed by vigorous stirring to obtain a transparent solution, which was then heated at 200°C for five hours in an autoclave [3]. This obtained solution was again stirred for 5-6 hours at 100°C to get a homogeneous gel. In the second step, the obtained gel was spin-coated on a quartz substrate, cleaned, and then degreased at 500°C. Finally, the obtained thin films were calcined at 200°C for three hours. A similar procedure has been followed to get the N-doped GQDs thin film. The optical and electrical studies of the thin film were performed using a UV-Visible spectrophotometer, and electrical studies were performed with the help of a Keithley 2400 source meter, respectively.

RESULTS AND DISCUSSION

High-resolution transmission electron microscopy (HR-TEM) analysis was performed to examine the surface morphology and particle size distribution of the GQDs. Figure 1(a) illustrates the formation of graphene quantum dots, while Figure 1(b) presents the corresponding particle size distribution histogram for 4% N-doped GQDs. The presence

of distinct dark spots with a quasi-spherical morphology in the HR-TEM image (Fig. 1(a)) confirms the successful synthesis of N-GQDs. The histograms in Fig. 1. (b) show the particle size distribution curves, and the average particle size is found to be 6.3 nm.

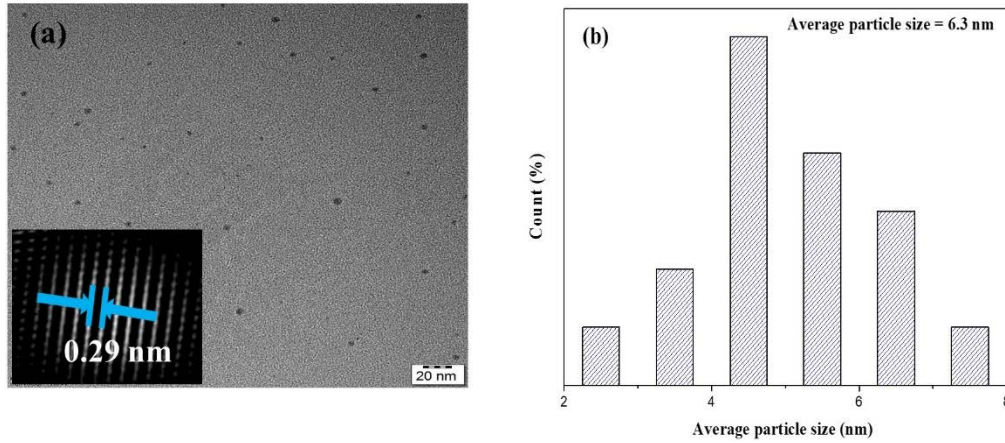


FIGURE 1. (a) The HR-TEM image, (b) histogram of particle size distribution of 4% N-GQDs thin film.

The UV-Visible study of the prepared GQDs thin film was investigated using UV-Visible spectroscopy in transmission mode in the wavelength region of 240 – 700 nm. Fig. 2 (a-c) depicts the transmittance and Tauc's plot of the prepared thin film, respectively. Fig. 2 (a) shows the high optical transmittance of 83% of the GQD thin film in the visible region. In addition to this, the optical band gap of the prepared thin film is calculated as follows [4],

$$\alpha h\nu = K(h\nu - E_g)^n \quad (1)$$

where $h\nu$, K , and n represent the energy of incident photons, band edge sharpness constant, optical band gap energy, and the transition type. The Tauc's plot of the GQDs thin film has been shown in Fig. 2 (c). The band gap energy of the prepared thin film was calculated from the intercept of the extrapolated linear part of the Tauc's plot on the energy axis (x-axis).

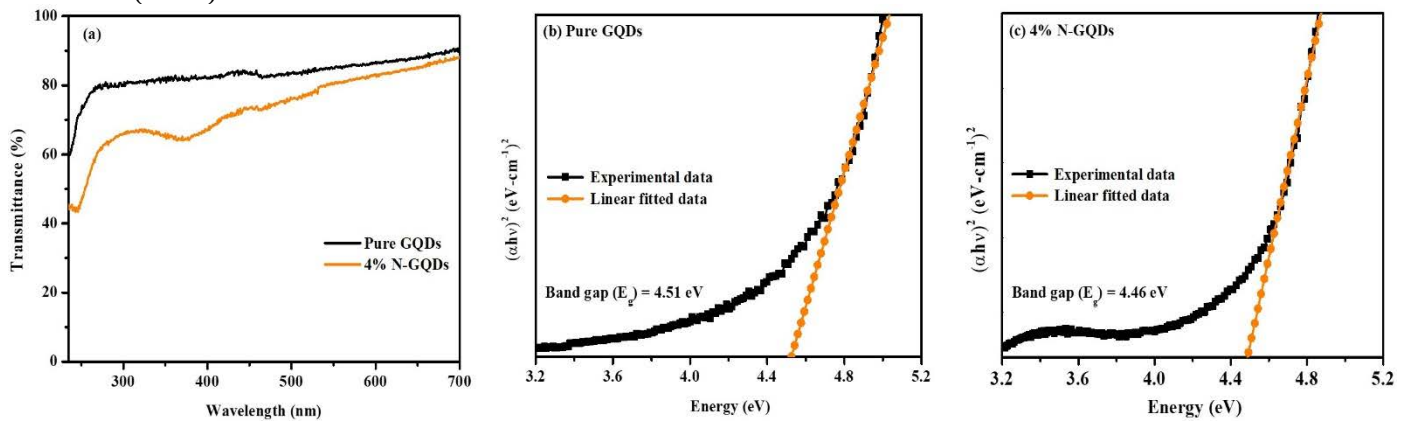


FIGURE 2. UV - Visible (a) transmittance spectrum, and (c, d) Tauc's plots of pure and doped GQDs thin film, respectively.

The temperature-dependent current-voltage (I-V) characteristics of pure and doped GQD thin films, measured over the temperature range of 293–513 K, are presented in Fig. 3(a, b). The linear nature of the I-V curves indicates the presence of ohmic conduction in the prepared thin films. It is observed that the current increases proportionally with the applied voltage, attributed to the enhanced electric field. Additionally, the current in all samples increases with rising temperature up to 513 K, which can be ascribed to the increased availability of charge carriers and enhanced carrier mobility at elevated temperatures, facilitating improved electrical conduction. Further, the values of electrical resistivity have been calculated from the inverse of the slopes of I-V curves shown in Fig. 3 (a, b), which are found to be $7.06 \times 10^5 \text{ Ohm-cm}$ and $4.63 \times 10^5 \text{ Ohm-cm}$ for pure and doped thin films, respectively. This decrease

in resistivity may be attributed to the increase in charge carriers resulting from nitrogen doping, which can broaden the band tail and ultimately reduce the resistivity.

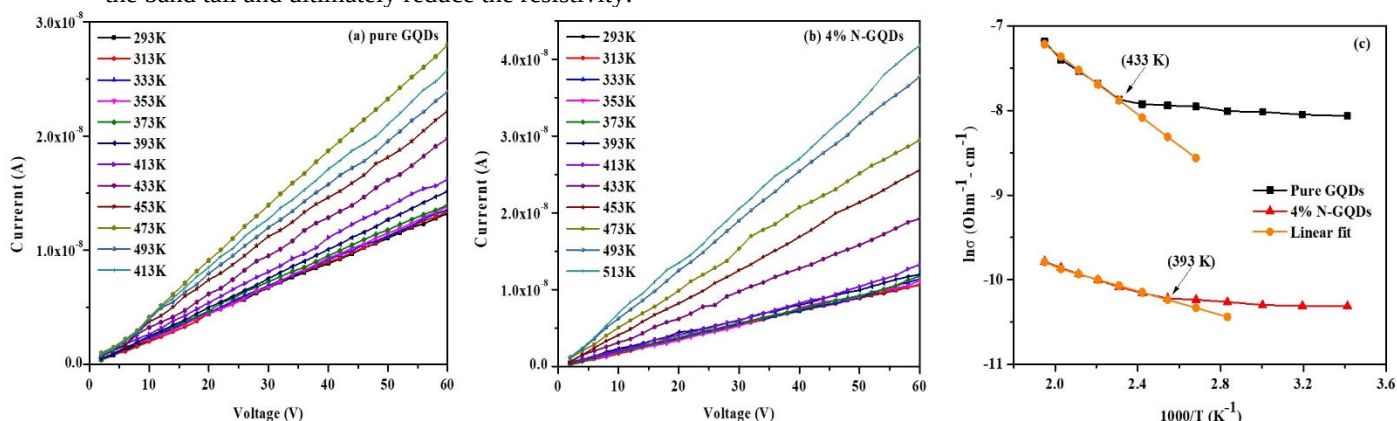


FIGURE 3. I-V characteristics of a) GQDs, b) activation energy plot of the prepared thin film.

Moreover, the conduction mechanism in prepared thin films was investigated using the Arrhenius equation [4],

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right) \quad (2)$$

where σ , σ_0 , E_a , k , and T denote the DC conductivity, pre-exponential factor, activation energy, Boltzmann constant, and absolute temperature, respectively. The activation energy for the pure GQD thin film was determined to be 0.311 eV, which decreases to 0.281 eV for the 4% N-doped GQD thin film, indicating enhanced charge transport due to doping. This increase in activation energy may be due to the fact that nitrogen may introduce some energy states near the conduction band edge, which may lead to a decrease in the activation energy of 4% N-GQDs thin film.

CONCLUSION

In this study, GQD thin film was prepared using hydrothermal synthesis and spin coating methods. The UV-Visible study shows a high absorption band in the UV region with a direct band gap of 4.51 eV. It was observed that the prepared thin film shows a high optical transmittance of 83% in the visible region. In addition, the high-temperature I-V characteristics have been studied, and the calculated value of resistivity depicts the semiconducting behavior of the pure and doped graphene quantum dot thin films, which show that the prepared thin films show their applicability as a transparent conducting material in optoelectronic devices.

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Engineering Self-Powered Photovoltaic Response in Multi-Heterostructure p-MoS₂ / n-MoSe₂ TMDC Devices Via Series and Parallel Architectures

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Abstract: Two-dimensional transition metal dichalcogenide (TMDC)-based devices hold great promise for photovoltaic and optoelectronic applications. However, enhancing key performance parameters such as open-circuit voltage (V_{OC}) and short-circuit current (I_{SC}) remains a critical challenge. In this study, we systematically compare TMDC p–n junctions composed of Nb-doped MoS₂ and intrinsic MoSe₂ configured in both series and parallel arrangements with ITO electrodes. The series-connected device exhibits a V_{OC} of approximately 0.5 V and an I_{SC} of ~26 nA, with a rectification ratio of 10. In contrast, the parallel configuration yields a significantly higher I_{SC} of ~170 nA, a V_{OC} of ~0.3 V, and an enhanced rectification ratio of 10³. These results highlight the crucial role of device architecture in optimizing the photovoltaic response of TMDC heterojunctions.

INTRODUCTION

The global push for sustainable energy has increased demand for efficient, flexible, and stable optoelectronic devices. While silicon (Si) and gallium arsenide (GaAs) offer high efficiency, they lack flexibility and long-term environmental stability [1]. Transition metal dichalcogenides (TMDCs) have emerged as strong alternatives due to their tunable bandgaps (1–2 eV), flexibility, strong light–matter interaction, and ability to form clean van der Waals heterostructures [1,2], making them suitable for next-generation optoelectronic applications. TMDC-based p–n junctions have demonstrated promising open-circuit voltage (V_{OC}) and short-circuit current (I_{SC}), which can be improved further by engineering band alignment and contact quality [3,4]. Low-bandgap TMDCs like MoSe₂ increase visible–NIR absorption, boosting I_{SC} [5], while strain and type-II alignment enhance charge separation [6]. MoS₂/WSe₂ devices, for example, show self-powered behavior with V_{OC} around 0.3 V [7]. Beyond materials, device configuration also plays a key role in shaping photovoltaic performance. Series and parallel geometries offer different ways to tune V_{OC} and I_{SC} . In this work, we directly compare series and parallel devices using Nb-doped MoS₂ and intrinsic MoSe₂ on ITO substrates. The series device shows $V_{OC} \approx 0.5$ V and $I_{SC} \approx 26$ nA, while the parallel setup yields higher $I_{SC} \approx 170$ nA but lower $V_{OC} \approx 0.3$ V. These results emphasize the importance of device architecture in optimizing TMDC-based photovoltaic performance.

EXPERIMENTAL DETAILS

Single-crystalline few-layer flakes of p-type Nb doped MoS₂ and n-type MoSe₂ were mechanically exfoliated from bulk crystals (HQ Graphene) using the Scotch tape method. Selected uniform flakes were transferred onto pre-patterned ITO-coated glass substrates via a PDMS stamp and 2D dry-transfer stage. Nb-doped MoS₂ (p-type) and intrinsic MoSe₂ (n-type) were used to fabricate p-n junctions in series and parallel configurations. Device schematics and optical images are shown in Fig. 1(a–b) for the series and Fig. 1(d–e) for the parallel geometry. Raman spectroscopy (HORIBA LabRAM HR, 532 nm, 3 mW) confirmed the material quality and crystallinity via characteristic peaks [Fig. 1(c), (f)].

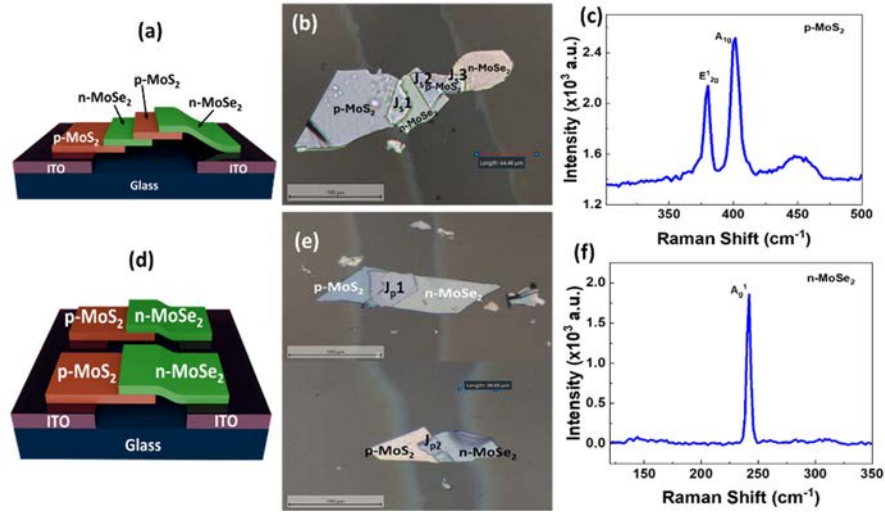


FIGURE 1. (a) and (b) show the schematic and optical image, respectively, of the p-MoS₂/n-MoSe₂/p-MoS₂/n-MoSe₂ series device. (c) displays the Raman spectrum of p-MoS₂, showing characteristic E'_{2g} and A_{1g} peaks. (d) and (e) show the schematic and optical image of the p-MoS₂/n-MoSe₂ parallel device. (f) presents the Raman spectrum of n-MoSe₂, highlighting the A_g' peak.

RESULTS & DISCUSSION

The current–voltage (I–V) characteristics of TMDC-based p–n heterojunctions in series and parallel configurations reveal how device geometry critically influences photovoltaic behavior. Under dark conditions, the parallel device exhibits stronger rectifying behavior with a rectification ratio of $\sim 10^3$, compared to ~ 10 for the series configuration, indicating superior junction asymmetry and current blocking. Under illumination (maximum power: 272 mW/cm²), the parallel device achieves a higher short-circuit current density ($J_{SC} \approx 52.28$ A/m²) and fill factor (FF $\approx 33\%$), while the series device records lower J_{SC} (≈ 12.68 A/m²) and FF ($\approx 18\%$). However, the series device exhibits a higher open-circuit voltage ($V_{OC} \approx 0.5$ V), arising from the additive voltage contributions of its two junctions. These contrasting performances stem from different charge transport mechanisms. In the parallel configuration, both Nb–MoS₂/n–MoSe₂ junctions share the same terminal voltage while their photocurrents add, effectively reducing series resistance and enhancing current output. The increased junction area further boosts carrier collection efficiency. However, V_{OC} is limited to the best-performing individual junction (typically ~ 0.3 V).

In contrast, the series configuration electrically connects two p–n junctions such that their individual V_{OC} values combine, making it beneficial for applications requiring higher voltage. But this comes at the cost of reduced current due to sequential carrier transport, increased interface resistance. Power-dependent I–V curves [Fig. 2(c), (d)] show that both I_{SC} and V_{OC} increase with illumination intensity in both configurations. Transient photoresponse [Fig. 2(e)] confirms stable and reproducible photocurrent generation at zero bias, demonstrating self-powered operation. Bias-dependent measurements [Fig. 2(f)] further reveal negative photocurrent at zero and reverse bias, driven by the built-

in electric field. As the bias approaches V_{OC} , the field is neutralized, and photocurrent drops to zero. Beyond V_{OC} , forward bias induces a positive photocurrent, confirming diode-like characteristics. These findings highlight the strategic importance of device geometry: parallel junctions favor high current output and efficient extraction, while series junctions are suited for applications prioritizing voltage gain.

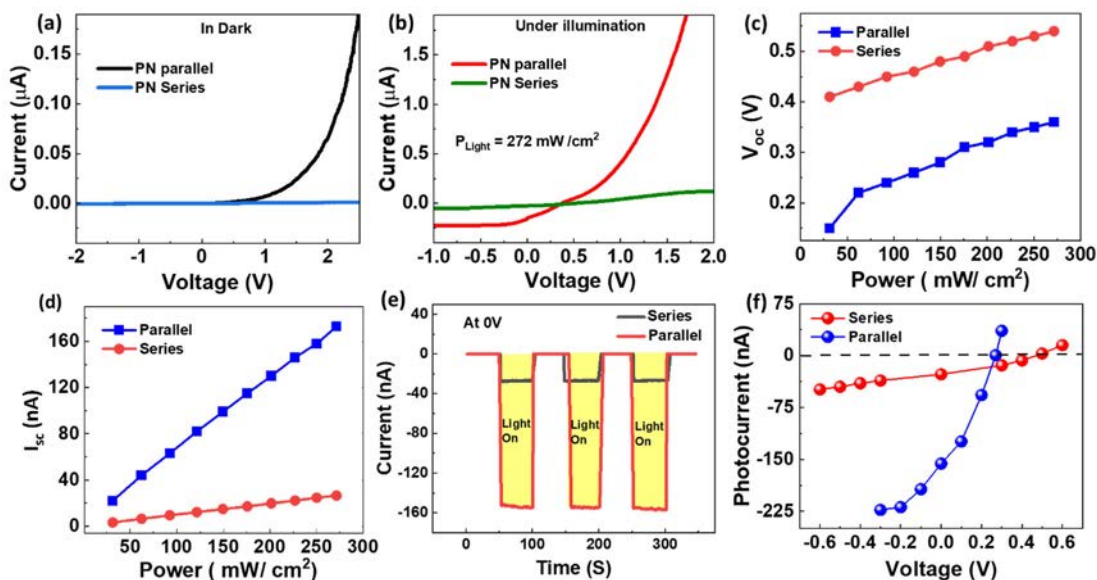


FIGURE 2. I-V characteristics of p-n series and parallel devices under (a) dark and (b) illuminated conditions. Power-dependent variation of (c) open-circuit voltage (V_{OC}) and (d) short-circuit current (I_{SC}) for both configurations. (e) Transient photoresponse at 0 V bias demonstrating stability and repeatability. (f) Bias-dependent photocurrent showing transition from negative to positive response across the built-in potential, confirming diode-like behavior.

CONCLUSION

The comparative analysis of TMDC-based p-n heterojunctions highlights the crucial influence of device geometry on photovoltaic performance. The parallel configuration generates a substantially higher short-circuit current (I_{SC}) as both junctions contribute simultaneously, enhancing overall carrier extraction. In contrast, the series configuration yields a higher open-circuit voltage (V_{OC}) due to the additive potential from each junction in the stack. This contrast underscores how parallel arrangements are favorable for maximizing current output, while series configurations are better suited for voltage enhancement, providing strategic flexibility in tailoring device design for targeted optoelectronic applications.

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Investigation of the $D0_{22}$ Phase Stability and Magnetotransport Properties in $Mn_{2.9}Ga_{1.1}$ Alloy

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Abstract. Bulk $Mn_{2.9}Ga_{1.1}$ alloys were synthesized by arc melting and annealed under argon, nitrogen, and vacuum conditions to investigate the effect of annealing environments on their structural, magnetic, and magnetotransport properties. Structural studies confirmed the transformation of the as-cast cubic γ -phase into the tetragonal $D0_{22}$ phase in all cases, with a minor Mn_8Ga_5 impurity phase. Magnetization studies revealed hard magnetic behavior with nearly the same coercivity and saturation magnetization, independent of the annealing environment. Temperature-dependent electrical resistivity showed metallic behavior with a comparable residual resistivity ratio, while Hall-effect analysis indicated that the anomalous Hall effect is mainly governed by intrinsic Berry curvature. Importantly, no significant variation in structural stability, resistivity behavior, or Hall response was observed across the annealing environments, underscoring the robustness of the $D0_{22}$ phase. These results highlight $Mn_{2.9}Ga_{1.1}$ as a stable, rare-earth-free alloy with promising potential for spintronic applications.

INTRODUCTION

Mn_3Ga is a multifunctional Heusler-like alloy that crystallizes in different crystallographic phases, including cubic ($L2_1$), hexagonal ($D0_{19}$), and tetragonal ($D0_{22}$), each exhibiting distinct physical properties and potential applications [1]. The cubic $L2_1$ phase generally shows soft magnetic behavior, while the hexagonal $D0_{19}$ phase displays non-collinear antiferromagnetism and unusual transport properties such as large anomalous Hall effect, making it attractive for exploring topological spin structures. Among these, the tetragonal $D0_{22}$ phase has emerged as particularly significant due to its rare earth-free hard magnetic properties, large uniaxial magnetocrystalline anisotropy, high coercivity, and Curie temperature above room temperature [2]. Beyond its robustness, this phase exhibits low Gilbert damping, metallic conductivity, and high spin-polarization, which are highly suitable for next-generation spintronic devices, such as magnetic tunnel junctions, spin-transfer torque memories, and spin-orbit torque oscillators [3,4]. Therefore, the $D0_{22}$ phase of Mn_3Ga uniquely combines hard magnetism with spintronic functionality, highlighting the need for detailed investigations of its structure-property relationships to fully exploit its technological potential.

EXPERIMENTAL DETAIL

The conventional arc-melting technique was used to prepare a bulk $Mn_{2.9}Ga_{1.1}$ alloy from high-purity Mn and Ga under an argon atmosphere. To ensure compositional homogeneity, the alloy ingots were repeatedly overturned and remelted during processing. The obtained alloys were subsequently annealed at 350 °C for 2 days under different environments, and then sectioned into rectangular specimens and mechanically polished into thin slices (~250 μm thick) for subsequent measurements. Structural characterization was performed using a powder X-ray diffractometer (PXRD) with a $Cu-K\alpha$ ($\lambda = 1.541 \text{ \AA}$) source. The magnetic and transport measurements were carried out on the same bulk samples using a Physical Property Measurement System (PPMS, Quantum Design, Dynacool). Magnetic measurements were performed under the magnetic field applied parallel to the sample surface. For transport characterization, the custom-built four-probe technique was employed to measure both longitudinal and Hall resistivities.

RESULT AND DISCUSSION

Figure 1(a) represents the room-temperature PXRD patterns of as-cast and annealed samples. The PXRD pattern of the as-cast alloy can be indexed as the cubic γ -phase, with a minor trace of hexagonal Mn_8Ga_5 phase. The as-cast

sample is annealed in argon, nitrogen, and under vacuum at 350 °C for 2 days, resulting in the transformation of the γ -phase into the tetragonal $D0_{22}$ phase; however, the Mn_8Ga_5 phase persists. From the PXRD patterns, it is evident that all annealed samples exhibit similar patterns, indicating their structural stability. To further confirm the phase formation, the PXRD patterns of annealed samples were analyzed using the Rietveld refinement with the FullProf software, confirming the formation of the $D0_{22}$ phase and yielding lattice constants of $a = 3.908 \text{ \AA}$ and $c = 7.125 \text{ \AA}$, and the Mn_8Ga_5 phase is shown in Figure 1(b).

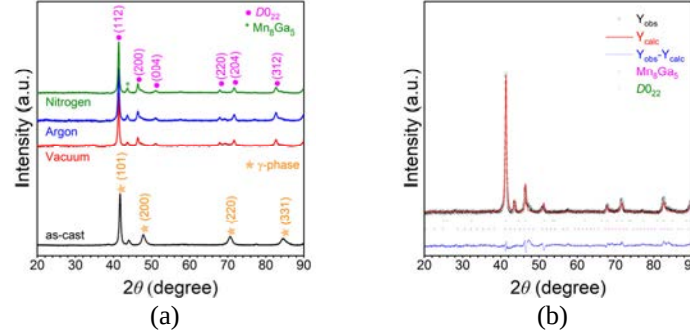


FIGURE 1. (a) Room-temperature PXRD pattern of ac-cast and annealed samples at 350 °C for 2 days in different environments, and (b) Rietveld refinement of the PXRD pattern annealed at 350 °C in vacuum.

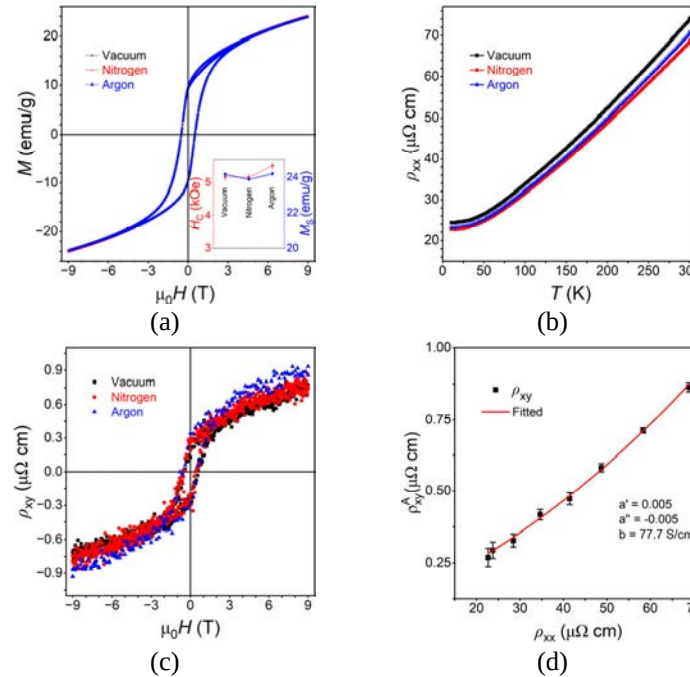


FIGURE 2. (a) Room-temperature M - H loops, (b) temperature-dependent electrical resistivity (ρ_{xx}), and (c) the variation of room temperature Hall resistivity (ρ_{xy}) with magnetic field ($\rho_{xy} - H$) of the annealed samples at different environments, and (d) Variation of anomalous Hall resistivity (ρ_{xy}^A) with ρ_{xx} and its fitting for vacuum annealed sample.

Figure 2(a) represents the room-temperature M - H loops of the annealed samples. It is observed that all the samples exhibit hard magnetic properties; however, their coercivity (H_c) and saturation magnetization (M_s) remain the same around $5.2 \pm 0.2 \text{ kOe}$ and $23.9 \pm 0.2 \text{ emu/g}$, respectively, highlighting the robustness after annealing under different environments. Figure 2(b) represents the temperature-dependent electrical resistivity ($\rho_{xx}(T)$) of the annealed samples without an external magnetic field. The data was obtained using a four-probe method during warming from 10 K to 300 K. The $\rho_{xx}(T)$ of all the samples exhibits a positive temperature coefficient of resistance (TCR), indicating the typical behaviour of metallicity. The residual resistivity (ρ_{10K}) of all the samples lies within the range of 22.7-24.4 $\mu\Omega\text{-cm}$, while at 300 K jumps within 70.8-74.2 $\mu\Omega\text{-cm}$. The residual resistivity ratio (ρ_{RR}), defined as ρ_{300K}/ρ_{10K} , falls within a narrow range of 3.03-3.05. In general, the material with a higher RRR signifies purity; however, the

relatively low value obtained in this study suggests the presence of impurity, which could be attributed to the presence of residual Mn_8Ga_5 phase. On the other hand, at low temperature ($T < 70$ K), ρ_{xx} exhibits a nearly squarelike temperature dependence, indicating that electron-magnon scattering is the dominant contribution. In contrast, the deviation from this behavior above 70 K highlights a crossover to electron-phonon scattering as the main resistivity mechanism [5]. Figure 2(c) illustrates the field-dependent Hall resistivity ($\rho_{xy}(H)$) at 300 K for all the annealed samples. The value ρ_{xy} of all the samples lies between $0.78 \mu\Omega\text{-cm}$ and $0.86 \mu\Omega\text{-cm}$. Interestingly, the $\rho_{xy} - H$ curves follow a similar trend to $M-H$ loops, confirming the direct dependence of ρ_{xy} on magnetization. To further analyse the anomalous Hall resistivity (ρ_{xy}^A) and its underlying mechanism, (ρ_{xy}^A) for vacuum annealed sample is measured at different temperature plotted against ρ_{xx} , and fitted using scaling relation $\rho_{xy}^A = a'\rho_{xx0} + a''\rho_{xxT} + b\rho_{xx}^2$ proposed by Tian *et al.* [6] is shown in Fig. 2(d). Here, $\rho_{xxT} = \rho_{xx} - \rho_{xx0}$ is the photon-induced resistivity contribution, and a' and a'' correspond to skew scattering induced by impurity and photon, respectively, while the b reflects the combined contribution from side jump and intrinsic Berry curvature. The fitting yields $a' = 0.005$, $a'' = -0.005$, and $b = 77.7 \text{ S/cm}$. The nearly negligible values of a' and a'' indicate that skew scattering has a little contribution in this system. The observed value of b indicates the intrinsic origin of the ρ_{xy}^A ; however, its relatively small magnitude compared to other systems is ascribed to the structural disorder and the presence of impurity phases.

CONCLUSION

Bulk $\text{Mn}_{2.9}\text{Ga}_{1.1}$ alloys were successfully synthesized, and their structural, transport, and magnetic properties were systematically investigated. Structural analysis confirmed the transformation of the as-cast cubic γ -phase into the tetragonal $D0_{22}$ structure upon annealing, although a minor Mn_8Ga_5 impurity remained irrespective of annealing environments. The annealed samples exhibited metallic conductivity with a low RRR, indicating the influence of disorder and secondary phases. Resistivity analysis revealed electron-magnon scattering dominating at low temperatures and electron-phonon scattering at higher temperatures. Hall measurements confirmed a strong correlation between magnetization and Hall resistivity, with scaling analysis indicating that the anomalous Hall effect is predominantly governed by intrinsic Berry curvature rather than skew scattering. These findings clearly demonstrate that the choice of annealing environment does not significantly affect the phase stability or functional properties of $\text{Mn}_{2.9}\text{Ga}_{1.1}$, underlining the robustness of the $D0_{22}$ structure and highlighting its potential as a spintronic material, while also emphasizing the need to minimize disorder and impurity phases to further enhance its functional properties.

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Synergistic Role of Voltage in Tuning Resistive Switching Phenomenon of $\text{Sr}_2\text{FeTiO}_6$ Thin Films

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Abstract. We observe a reversible transition from volatile to non-volatile resistive switching in $\text{Ag}/\text{Sr}_2\text{FeTiO}_6$ (SFTO)/ SrRuO_3 (SRO)/Si device upon applying higher voltage in the presence of a magnetic field. This behavior highlights the tunability of resistive switching under combined electric and magnetic stimuli and points toward the role of magnetoelectric coupling in complex oxides. The ability of the device to reversibly switch between volatile and non-volatile states makes it a strong candidate for use as a selector element in crossbar memory architectures. Furthermore, this switching characteristic opens new possibilities for developing multistate, high-density data storage in future memory technologies.

INTRODUCTION

Resistive switching (RS) phenomena in transition metal oxides have emerged as a promising platform for next-generation memory and neuromorphic computing applications due to their simple metal–insulator–metal (MIM) architecture, scalability, and low power consumption. RS devices generally operate by transitioning between high and low resistance states under the influence of an external electric field. These changes in resistance may be temporary (volatile) or permanent (non-volatile), depending on the nature of the switching. Although both switching behaviors have distinct advantages, integrating reversible control of both switching within a single device offers a powerful route toward dynamic and reconfigurable memory control. However, a major challenge in this field is achieving reliable multi-state switching behavior, essential for enhancing data density and enabling neuromorphic functionalities. In this regard, transition metal oxides, particularly complex perovskites, offer rich physics and functional tunability due to the interplay of multiple degrees of freedom like charge, spin, lattice, and orbital. In recent years, attention has turned toward exploring the impact of additional external stimuli such as magnetic fields, light, or temperature on RS behavior. Among these, magnetic field interactions with RS mechanisms remain untapped areas, particularly in complex oxide systems where magnetoelectric coupling may offer additional degrees of control. Such coupling effects, when leveraged properly, could enable tunable and reconfigurable devices that support multistate or hybrid volatile–nonvolatile functionalities.

In this work, we investigate the resistive switching characteristics of an $\text{Ag}/\text{Sr}_2\text{FeTiO}_6$ (SFTO)/ SrRuO_3 (SRO)/Si device and report a reversible transition from volatile to non-volatile RS behavior upon increasing the applied voltage in the presence of a small magnetic field. This observation underscores the synergistic role of electric and magnetic fields in modulating the switching characteristics of SFTO-based heterostructures and suggests a potential influence of magnetoelectric coupling. The ability to dynamically toggle between volatile and non-volatile states not only reveals new insights into field-driven switching mechanisms in complex oxides but also positions the device as a promising selector element in crossbar memory arrays. Furthermore, the multilevel switching capability observed under combined field stimuli opens pathways for high-density, multistate memory architectures in future data storage technologies.

EXPERIMENTAL SECTION

SFTO ceramic pellets were prepared via the conventional solid-state reaction route. Stoichiometric amounts of SrCO_3 , TiO_2 , and Fe_2O_3 were thoroughly mixed and preheated at 900 °C, followed by calcination and sintering at 1400 °C and 1600 °C, respectively, in accordance with procedures reported in the literature [1,2]. The thin films were then grown on SRO coated substrates using the pulsed laser deposition (PLD) technique, following the deposition parameters reported in previous study [3].

RESULTS AND DISCUSSION

The XRD pattern of the SFTO film in Fig. 1(a) confirms a cubic crystal structure with $Pm\bar{3}m$ symmetry, consistent with previous reports [1,4,5]. The inset shows the 2θ scan (5° – 90°), highlighting the most intense Si substrate peak.

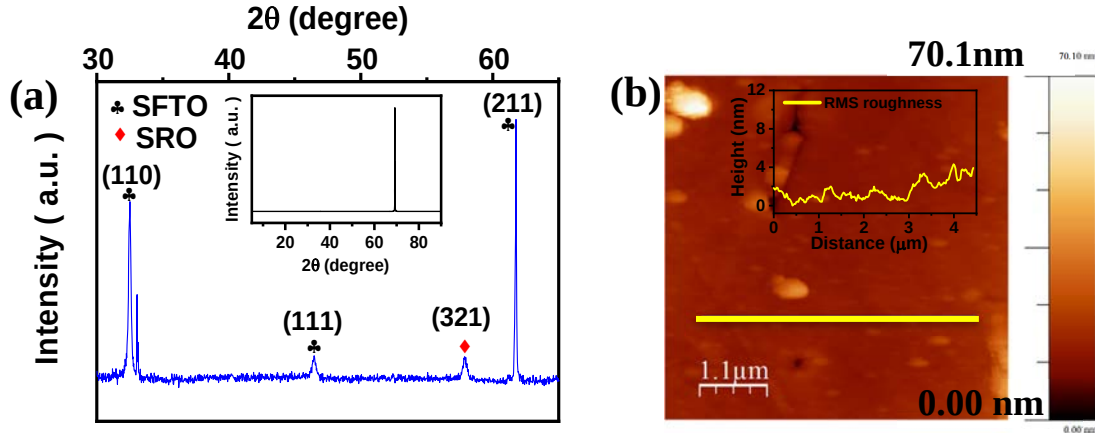


FIGURE 1. (a) XRD pattern of the SFTO thin film. (b) AFM topography image with inset displaying the corresponding RMS roughness plot.

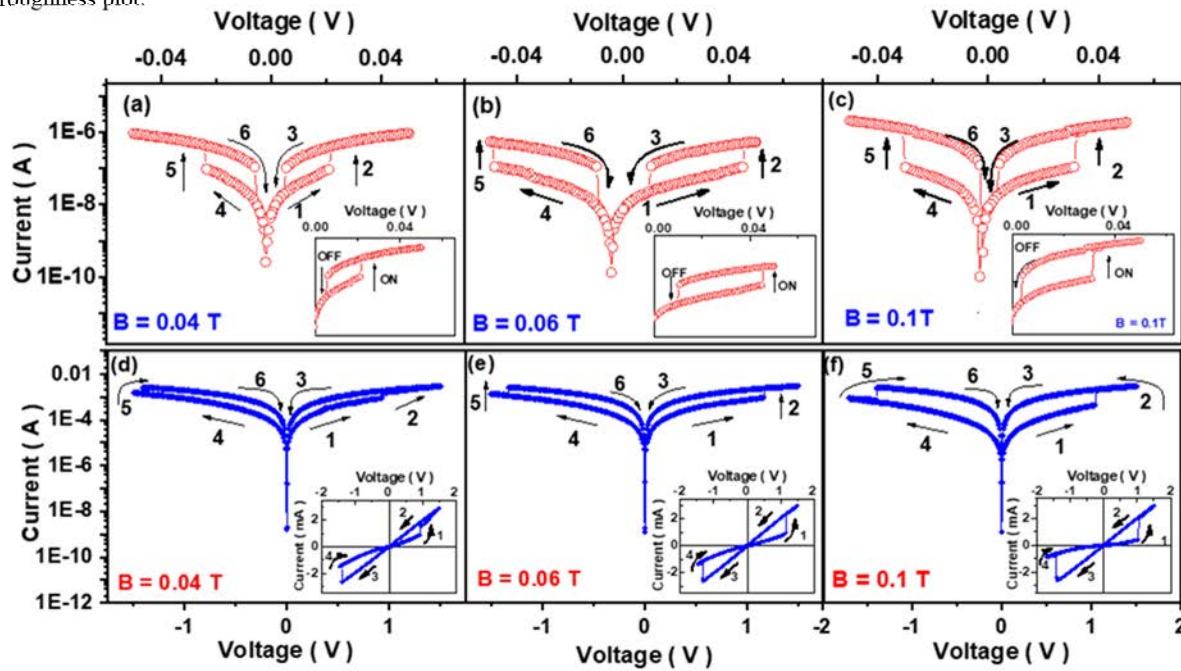


FIGURE 2. Semi-log plots of I-V curves indicating two distinct switching modes (a-c) volatile, and (d-f) non-volatile resistive switching.

roughness of 110 nm. Electrical measurements were performed using a Keithley 6412B source meter in two-probe configurations. The I-V characteristics presented in Fig. 2(a-c), measured at low voltage and under a small magnetic field varying from 0.04 T to 0.1 T. A voltage sweep of $0 \rightarrow 0.05 \rightarrow -0.05 \rightarrow 0$ was applied. During a forward voltage sweep from 0 to 0.05 V, the device enters a low-resistance ON state (SET), and as the voltage is reduced back to 0 V, the device switches back to the high-resistance OFF state (RESET).

A similar switching pattern was also observed under negative voltage sweeps, where the device turns ON from 0 to -0.05 V and switches OFF as the voltage returns to zero. This symmetric, non-retentive behaviour confirms the volatile nature of the switching under low voltage and magnetic field conditions. As the applied voltage increases to 1.5 V, a noticeable change in switching of the device was observed. The device shifts from volatile to bipolar non-volatile

switching, where the resistance state persists even when the polarity is reversed. This stable switching behaviour is clearly illustrated in Fig. 2(d–f), with the inset showing the corresponding linear I–V curves. The applied voltage in resistive switching devices can modulate magnetic anisotropy and magnetization through ME effects, thus helping to stabilize the conductive filaments responsible for non-volatile switching. This voltage-induced modulation of switching behaviour are generally driven by effects like voltage-controlled magnetic anisotropy (VCMA) and spin-orbit torque (SOT), which plays a vital role in retaining their resistance states reliably [6,7]. This stable and robust retention makes them well-suited for use in memory and neuromorphic computing applications.

CONCLUSION

The SFTO film showed a well-defined cubic crystal structure with pm-3m space group symmetry with a smooth surface with RMS roughness of 1.89nm, as confirmed through structural and morphological studies. It was observed at lower voltages and under a magnetic field, the device exhibits volatile resistive switching with no memory retention. However, with rising voltage a transition from volatile to stable bipolar non-volatile switching was observed, possibly driven by magnetoelectric effects like VCMA and spin-orbit torque. This switching behavior reflects core ideas in spintronics and points toward the device's potential use in spin-based non-volatile memory and neuromorphic computing systems. Interestingly, the volatile switching at lower voltages could make the SFTO device a strong fit as a selector element in crossbar memory arrays, where managing sneak-path currents is key to reliable performance. With its ability to support both switching modes, SFTO offers flexibility and compactness, traits that are valuable for future memory technologies aiming for high density and efficiency.

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Mn-Doped $\text{Cs}_2\text{AgInCl}_6$ Microcrystals for Lead-Free X-Ray Scintillation

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Abstract. Double perovskites are being widely considered as safer alternatives for optoelectronic applications, offering a replacement for toxic lead-based systems. This report, demonstrates the effect of Mn^{2+} doping on the scintillation behavior of $\text{Cs}_2\text{AgInCl}_6$ microcrystals. Compositions with varying Mn concentrations were prepared via an acid precipitation approach utilizing halide-based precursors. Compositional analyses performed using XPS, confirmed successful Mn incorporation. Radioluminescence measurements revealed that Mn doping enhances the radioluminescence emission intensity, with the 10% Mn-doped sample showing optimal performance. The improved response is attributed to defect-assisted luminescence associated with aliovalent Mn doping. These findings demonstrate the promise of Mn-doped $\text{Cs}_2\text{AgInCl}_6$ as a lead-free scintillator material for X-ray detection and imaging.

INTRODUCTION

Over the past few years, halide perovskites have drawn increasing attention owing to their broad applicability in optoelectronic components such as photodetectors, scintillators, and light-emitting systems. This interest is mainly driven by their excellent properties, with a direct and tuneable bandgap, long charge carrier diffusion length, and high mobility [1]. One of the most studied halide perovskites is APbX_3 , where A is a monovalent cation and X is a halide ion. This material has shown remarkable performance in various optoelectronic applications due to its excellent optical and electronic properties. However, despite its advantages, the occurrence of deadly lead and its poor environmental stability, especially under heat, moisture, and light exposure pose serious challenges, limiting its practical and long-term use [2]. Lead-free halide double perovskites having stoichiometry $\text{A}_2\text{M(I)M'(III)Cl}_6$ have developed as potential alternatives to lead-based perovskites, addressing key concerns such as toxicity and poor environmental stability. These materials not only offer better resistance to heat, moisture, and light but also allow for low-cost, solution-based synthesis. Despite these advantages, they face inherent limitations, most notably, a wide and indirect bandgap, low emission which can hinder their efficiency in optoelectronic applications. Among the family of halide double perovskites, $\text{Cs}_2\text{AgInCl}_6$ has attracted attention due to its direct bandgap, which is favorable for optoelectronic applications. However, its inherently low photoluminescence and limited sensitivity to high-energy radiation remain key limitations [3]. Elemental doping offers an effective strategy to enhance these properties. Notably, Mn^{2+} incorporation has been shown to significantly improve both the optical and nonlinear optical responses of $\text{Cs}_2\text{AgInCl}_6$, highlighting its potential in advanced photonic and radiation detection applications [4, 5].

Mn^{2+} , as an aliovalent dopant in $\text{Cs}_2\text{AgInCl}_6$, is expected to substitute at the Ag^+ site, leading to the formation of cationic vacancies and excess electron concentration after doping as confirmed by DFT and positron annihilation lifetime spectroscopy analysis [6]. These vacancies can effectively modulate the material's optoelectronic properties. In this study, we synthesized Mn-doped $\text{Cs}_2\text{AgInCl}_6$ microcrystalline powders, confirmed the successful incorporation of Mn through X-ray photoelectron spectroscopy (XPS), and evaluated their scintillation response under X-ray excitation.

EXPERIMENTAL

In the present work, undoped and Mn-doped $\text{Cs}_2\text{AgInCl}_6$ microcrystals were prepared using a earlier reported halide-precursor-based acid precipitation method [7, 8]. For the pristine sample, 1 mmol of silver chloride (AgCl , 99.99%) and 1 mmol of indium chloride (InCl_3 , 99.999%) were first mixed in 10 mL of concentrated hydrochloric acid (HCl , 37 wt%). The mixture was stirred at 70 °C for 30 minutes to ensure complete dissolution. After this, 2 mmol of cesium chloride (CsCl , 99.99%) was introduced into the solution and the stirring was sustained for another 20 minutes. The formed precipitate was then collected by removing the supernatant, followed by washing several repetitions with ethanol, and finally dry for 12 hours at 80 °C. For Mn-incorporated samples, the same synthesis route was adopted, with the addition of a calculated amount ($x/100$ mmol) of manganese chloride (MnCl_2) along with AgCl to obtain the required doping level ($x\%$).

RESULTS AND DISCUSSION

XPS was carried out using AXIS SUPRA XPS instrument to verifies the effective substitutions of Mn^{2+} into the $\text{Cs}_2\text{AgInCl}_6$ double perovskite matrix. As presented in Figure 1(a), the full survey spectrum confirms the presence of Cs, Ag, In, Cl, and Mn elements in the sample. Furthermore, highly resolved deconvolution of the Cs 3d, Ag 3d, In 3d, and Mn 2p core-level spectra (Figures 1(b–f)) reveals oxidation states of +1 for Cs and Ag, +3 for In, and +2 for Mn, respectively [4]. The structural and optical characteristics of the synthesized material have been verified and are detailed in our previous report [6].

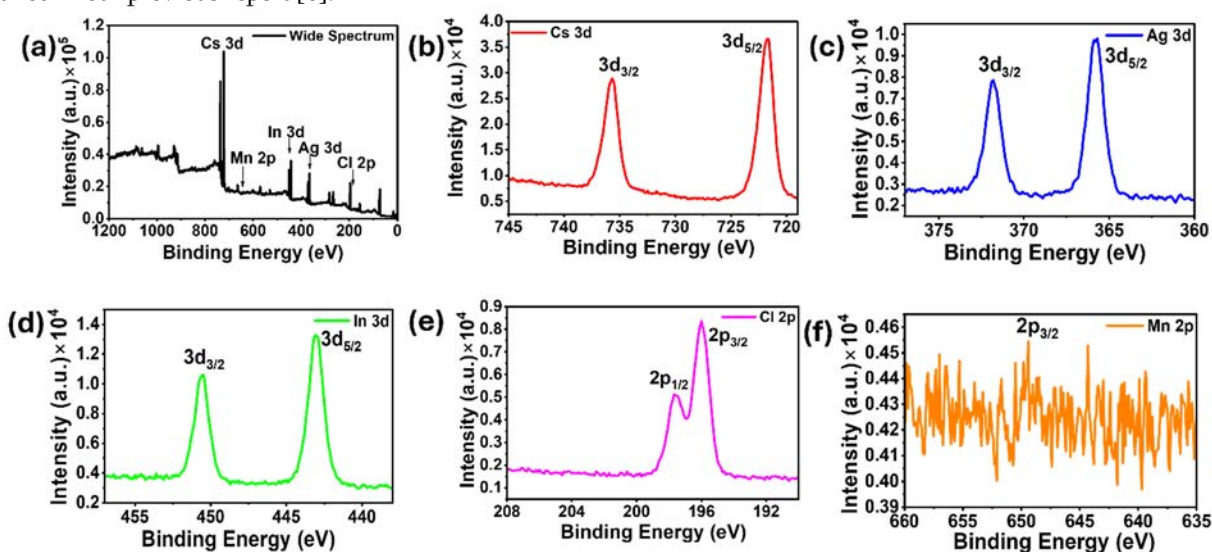


FIGURE 1. (a) Overview XPS spectrum, (b–f) highly resolved core-level spectra associated to Cs 3d, In 3d, Ag 3d, Cl 2p, and Mn 2p, respectively.

In this study, lead-free Mn^{2+} doped $\text{Cs}_2\text{AgInCl}_6$ microcrystals were investigated for their X-ray detection capabilities, as presented in Fig. 2. The undoped $\text{Cs}_2\text{AgInCl}_6$ sample displayed only a weak radioluminescence signal. However, upon Mn^{2+} doping, a prominent radioluminescence emission peak centered around 630 nm was observed, assigned to the spin-forbidden ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ transition of Mn^{2+} [9]. The radioluminescence intensity was found to increase with rising Mn doping concentrations, with the highest emission recorded for the 10% Mn-doped sample. The radioluminescence measurements were carried out using a home-built black box setup equipped with a monochrome CCD detector to capture the emission under X-ray excitation.

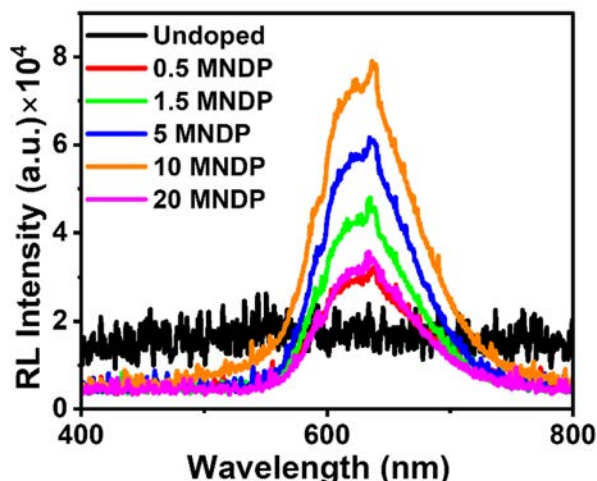


FIGURE 2. RL response of $\text{Cs}_2\text{AgInCl}_6$ and $x\%$ -Mn doped $\text{Cs}_2\text{AgInCl}_6$ (denoted as x MNDP) ($x=0.5, 1.5, 5, 10$, and 20).

CONCLUSION

In summary, this communication presents the effect of aliovalent Mn^{2+} doping on the radioluminescence response of $\text{Cs}_2\text{AgInCl}_6$ double perovskite. Undoped and Mn-doped samples were synthesized using a precipitation method, and the successful incorporation of Mn was confirmed through XPS. Mn^{2+} doping largely increase the radioluminescence response when compared to the undoped sample, with the 10% Mn-doped composition exhibiting the highest emission intensity. These results highlight the potential of aliovalent doping strategies for defect engineering and suggest a potential pathway for developing non-toxic scintillators for X-ray imaging applications.

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Effect of Ag Ion Irradiation on the Electrical Transport Properties of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin films

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Abstract. We report the effect of Swift Heavy Ion (SHI) irradiation (100 MeV Ag) on the structural and electrical transport properties of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin films deposited on Si-substrate. The irradiation is performed at two different ion fluences of $1\text{E}11$ and $1\text{E}12$ ions/cm². The structural analysis using the X-ray diffraction method shows, the strain present in the film released at higher fluences shows the annealing effect. The resistivity measurements show the metal-insulator transition in all samples, with an overall decrease in resistivity in a magnetic field of 0.2 T, confirming the negative magneto-resistance behavior. Metal-Insulator (M-I) transition temperature increases towards higher temperatures at initial fluence and decreases for higher fluence. The experimental data at low temperature below $T_{\min}$ are fitted using the Kondo-like expression and the metallic-like conductivity expression above the minimum temperature. The observed increase in resistivity is explained using ion beam-induced defects in the LSMO thin films. The negative magneto-resistance is explained by the suppression of magnetic domain boundary scattering of charge carriers by a magnetic field.

INTRODUCTION

The divalent doped rare earth manganite attracts a lot of attention, has interesting properties such as paramagnetic to ferromagnetic and insulator to metal transition. The transition temperature of these phases varies according to the divalent ion and the substitution amount. Out of the possible doped manganates, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($0.17 \leq x \leq 0.33$) has special interest due to its high Curie temperature (369 K), systematic electrical and magnetic properties variations, and large spin polarization (nearly 100 %) [1,2].

The physical properties of perovskite manganites can be tailored by various methods, such as Jahn-Teller distortions, cationic size mismatch, oxygen vacancy and charge ordering [3]. However, these techniques produce the disorder/stress have limitations due to solubility, while ion bombardment techniques produce the disorder in a controlled manner beyond the thermodynamic limit. The magnetoresistance in LSMO can be induced at low magnetic fields naturally or by modifying the Mn-O-Mn bond angle and length [4]. In this paper, the electrical transport properties of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ are studied, showing the metal-insulator transition with a sharp rise in resistivity at low temperatures, explained using the Kondo effect. The experimental data are analyzed by considering the various scattering mechanisms.

EXPERIMENTAL DETAILS

The LSMO films were grown using the PLD method on Si(100) substrate. The deposition was performed at a base pressure of 10^{-8} mbar. The substrate temperature at 700°C and oxygen partial pressure of 0.2 mbar is kept fixed. Further films were annealed at the same temperature in oxygen with a partial pressure of 500mbar for 30 minutes.

After the deposition, these films are irradiated with Ag 100 MeV ions using the 15UD Tandem accelerator at Inter University Accelerator Center (IUAC), New Delhi, at two different fluences, $1\text{E}11$ and $1\text{E}12$ ions/cm². The structural characterizations were examined with X-ray diffraction (XRD) in glancing angle mode using Philips X'pert PRO (Model PW 3040) diffractometer. The resistivity is measured using the standard four-probe technique at two different magnetic fields of 0T and 0.2T.

RESULTS AND DISCUSSION

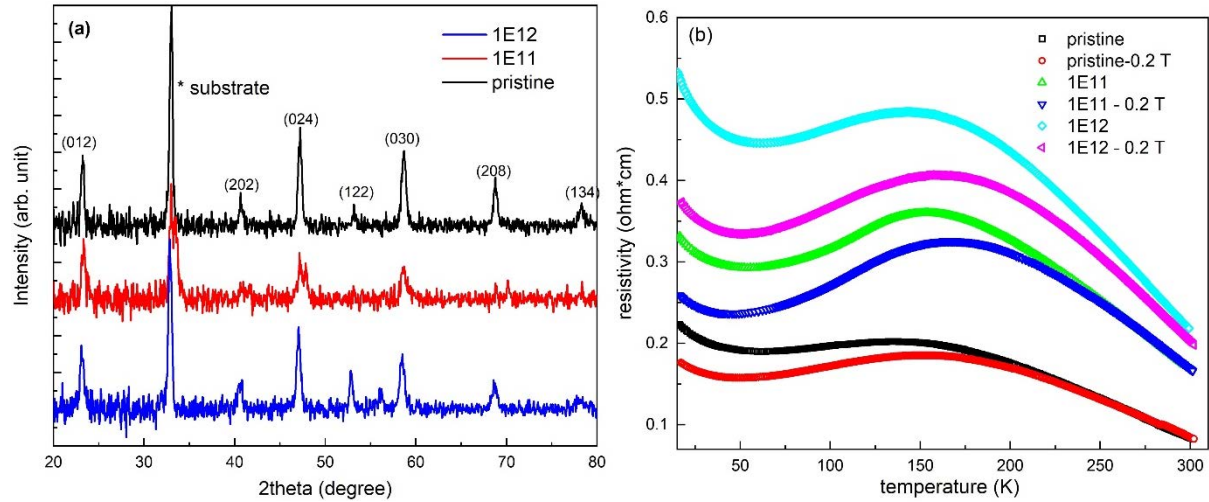


FIGURE 1: (a) XRD pattern of pristine and Ag-100 MeV irradiated LSMO thin films. All the peaks were marked with corresponding Miller indices. (b) Resistivity vs temperature variation for the LSMO thin films with and without a magnetic field.

Figure 1(a) shows the X-ray diffraction pattern of pristine and Ag-100 MeV irradiated samples. It shows the polycrystalline nature with a slight shifting of the XRD peak towards the higher angle side (due to strain due to irradiation) at the fluence of 1E11 ions/cm². The XRD peaks shift towards the lower angle side at 1E12 ions/cm², showing the ion beam-induced annealing effects. No structural phase transition was obtained up to the highest studied fluence, 1E12 ions/cm². Figure 1(b) shows the resistivity measurements from 15K- 300K of pristine and irradiated samples. Initially, the resistivity is found to increase with a decrease in temperature, showing the insulating type behavior. After a certain temperature (called peak temperature T_p), the resistivity variations show the metallic type behavior, i.e., resistivity decreases with a decrease in temperature. The further decrease in temperature gives a minimum in resistivity (denoted by T_{min}), and an increase in resistivity with a further decrease in temperature. This type of variation in resistivity is direct evidence of Kondo-like scattering, which is generally found in materials with a small amount of magnetic impurity and observed in manganites [3]. The values of T_{min} and T_p and their variation with the Ag-100 MeV ion irradiation and magnetic field are shown in Table 1. The increase in T_p and decrease in T_{min} with the magnetic field are due to the formation of magnetic domains [4].

Sample Name	Peak Temperature (T_p) (K)		Minimum Temperature (T_{min})	
	0T	0.2 T	0T	0.2 T
Pristine	136	151	62	51
1E11	154	166	55	44
1E12	143	156	63	50.5

The smaller values of peak temperature are possibly due to lower grain size [1]. The resistivity increases with ion fluence due to an increase in the defects or scattering centers [2]. The peak temperature shifts towards the high temperature side at 1E12, indicating the decrease in the grain size due to ion beam-induced defects at 1E11 fluence and decreases for the higher fluences due to an increase in grain size by ion beam annealing effects. The overall resistivity is suppressed significantly for all samples under the influence of a magnetic field. The resistivity minimum temperature shifts towards the lower side of the temperature with the applied magnetic field for all samples. This type of variation can be explained on the basis of suppression in magnetic scattering centers [2].

The rapid variation of resistivity with magnetic field suggests the spin-dependent scattering at low temperatures. To confirm the same, the resistivity data below T_{min} is fitted using the Kondo-like expression (equation 1),

$$\rho = \rho_0 + \rho_{0.5}T^{0.5} - \rho_1 \ln(T) + \rho_5 T^5 \quad (1)$$

Here in equation (1), the first term ρ_0 , called the residual resistivity, is due to the residual defects, impurity scattering, and grain boundary scattering, $\rho_{0.5}$ represents electron-electron scattering, ρ_1 represents the contribution due to Kondo-like spin-dependent scattering, and the last term ρ_5 is due to inelastic electron-phonon scattering.

The experimental data above $T_{\min}$ and below T_p are fitted using the metallic-like conductivity expression

$$\rho = \rho_0 + \rho_2 T^2 + \rho_5 T^5 \quad (2)$$

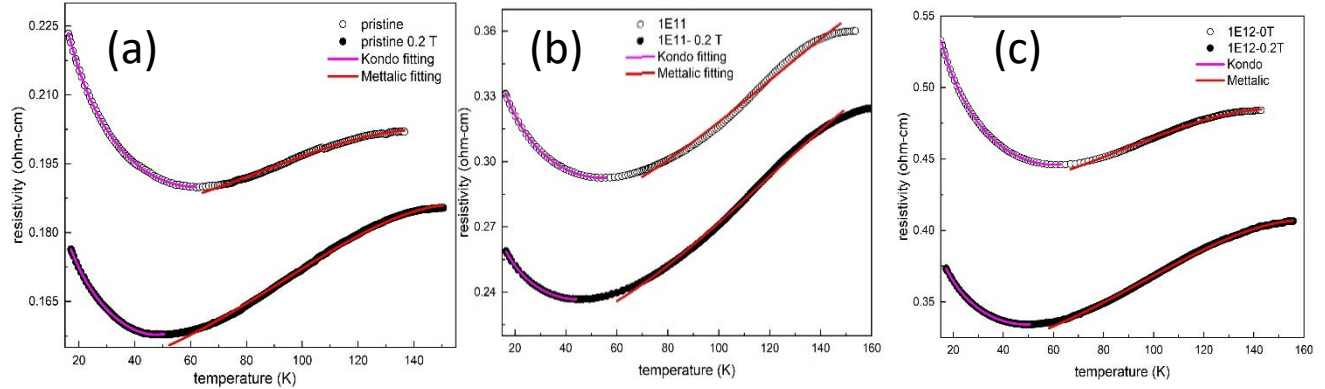


FIGURE 2: Kondo-like (eq. 1) and metallic (eq. 2) like resistivity fitting of LSMO pristine and irradiated samples in the low temperature region. The solid lines show the fitting using these equations.

In equation (2), the first term ρ_0 is residual resistivity, ρ_2 represents the contribution due to delocalized electron-electron scattering, and ρ_5 corresponds to electron-phonon scattering at higher temperatures.

The data fitted using equations 1 and 2 are shown in Figure 2 (a-c) fits well with the experimental data. The fitting results show that the electron-phonon scattering parameter (ρ_5) is very small in the low temperature range and has no sensitivity to the magnetic field. The e-e scattering ($\rho_{0.5}$) has a significant contribution and is suppressed by the magnetic field. The sharp rise in low temperature resistivity is due to the exchange interaction between a localized electron and conduction electrons, which is called the Kondo effect [2-5]. The decrease in resistivity with magnetic field is due to the suppression of spin-dependent scattering [4-6]. The magnitude of the scattering coefficient indicates that spin-dependent scattering (ρ_1) is dominant in the low temperature region, and localized e-e scattering is dominant in the metallic region [3-6].

CONCLUSION

We have studied the electrical transport properties of pristine and Ag-ion irradiated LSMO samples. The sample shows the Kondo-like scattering at low temperatures and variable range hopping above the M-I transition temperature with and without a magnetic field.

ACKNOWLEDGMENTS

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Thermopower in a Correlated Disordered 1D Chain

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Abstract. We investigate the thermoelectric transport properties of a one-dimensional (1D) tight-binding chain subject to correlated quasiperiodic modulations in both on-site energies and nearest-neighbor hopping integral. This is achieved by combining the Aubry–Andre–Harper (AAH) model, which modulates site energies and hopping integrals, with the Su–Schrieffer–Heeger (SSH) model, which has alternating hopping parameters ($t_1 \neq t_2$). Using the Landauer–Büttiker formalism, we calculate both the electronic and phononic transmission functions and evaluate the Seebeck coefficient (S) as a function of chemical potential (E_F). Our analysis focuses on the off-diagonal generalized AAH disorder and its interplay with hopping dimerization. We observe a significant enhancement in the S when transitioning from the pure AAH model to the correlated AAH + SSH disordered system, highlighting the role of structural modulation and electronic localization in optimizing thermoelectric performance at the nanoscale.

INTRODUCTION

The AAH model is among the most well-known instances of a correlated system [1]. Beyond a threshold disorder strength, a transition from a metallic to an insulating phase occurs for a 1D tight-binding AAH system [1,2]. The AAH model has previously been experimentally implemented in both 1D and 2D. Diverse AAH systems are being used by researchers worldwide to identify various functional operations [3]. Three distinct AAH model generalizations, diagonal, off-diagonal, and generalized, are considered in which the cosine form is used to modulate on-site energies, hopping integrals, or both [4]. With the right configuration, the so-called AAH phases, which are further linked to cosine modulations, may be adjusted individually.

The concepts of topology and topological invariants in condensed matter physics are explored through a beautiful model known as the SSH model [5,6]. As a tight-binding model, the SSH model represents a single spinless electron on a two-site unit cell of a 1D lattice. The two locations are designated A and B in a unit cell [7], where two alternative hopping parameters are considered within the unit cell, and a second is considered with the neighboring unit cell [6].

In this work, we investigate the combined effect of AAH disorder and SSH hopping dimerization on the thermopower of a 1D chain. We focus on the off-diagonal dimerization in pure AAH and AAH + SSH disordered systems. The detailed methodology is presented in the following section, followed by a comprehensive discussion of the results and a summary of our key findings.

METHODOLOGY

In order to study the interaction between topology and quasiperiodic disorder in 1D systems, we build a tight-binding Hamiltonian that includes on-site energy modulation via the AAH model and modulated hopping via the SSH model. Thus, we investigate the effects of correlated disorder on thermopower. Fig. 1 illustrates the disordered 1D chain that represents the tight-binding Hamiltonian.

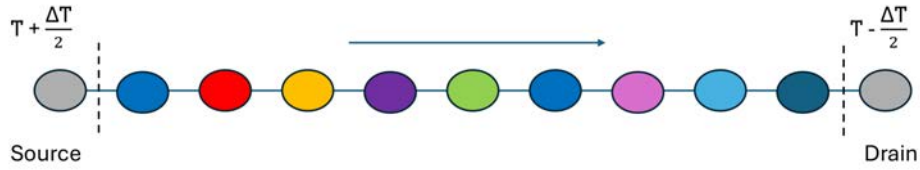


FIGURE 1. 1D chain with AAH modulation and dimerized hopping, coupled to two heat baths.

The total Hamiltonian is given by:

$$H_{Tot} = H_{SSH} + H_{AAH}. \quad (1)$$

The off-diagonal AAH Hamiltonian is written as [4]:

$$H_{AAH} = \sum_n \epsilon_n c_n^\dagger c_n + \sum_n (t_n c_{n+1}^\dagger c_n + h.c.), \quad (2)$$

where $c_n^\dagger, c_n$ are the creation, annihilation operators at site n and ϵ_n, t_n are the on-site energy and nearest neighbor hopping integral. In the presence of cosine modulation, the nearest-neighbor hopping integral factor takes the form:

$$t_n = t[1 + \lambda \cos(2\pi b n + \phi_\lambda)],$$

where λ is the modulation strength, factor b is an irrational number which makes the nearest-neighbor hopping integral quasiperiodic, and ϕ_λ is the phase factor.

The SSH Hamiltonian, accounting for dimerized hopping, is expressed as [7]:

$$H_{SSH} = t_1 \sum_n (c_{n,B}^\dagger c_{n,A} + h.c.) + t_2 \sum_n (c_{n+1,B}^\dagger c_{n,A} + h.c.). \quad (3)$$

Here t_1 and t_2 are the parameters of hopping within the unit cell and the hopping connecting neighboring unit cells.

To study transport properties, we compute the electronic transmission probability with the help of Green's formalism. The transmission probability is calculated as [4]:

$$T_p = \text{Trace}[\Gamma_s G \Gamma_D G^\dagger] \quad (4)$$

Here, G is the retarded Green's function Γ_s and Γ_D are the coupling matrices (or the broadening functions) of source and drain contacts.

We determined the thermoelectric quantity S from the Landauer formalism, and it is shown as [7]:

$$L_n = -\frac{1}{h} \int dE T_p(E) \left(\frac{\partial F}{\partial E} \right) (E - E_F)^n \quad (5)$$

$$S = \frac{L_1}{e T L_0} \quad (6)$$

RESULTS AND DISCUSSION

In this study, we begin by outlining the key parameters and model configurations. For the calculations using the AAH model, we have chosen a parameter set in which the hopping modulation strength is set to $\lambda = 0.5$ eV. Additionally, the system size is fixed at $N = 30$ atomic sites. To model the SSH hopping modulation, we utilized a theoretical framework that incorporates alternating hopping amplitudes. The combined AAH+SSH model thus allows us to investigate the interaction between quasiperiodic and bond alternation in determining thermoelectric properties.

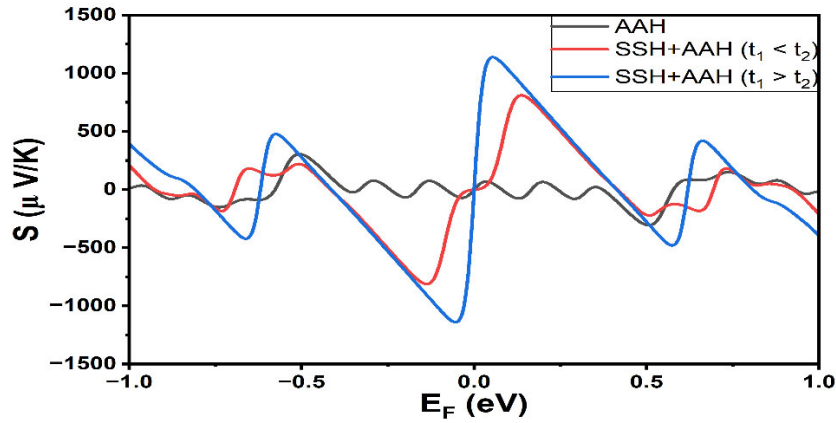


FIGURE 2. S as a function of E_F where AAH includes the cosine modulation (diagonal) with $\lambda = 0.5\text{eV}$, and AAH+SSH disordered system includes the hopping dimerization (along with the hopping modulation $t_1 \neq t_2$ and $\lambda = 0.5\text{eV}$) and $\phi_\lambda = 0$.

Figure 2 illustrates the variation of the S as a function of the E_F for three different cases: a pure AAH 1D chain with nearest-neighbor hopping integral modulation and disorder strength $\lambda = 0.5\text{eV}$, and two variants of a combined AAH+SSH 1D chain with alternating hopping amplitudes ($t_1 < t_2$, $t_1 > t_2$ respectively). The introduction of SSH-type hopping modulation in conjunction with AAH potential leads to a pronounced enhancement in S , exhibiting sharp peaks with values reaching approximately $\pm 1200\mu\text{V/K}$. This increase in thermopower highlights the role of hopping modulation in topologically modulated, correlated disordered systems, which holds great promise for enhancing thermoelectric performance in low-dimensional devices.

CONCLUSION

To study the effect of correlated disorder and hopping modulation on thermoelectric properties, we have analyzed the behavior of the S in various combinations of parameters of a 1D tight-binding chain. For this purpose, we have compared the values of S obtained for a pure AAH modulated system along with that in systems incorporating a combination of AAH and SSH (for alternating hopping amplitudes). It is observed from our results that the interplay between off-diagonal (hopping) disorder leads to a significant modification of the energy-dependent thermoelectric response. As evident from Fig. 2, this interplay not only enhances the magnitude of S but also introduces sharp features near specific Fermi energy values, with peak values reaching $\pm 1200\mu\text{V/K}$. Such enhancements are highly desirable, as they indicate improved thermoelectric efficiency in these low-dimensional systems.

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Effect of MWCNT Based Source and Drain Contacts in Organic FETs

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Abstract. This work explores the effect of using multi-walled carbon nanotube (MWCNT) yarns as source and drain electrodes in organic field-effect transistors (OFETs), replacing traditional Au/Ag or other metal contacts. The device was fabricated using spin-coated PBTTT-C14 thin film and chemical vapor deposition (CVD) grown MWCNT yarns. Electrical measurements revealed device transfer characteristics and mobility behaviour. Simulations were conducted using a hopping percolation model assuming an exponential density of states. While the theoretical model showed a linear mobility dependence on carrier density (on a log-log scale), experimental results displayed a nonlinear behaviour. This mismatch can be attributed to a dynamic barrier between MWCNT electrodes and the organic semiconductor due to the gate field. The findings highlight MWCNTs' potential in flexible electronics and emphasize the need to account for contact effects in modelling.

INTRODUCTION

OFETs are at the forefront of flexible, low-cost electronics for applications like wearable sensors and displays. As for the contacts, while gold and silver offer high conductivity, they are limited and thus costly, making them unsuitable for scalable production. CNTs, with their excellent conductivity, mechanical strength, and compatibility with flexible substrates, offer a promising alternative for energy storage devices [1] as well as contacts. Their quasi-one-dimensional nature also enhances charge transport efficiency. Among CNTs, multiwalled carbon nanotubes (MWCNTs) are particularly attractive due to their ability to carry high current densities and their potential for quasi-ballistic transport [2]. The metal-CNT contact geometry significantly influences resistance. Side-contacted and end-contacted configurations exhibit different electron injection behaviours, as shown in prior studies [2]. Additionally, interwall coupling in MWCNTs can induce pseudo gaps near the Fermi level during low-frequency motion, affecting the density of states and charge transport [3]. Studies also show that charge injection in organic semiconductors is mobility-dependent, and contact-limited devices can suppress performance regardless of bulk mobility [4]. In this work, we investigate MWCNT yarns as source and drain contacts in OFETs using PBTTT-C14 film. We analyse mobility trends and compare experimental results with simulations, aiming to better understand contact resistance effects and advance CNT-integrated flexible electronics.

FABRICATION AND MEASUREMENT

The fabrication process began with the preparation of a silicon substrate. Standard cleaning procedures were followed, starting with a rinse in deionized (DI) water, followed by immersion in isopropyl alcohol (IPA) and treatment in an ultrasonic bath. The substrate was then cleaned in acetone and again ultrasonicated to ensure complete removal of surface contaminants. The semiconducting layer was prepared by dissolving 50 mg of PBTTT-C14 in 10 mL of chlorobenzene and stirred at 100 °C for 20 minutes on a hot plate. The solution was then drop-cast onto the cleaned substrate and spin-coated at 1000 rpm for 30 seconds to form a uniform thin film. For Contacts, MWCNT yarns extracted from MWCNT forests grown by CVD [5]. The MWCNT yarns were carefully aligned and placed onto the PBTTT-C14 thin film manually. To improve adhesion and interface quality, a few drops of the polymer solution were added over the electrodes, followed by annealing at 150 °C for 50 minutes to complete the device.

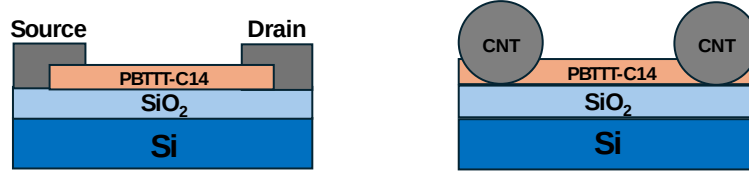


FIGURE 1. (a) OFET device with metal contacts; **(b)** Schematic of the fabricated device.

Numerical simulations were carried out using MATLAB to model the charge carrier mobility and current-voltage characteristics. The OFET structure was defined with a channel length of 800 μm , a width of 10 mm, and a layer thickness of 200 nm. The dielectric constant of PBTTT-C14 was taken as 2.85.

The simulation employed a percolation-based model using an exponential density of states. The carrier concentration was calculated from the gate voltage using the expression for induced charge, and mobility was derived from both the experimental drain current and a theoretical hopping model: [6]

$$\mu(\rho) = \left(\frac{\sigma_0}{e}\right) \times \left(\frac{T}{T_0}\right)^4 \times \left[\frac{\sin\left(\frac{\pi T}{T_0}\right)}{(2\alpha)^3 B_c}\right] \times \rho^{\frac{T_0}{T-1}} \quad (1)$$

Here, σ_0 represents the conductivity prefactor, while α^{-1} denotes the effective overlap length between localized states. T_0 characterizes the width of the exponential density of states (DOS), and B_c is the critical threshold for percolation to begin. Parameters used were: $T_0=500$ K, $T=300$, $\sigma_0=3 \times 10^6$ S/cm, $\alpha=10^{12}/0.12$, and $B_c = 2.5$.

RESULTS AND DISCUSSION

The electrical characteristics of the fabricated OFET with CNT yarn electrodes were evaluated through transfer curve measurements at a fixed drain-source voltage (V_{DS}) of -6V. Figure 2(a) shows transfer (I_D - V_G) characteristics exhibited typical p-type transistor behaviour, confirming the functionality of the PBTTT-C14 as the active semiconducting layer. Charge carrier mobility (μ) was extracted from the experimental data using the standard field-effect transistor equation in the linear region. The mobility was plotted as a function of carrier density. The calculated mobility showed increasing behaviour with gate bias as shown in Fig. 2(b), as expected, but deviated from linearity when plotted against charge carrier density on a log-log scale as shown in Fig. 2(c).

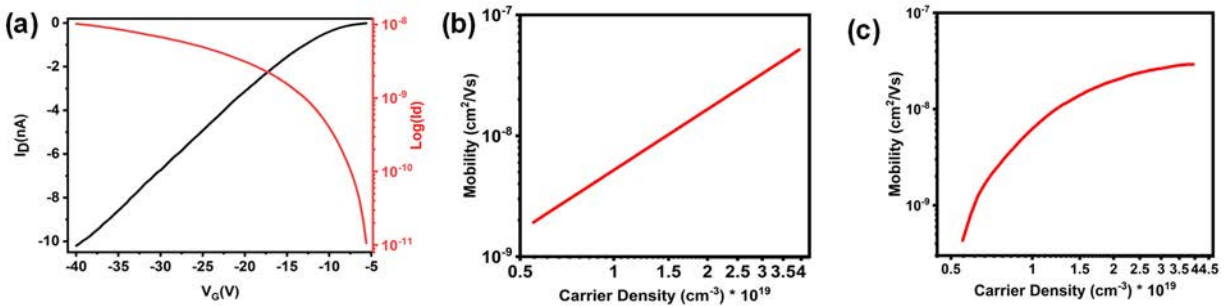


FIGURE 2. (a) Transfer characteristics of the OFET device; Dependence of Mobility on the Charge Carrier Density **(b)** From the Simulations, **(c)** of the device.

This mismatch between theoretical and experimental data is likely due to a dynamic contact barrier introduced by the MWCNT yarn electrodes. Unlike conventional metal electrodes, which possess a fixed Fermi level (Fig. 3a), MWCNTs have their own discrete energy states, including HOMO and LUMO levels (Fig. 3b). In metal-semiconductor contacts, the energy alignment at the interface is mostly governed by the work function difference, and the gate field primarily shifts the energy bands of the organic semiconductor. However, in the case of MWCNT contacts, the gate field not only affects the organic layer but also shifts the energy levels of the MWCNTs themselves. As shown in Fig. 3(a), with metal electrodes, the energy level alignment remains stable under gate bias, leading to a consistent Schottky barrier. In contrast, Fig. 3(b) illustrates that the energy levels of MWCNTs shift along with the semiconductor bands under gate bias, causing the Schottky barrier height to become variable. This dynamic behaviour affects the charge injection efficiency, resulting in the observed nonlinear dependence of mobility on carrier density.

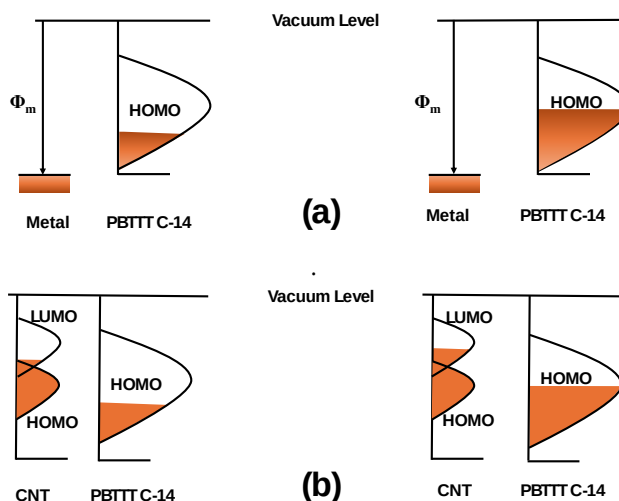


FIGURE 3. Energy Levels of Drain and Organic Layer of **(a)** Metal Contact, **(b)** CNT Contact.

CONCLUSIONS

This study demonstrates the feasibility of using MWCNT yarns as source and drain electrodes in OFETs, offering a cost-effective alternative to traditional metal contacts and their effect on the charge carrier mobility with respect to the gate field. While theoretical models predict an exponential mobility-carrier density relationship, experimental results reveal deviations likely caused by contact resistance at the MWCNT-semiconductor interface. Future work will focus on refining simulation models and optimizing MWCNT integration to reduce injection barriers and enhance charge transport.

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Structural, Morphological and Optical Properties of β -Ga₂O₃ Microrods grown by Facile Hydrothermal method

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Abstract: In this present work, structural, optical and morphological properties of β -Ga₂O₃ microrods grown by a simple and cost-effective hydrothermal method, have been investigated by using X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscope (FESEM) and UV-Visible Spectrophotometer. The monoclinic phase with space group C2/m of the Ga₂O₃ nanorods were confirmed by X-Ray diffraction. The average length and width of the β -Ga₂O₃ microrods have been calculated 975 nm and 325 nm respectively. The reflectance spectra shows that Ga₂O₃ microrods reflect 81% of illuminated light in the Visible region and have a bandgap of 4.7eV.

INTRODUCTION

β -Ga₂O₃ is a unique next generation Ultra-wide bandgap semiconductor for high thermal and high-voltage applications. Power electronics or high frequency electronics markets are dominated by SiC and GaN like Ultra-wide bandgap materials but β -Ga₂O₃ has drawn the special attention of researchers because of its higher band gap which provides better thermal resistance and higher critical electric field resulting in high operational voltage and higher Baliga figure of merit which make it efficient for high frequency operation. Ga₂O₃ has several polymorphs, known as α , β , γ , δ and ϵ . Out of these β -Ga₂O₃ is the most thermally and chemically stable state. β -Ga₂O₃ monoclinic crystal structure with C2/m space group, has an ultra-wide band gap (~4.8eV), high critical field (~8 MV), dielectric constant (10.2-12.4) and higher Baliga figure of merit (~3000).^{1,2} Ga₂O₃ has been grown by using various growth method such as Czochralski method, melt grown method, Chemical Vapor deposition (CVD), MOCVD, LPCVD, Sputtering and wet chemical methods etc.¹ The Hydrothermal method is relatively cost effective and simple method to achieve control over morphology for crystal growth. For the growth of 1D/2D microstructure, hydrothermal method is the more suitable method than another chemical route.

In this work, β -Ga₂O₃ Microrods have been grown using the simple and cost-effective hydrothermal method via wet chemical route. The structural, morphological and optical properties have been studied using X-Ray diffraction, Field emission scanning electron microscope, UV-Visible Spectroscopy.

METHODOLOGY

Gallium Nitrate hydrate Ga(NO₃)₃.x H₂O (Sigma Aldherich, 99.9%) was used as a precursor for the growth of β -Ga₂O₃ nanorods for hydrothermal synthesis.³ 0.5 M of Ga(NO₃)₃.x H₂O was dissolved in 50 ml of DI water and kept for stirring at 600 rpm for 1hour. Subsequently the Hexamethylenetetramine (HMTA) is added as stabilizer in 1:1 to obtain transparent and homogeneous solution. Then obtained solution was transferred into a Teflon beaker with a stainless-steel autoclave and kept in an oven at 140°C for 30 minutes. A white precipitate of GaOOH was obtained, which was washed with DI water, using centrifuge at 5000 rpm to remove all the residual reactant. Further obtained precipitate was kept in the oven for drying at 70°C overnight. The obtained powder was further calcined at 1000°C for 2 hours in a high-temperature muffle furnace to convert GaOOH into β -Ga₂O₃.

Characterization

The crystallographic structural properties of the sample have been studied by X-ray Diffraction analysis using Rigaku Smartlab High Resolution X-Ray Diffractometer with CuK α radiation source with wavelength (0.154 nm). This

synthesized sample was scanned over a range from 10- 70° angle with step size of 0.02. A morphological study has been done by using Zeiss, Germany, Supra55, FESEM. The reflectance spectra of the powder sample were obtained by using an Agilent Cary 5000 UV-Vis-NIR Spectrophotometer. Further optical properties have been studied by plotting Tauc's plot.

RESULTS AND DISCUSSION

Structural Properties

Figure 1(a) shows the XRD pattern of the microrods sample. The XRD pattern was indexed using the International Centre for Diffraction Data (ICDD) of β - Ga_2O_3 for monoclinic phase with card no. 00-041-1103 by using Xpert HighScore software. The XRD pattern confirms the growth of polycrystalline gallium oxide microrods. The intense peak appeared at $2\theta = 35.34^\circ$, shows a strong (111) plane diffraction indicating the growth of microrods orientation in (111) plane. This intense maximum peak, followed by several secondary maxima peaks, confirms the monoclinic phase with C2/m space group.

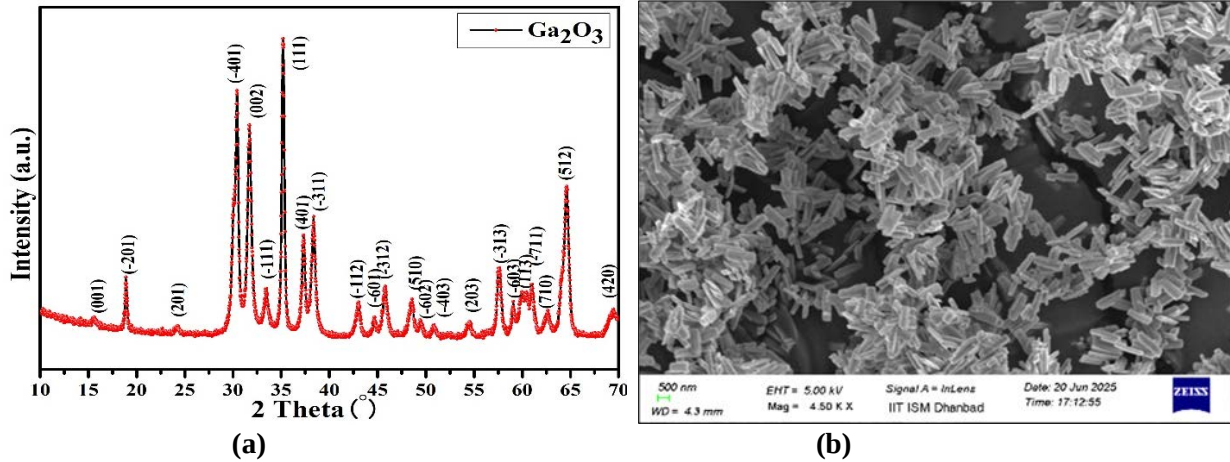


FIGURE 1: (a) XRD pattern of β - Ga_2O_3 Microrods (b) FESEM Image of β - Ga_2O_3 microrods

Morphological Properties

To study the surface morphology of the β - Ga_2O_3 microrods, FESEM has been used in imaging mode. The growth of the uniform β - Ga_2O_3 microrods is confirmed by the high resolution FESEM images in figure 1(b). This micrograph has been analyzed by the ImageJ software to estimate the dimensions of microrods. The average dimension of microrods is 975 nm in length and 325nm in width.

Optical Properties

The optical properties of β - Ga_2O_3 microrods have been studied using UV-VIS Spectroscopy. The reflectance spectra of the sample has been recorded over a range 200nm to 800nm. Figure 2(a) shows high reflectance up to 81% and a sharp absorption band edge in the spectra around 265 nm which shows the sharp inter-band transition from top of valence and bottom of conduction band in wide bandgap material with high crystallinity. To study the absorption behavior, reflectance data was converted using Kubelka Munk function⁴.

$$F(R) = \frac{(1-R)^2}{2 \cdot R} = \frac{K}{S};$$

Where R is Reflectance, K is absorption Coefficient and S is scattering constant. The reflectance spectra show the higher reflectance in visible region which predicts that material is highly transparent in Visible to NIR region. The Bandgap energy between the valence band and the conduction band, for the sample, was estimated by using Tauc's Plot.

$$F(R)h\nu = A (h\nu - E_g)^{1/2}$$

Where A = constant and $h\nu$ = photon energy.

E_g is determined by extrapolating the linear region of the plot. From figure 2(b) Tauc's plot, the estimated direct bandgap energy for the Ga_2O_3 nanorods is $E_g = 4.7$ eV.

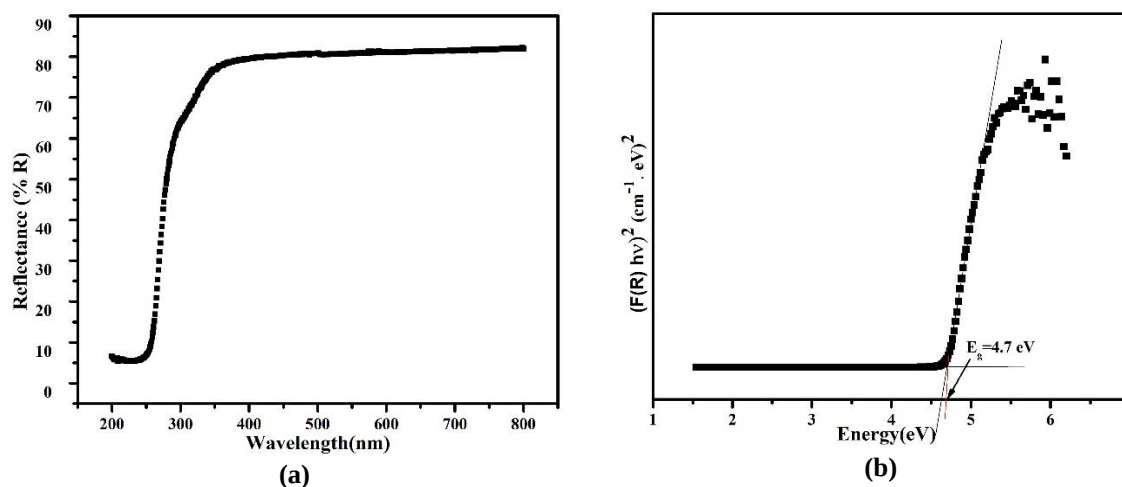


FIGURE 2. (a) UV-VIS reflectance spectra, and (b) Tauc's Plot for β - Ga_2O_3 microrods

CONCLUSION

In summary the β - Ga_2O_3 microrods were grown using hydrothermal method. The structural study confirms the polycrystalline phase of the β - Ga_2O_3 microrods with a monoclinic crystal structure and space group C2/m. The FESEM image shows the growth of microrods with an average length of 975 nm and 325 nm width. The reflectance spectra show the high absorption in the UV region while transparent in the visible region and Tauc's plot estimates the bandgap around 4.7 eV. This concludes that the β - Ga_2O_3 is a potential candidate for UV optoelectronic and power devices.

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Magneto-Dielectric Behavior in Honeycomb-Layered $\text{Na}_3\text{Co}_2\text{SbO}_6$

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Abstract. In the present work, the structural, magnetic, dielectric, and magneto-dielectric behavior of the honeycomb-layered $\text{Na}_3\text{Co}_2\text{SbO}_6$ is reported. It is known in the literature for its ‘zig-zag’ AFM structure at low temperatures (T_N -9 K). Co^{2+} ($S=3/2$) is responsible for adopting the honeycomb structure in the studied compound, which was isolated with non-magnetic Sb. Detailed magnetic measurements confirm its antiferromagnetic transition around 9 K and the perfect overlap of Zero Field Cool (ZFC)-Field cool (FC) magnetic pattern at low field ($H=100$ Oe), suggesting the high quality of the magnetic sample. In the dielectric data, we have not found any anomaly across the magnetic transition, ruling out its type-II multiferroic aspects. However, intrinsic magneto-dielectric behaviour was observed in the magnetic state of the studied compound.

INTRODUCTION

The primary aim of studying the $\text{Na}_3\text{Co}_2\text{SbO}_6$ -based materials is due to their possible electrochemical properties [1]. $\text{Na}_3\text{Co}_2\text{SbO}_6$ crystallizes in a CdI_2 -type structure in which edge-sharing CoO_6 octahedral layers are intercalated by Na atoms (octahedral interstices). The honeycomb ordering consists of Co^{2+} ($S=3/2$) magnetic ions separated by a non-magnetic Sb atom. Based on its neutron diffraction data, the magnetic ground state of the titled compound was found to be ‘zig-zag’ AFM structure [2]. Due to its interesting magnetic structure as mentioned above, the frustration in the titled compound can not be ruled out. It has been reported in the literature that one of the main causes of ferroelectricity in a special class of antiferromagnetic materials is associated with the frustration among magnetic atoms, and thus, there is a breaking of the inversion symmetry [3]. Due to this, they share both magnetic and ferroelectric transitions at the same temperature and are termed as type-II multiferroics [3]. In the past, we have reported some new type-II multiferroic materials as a virtue of frustration among various magnetic atoms in Tb_2BaMO_5 ($M=\text{Ni}, \text{Co}$) [4,5]. Therefore, the present work aims to explore the magneto-electric, magneto-dielectric behaviour of the Honeycomb-layered $\text{Na}_3\text{Co}_2\text{SbO}_6$.

EXPERIMENTAL DETAILS

Polycrystalline $\text{Na}_3\text{Co}_2\text{SbO}_6$ was prepared by the conventional solid-state route as described by Wong et.al [2]. X-ray diffraction (XRD) pattern ($\text{Cu K}\alpha$) confirms single-phase behaviour of the titled compound. The obtained XRD pattern was further fitted with Rietveld refinement using the Fullprof program and considering a monoclinic structure (space group: $C2/m$), which is presented in Figure 1a. From the best fit of the data, the lattice parameters ($a=5.357$ Å, $b=9.286$ Å, and $c=5.648$ Å) obtained are well matched with the literature [2]. Magnetic measurements (temperature-dependent magnetization and isothermal magnetic hysteresis) have been carried out with the help of a commercial 7 Tesla-SQUID magnetometer (Quantum Design USA). Dielectric and magneto-dielectric measurements have been carried out by using an LCR Meter (Keysight-E4980AL) integrated with the Commercial (Quantum Design) Physical Properties Measurements System.

RESULT & DISCUSSION

After confirming its structural aspect, we have studied the magnetic, dielectric, and magneto-dielectric behavior of the titled compound and discussed it in the following sections:

Magnetic Measurements

Figure 1 b shows the zero-field cooled (ZFC)-Field cooled (FC) magnetization data of the titled compound as a function of temperature (2-300 K) in the presence of a 100 Oe magnetic field. The perfect overlap of ZFC-FC rules out any possibilities of spin disorder/magnetic impurities in the present studied compound. The sharp peak around 9 K is associated with the antiferromagnetic transition. Further, we have also recorded the ZFC curve in the presence of $H=5$ kOe and presented it in the inset of figure 1b. $\chi(T)^{-1}$ data above 100 K has been fitted according to the Curie-Weiss law, and the effective magnetic moment (μ_{eff}) value comes out to be of the order of $4.8 \mu_B$, which is higher than the calculated μ_{eff} ($3.87 \mu_B$). The higher value of the effective moment of the titled compound can be explained in terms of the orbital contribution from the Co^{2+} magnetic atom. The value of the paramagnetic Curie temperature is found to be 14 K, suggesting weak ferromagnetic interaction. We have also collected isotherms of magnetic hysteresis (M - H) curves below and above the magnetic transition temperature (2, 5, and 100 K). The corresponding magnetic hysteresis is presented in Figure 1c. The obtained pattern, at 2 and 5 K, indicated that a small portion of ferromagnetism is associated with the antiferromagnetic behaviour, because of its interesting honeycomb arrangement of magnetic atoms and zig-zag AFM pattern [2].

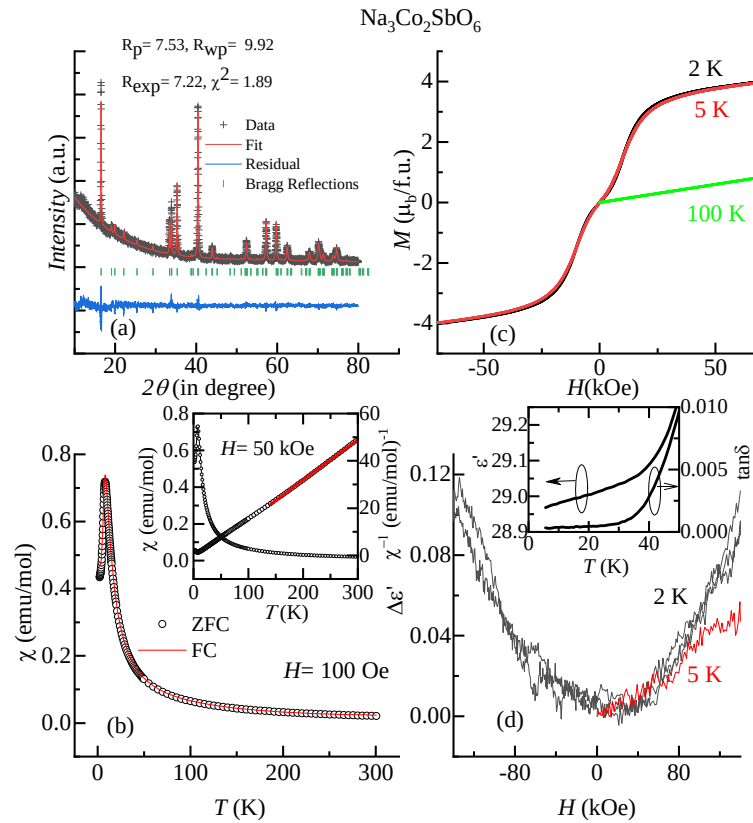


FIGURE 1. (a) X-ray diffraction pattern along with Rietveld Refinement, (b) ZFC-FC curves in the presence of $H=100$ Oe, (c) M - H Curves for some selected temperatures, as mentioned in the text, (d) magneto-dielectric behaviour for some selected temperatures, as mentioned in the text. Inset of (b) shows the temperature-dependent magnetization data with $H=5$ kOe with the Curie-Weiss fitting. Inset of (d) shows the temperature-dependent dielectric and $\tan\delta$ data.

Dielectric and magneto-dielectric behavior

As the motivation of the present work is to explore the magneto-electric and magneto-dielectric behavior of the titled compound, detailed dielectric measurements have been carried out from 5-300 K. The obtained pattern rules out the possibilities of any type-II multiferroic aspect, as there was no anomaly across the magnetic transition (T_N -8 K). The inset of Fig. 1(d) shows the dielectric (left frame) and $\tan\delta$ (right frame) data across the magnetic transition temperature for the frequency of 100 kHz. However, in this temperature regime, the value of $\tan\delta$ is very low (0.005), mimicking its highly insulating behaviour. As the sample is highly insulating in the magnetic state, we have recorded the dielectric constant for some selected temperatures, i.e., 2 and 5 K, as a function of magnetic field up to 140 kOe and presented in Fig. 1d. The obtained pattern shows the systematic behaviour as a function of magnetic field, revealing the intrinsic magneto-dielectric behavior, however weak, in the studied compound.

In summary, the present work reports the magnetic, dielectric, and magnetodielectric behavior of the honeycomb-layered $\text{Na}_3\text{Co}_2\text{SbO}_6$. The studied compound shows the antiferromagnetic transition around 9 K. In the magnetic state, a small portion of ferromagnetic properties has also been observed along with the antiferromagnetic fraction, as revealed by magnetic hysteresis curves. Temperature-dependent dielectric data endorse no magneto-electric behavior, but weak intrinsic magneto-dielectric behavior in the magnetic state of $\text{Na}_3\text{Co}_2\text{SbO}_6$.

ACKNOWLEDGMENTS

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Superparamagnetic Behavior of Ni-Mn-Ga Melt Spun Ribbon

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Abstract. The superparamagnetic behavior of $\text{Ni}_{50}\text{Mn}_{29}\text{Ga}_{21}$ alloy has been studied in ribbon form. The crystal structure was observed to change from 7M orthorhombic to monoclinic from bulk to ribbon. Systematic investigations on the magnetic properties on as cast ribbon reveal the presence of superparamagnetic nature. Blocking temperature and in the ribbon was found to be 45 K which evidences the presence of superparamagnetic nature in the ribbons. The average particle size of 8 nm was estimated from the blocking temperature and magnetocrystalline anisotropy constant (K_{eff}).

INTRODUCTION

Among the non-stoichiometric compositions explored in the Ni-Mn-Ga system, $\text{Ni}_{50}\text{Mn}_{29}\text{Ga}_{21}$ has received considerable attention due to its large magnetic-field-induced strain, due to high magnetocrystalline anisotropy and low twinning stresses associated with modulated crystal structure in the martensitic phase [1-4]. In contrast, superparamagnetism is considered a distinctive characteristic of magnetic nanoparticles and holds significant promise for modern technological applications such as contrast agents for magnetic resonance imaging (MRI), hyperthermia, and ferrofluid technology [5]. To investigate how reducing particle size affects melt-spun ribbons Ni-Mn-Ga are particularly suitable. The rapid solidification from the liquid state allows for a finite grain size along with changes in atomic ordering and crystal structure. During annealing, the migration and annihilation of vacancies facilitate atomic rearrangement, which, together with the behavior of internal stresses and dislocations, alters the transformation temperature of martensitic state (T_M), Curie temperature (T_C), and saturation magnetization of the ribbons [6]. Neutron diffraction studies [7] indicate that the magnetic moment in these alloys is predominantly located on manganese atoms, with $\mu_{\text{Mn}} = 3.5 \mu_B$, while the moment on nickel atoms is relatively small at $\mu_{\text{Ni}} = 0.33 \mu_B$. Magnetization reaches its maximum for stoichiometric Ni_2MnGa and decreases in off-stoichiometric, Mn-rich alloys due to local antiferromagnetic ordering of excess Mn atoms, as well as in Mn-deficient alloys due to the reduced number of Mn atoms [7-8].

Temperature-dependent magnetization measurements, $M(T)$, may reveal key characteristics of a superparamagnetic nature. The temperature, below which the magnetic moments of the particles become immobilized, is typically regarded as average blocking temperature (T_B) is a crucial parameter in characterizing the magnetic behavior of a magnetic nanoparticle system. The blocking temperature, T_B usually determined by analyzing the zero-field-cooled and field-cooled (ZFC and FC) magnetization curves. Above T_B , thermal fluctuations are sufficient to reverse the direction of the magnetic moment, and no hysteresis is observed. When particles interact, magnetic dipole-dipole interactions become significant and more pronounced. Depending on the orientation of the dipoles, this dipole interaction can be either ferromagnetic or antiferromagnetic. In this work, we aim to explore how reduced particle size influences the structural and magnetic properties of $\text{Ni}_{50}\text{Mn}_{29}\text{Ga}_{21}$ alloy ribbons produced using the melt-spinning technique.

EXPERIMENTAL PROCEDURES

An as-cast ingot with a nominal composition of $\text{Ni}_{50}\text{Mn}_{29}\text{Ga}_{21}$ was prepared using conventional argon arc melting, using high pure Ni, Mn and Ga elements. The alloy was subsequently induction melted in a quartz crucible

fitted with a circular nozzle of 1 mm diameter and ejected by applying argon pressure onto the polished surface of a copper wheel. This process was conducted under an argon atmosphere. The resulting as-quenched ribbons were obtained as flakes measuring 3 mm in width, 30–80 mm in length, and 40 μm in thickness. The microstructure and elemental chemical composition of the ribbons were examined using a field emission scanning electron microscope (FESEM) equipped with a wavelength dispersive spectroscopy (WDS) microanalysis system. Magnetization measurements were carried out using a physical properties measurement system (PPMS-9T-Quantum Design) with the vibrating sample magnetometer module, over a temperature range of 5 to 320 K. The magnetic field, applied up to 90 kOe, was oriented along the ribbon axis (rolling direction).

RESULTS AND DISCUSSION

The X-ray diffraction pattern obtained at room temperature for the melt-spun ribbon under investigation is presented in Fig. 1 (a). The pattern corresponds to a seven-layered modulated (7M) structure with a monoclinic lattice, yielding lattice parameters $a = 4.241(3)$ Å, $b = 5.547(2)$ Å, $c = 4.214(2)$ Å, and $\beta = 92.45(7)^\circ$. The bulk alloy with the same composition exhibits an orthorhombic crystal structure (pnnm space group) with 7M modulation [6]. The diffraction peak intensities from the (0 2 14), (2 0 14), and (0 4 14) planes, observed at 55.3° , 63.8° , and 83.8° respectively in the melt-spun ribbon (shown in Fig. 1 (a)), are relatively higher than those reported for the bulk polycrystalline alloy of the same composition [5]. This suggests that the $\text{Ni}_{50}\text{Mn}_{29}\text{Ga}_{21}$ ribbons possess a preferential [6] orientation, indicating the presence of some degree of texture.

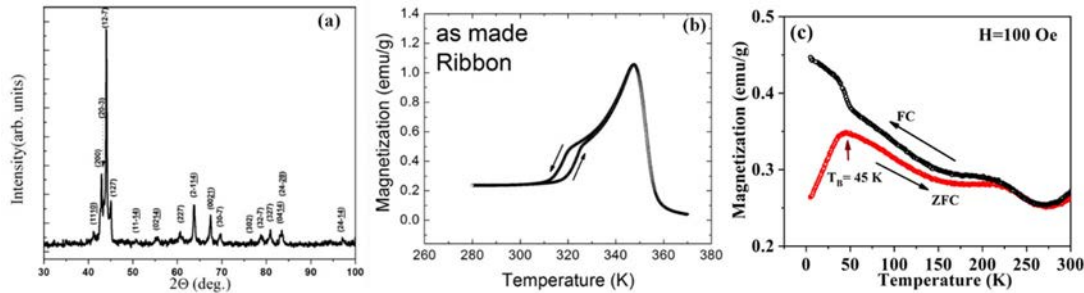


FIGURE 1(a): The XRD pattern for the melt-spun ribbon at room temperature, **1(b)** Temperature dependence of magnetization in the as-made ribbon and **1(c)** ZFC and FC magnetization indicating the blocking temperature (T_B)

The temperature-dependent magnetization $M(T)$ curves were measured under an applied magnetic field of 100 Oe using a PPMS, as shown in Fig. 1 (b). The structural transformation temperatures— M_s , M_f , A_s , and A_f —derived from the $M(T)$ data are found to be 320 K, 313 K, 319 K, and 326 K, respectively. The Curie temperature (T_C) of the ribbon was estimated from the minimum of the first derivative of the $M(T)$ curve and is determined to be 357 K.

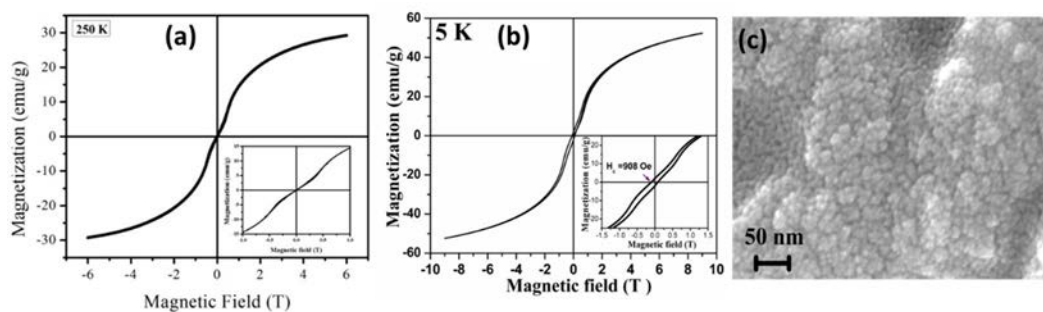


FIGURE 2 Magnetic hysteresis loops measured (a) at 250 K, (b) at 5 K and (c) SEM micrograph displaying the nano sized particles

Figure 1 (c) shows the ZFC and FC magnetization measurements of melt spun ribbon. The magnetization measurements were carried out in the temperature range 5 - 320 K at an applied magnetic field of 100 Oe. The average blocking temperature (T_B), was estimated to be 45 K in melt spun ribbon. Fig. 2 (a) and Fig. 2 (b) display the magnetic hysteresis loops measured at 250 K and 5 K respectively. The as-spun ribbon at 250 K has a low magnetization with

very low hysteresis. The slow rise in the magnetization with field is indicative of substantial amount of disorder-induced magnetic anisotropy in this ribbon. The absence of magnetic hysteresis with a small remanence and coercivity (H_c), may suggest the possible existence of a long-range magnetic dipole-dipole interaction. This may lead to the presence of superparamagnetic behaviour. The increase in magnetization with decreasing temperature and the presence of a symmetric hysteresis loop at 5 K, indicating a transition from superparamagnetic to ferromagnetic behavior. Above T_B , the magnetization is free to align with the fields during the measurement time. The M-H loop should exhibit no hysteresis as displayed in Fig. 2 (a). Consequently, a hysteresis loop response is observed below T_B (Fig. 2 (b)). This may be due to insufficient thermal energy which may not allow the particle moments to align with applied fields. This is consistent with the theory of superparamagnetism. The effective magnetic crystalline anisotropy was estimated by using formula

$$H_c = 0.96 \frac{K_{eff}}{M_s} \left[1 - \left(\frac{T}{T_B} \right)^{0.77} \right]$$

The blocking temperature, coercivity and saturation magnetisation are observed to be $T_B = 45$ K, $H_c = 908$ Oe (at 5K) and $M_s = 58$ emu/g (calculated from approach to saturation method) respectively. The K_{eff} is found to be 5.446×10^4 J/m³. The average particle size of the melt spun ribbon was estimated by using formula $T_B = V \frac{K_{eff}}{25K_B}$ and is found to be 8 nm. To confirm this FESEM micrograph of as spun ribbon was recorded as shown in Fig. 2 (c). The average particle size estimated from this micrograph is well in agreement with the particle size estimated using T_B and K_{eff} as discussed above. This concludes the existence of superparamagnetism in $Ni_{50}Mn_{29}Ga_{21}$ melt spun ribbon.

CONCLUSIONS

The superparamagnetic nature in $Ni_{50}Mn_{29}Ga_{21}$ system was systematically investigated by using melt spun ribbon. The crystal structure of the as cast ribbon was found to be seven-layered monoclinic structure. Systematic investigations on the magnetic properties reveal the existence of superparamagnetic nature in the ribbon. The presence of nanoparticles in the ribbon was confirmed by estimating the average particle size of 8 nm from blocking temperature (T_B) and magnetocrystalline anisotropy constant (K_{eff}) which was further confirmed from the electron micrographs.

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The effect of doping Selenium in MnBi_2Te_4 antiferromagnetic van der Waals layered material

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Abstract. Tuning spin alignment in antiferromagnetic topological insulator, MnBi_2Te_4 , was attempted by introducing selenium in place of tellurium. MnBi_2Te_4 exhibits a long-range antiferromagnetic ordering with a $T_N = 25$ K with a strong out of plane anisotropy. Here, the Mn spins are pointing out of basal plane and coupled antiparallelly along the c-axis. On the other hand, $\text{MnBi}_2\text{Te}_{4-x}\text{Se}_x$ ($x = 0.6, 0.65, 0.7$) show a sharp increase in magnetization at $T = 11$ K and a broad hump between 130 K-170 K. Though the ferromagnetic like signatures are welcome, these arise due to the formation of Mn doped Bi_2Te_3 with MnSe as secondary phase, rather than $\text{MnBi}_2\text{Te}_{4-x}\text{Se}_x$ phase.

INTRODUCTION

Recently discovered MnBi_2Te_4 (MBT) is an antiferromagnetic van der Waals layered material having Neel temperature $T_N = 25$ K. MBT consists of Te-Bi-Te-Mn-Te-Bi-Te septuple layers (SLs) stacked in ABC sequence along the c-direction. Therefore, structure can be realized as derived from topological insulator, Bi_2Te_3 , by placing a Mn-Te layer in between its Te-Bi-Te-Bi-Te quintuple layers (QLs). Magnetic contribution in this TI comes from Mn atoms. The exchange coupling interaction within the layer between Mn-Mn is ferromagnetic along an out of plane easy axis whereas it is antiferromagnetic (AFM) between neighboring SLs resulting in A type AFM ground state [1]. This magnetic alignment is similar to that in MnTe.

The study of magnetic properties along with controlling the spin interactions by means of doping in MnBi_2Te_4 plays a vital role in advancing our understanding in the field of spintronics. Therefore, in this paper we plan to alter the magnetic interactions of MBT by doping Se in place of Te in the Mn-Te layer within the septuple layers of MBT. MnTe and MnSe both are antiferromagnets but unlike MnTe which has a spin propagation vector along (001) direction, MnSe has along (111) direction [2]. The objective was to cant Mn spins giving rise to a weak ferromagnetic signal along the out of plane easy axis.

EXPERIMENTAL

The samples $\text{MnBi}_2\text{Te}_{4-x}\text{Se}_x$ ($x=0, 0.6, 0.65, 0.7$) were synthesized using self-flux method. To make sure that selenium replaces Te in Mn-Te layer we synthesized $\text{MnTe}_{1-x}\text{Se}_x$ ($x=0, 0.6, 0.65, 0.7$) and Bi_2Te_3 as two precursors and mixed them in 1:1 stoichiometric ratio. Then fine powder was sealed in evacuated quartz tubes, annealed at 900 °C for 12 h. Then the temperature was reduced to 600 °C at 10 °C /h and to optimize the growth conditions, we performed a slow cooling to 585 °C at 0.1 °C/h, annealed for 3 days and eventually tubes were quenched in ice cooled water to obtain shiny single crystals. These samples were characterized by powder XRD, TEM for their structure, and a SQUID magnetometer for magnetic properties. Phonon modes were studied using Raman spectroscopy.

RESULTS AND DISCUSSION

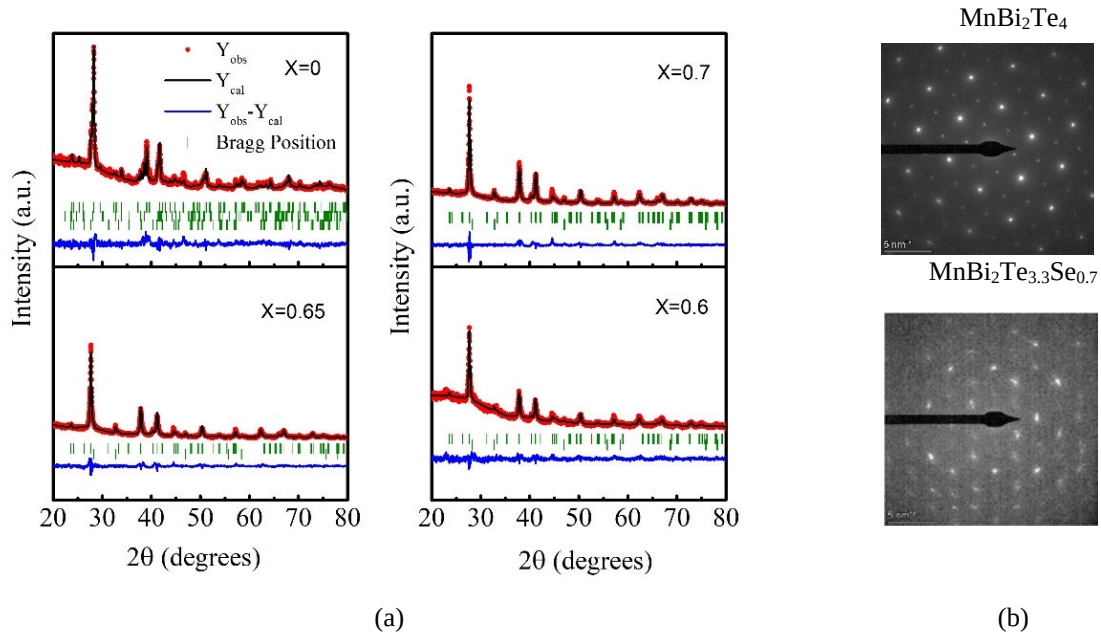


FIGURE 1. (a) The Rietveld refined X-ray diffraction patterns of $\text{MnBi}_2\text{Te}_{4-x}\text{Se}_x$ ($x=0, 0.6, 0.65, 0.7$) and (b) SAED pattern for MnBi_2Te_4 and $\text{MnBi}_2\text{Te}_{3.3}\text{Se}_{0.7}$

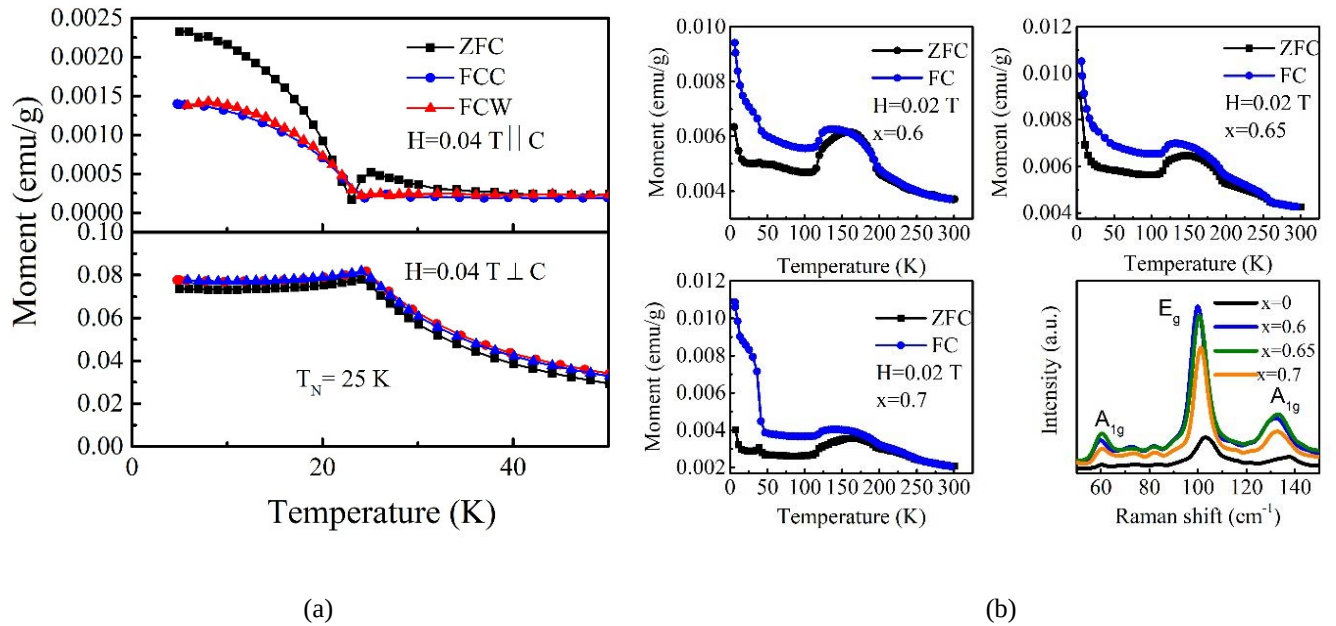


FIGURE 2. (a) Temperature dependent magnetization $M(T)$ of MnBi_2Te_4 along c -direction and perpendicular to c -direction. (b) $M(T)$ patterns of $\text{MnBi}_2\text{Te}_{4-x}\text{Se}_x$ ($x = 0.6, 0.65, 0.7$) and Raman modes in the four samples.

The powder XRD of all four samples reveals centrosymmetric rhombohedral (Sp. Gr. R-3m) structure of MBT along with flux generated impurity phases as shown in Figure 1 (a). SAED patterns recorded using TEM shows sharp spots in the case of MnBi_2Te_4 indicating high quality single crystals with trigonal symmetry (Figure 1(b)). In the case of $\text{MnBi}_2\text{Te}_{3.3}\text{Se}_{0.7}$ the spots are slightly diffused which could be due to the presence of strain. A careful analysis of TEM images, EDS and refinement of powder XRD patterns of Se doped MBT reveals the formation of Mn doped Bi_2Te_3 with MnSe as secondary phase instead of the expected $\text{MnBi}_2\text{Te}_{4-x}\text{Se}_x$. It appears that selenium doping influences a phase separation resulting in Mn doped Bi_2Te_3 and MnSe phases. The structural parameters of all the four compounds are summarized in Table 1.

TABLE 1. Magnetic ordering temperatures, Lattice parameters, Raman modes

Sample	Ordering temperatures (K)		Lattice parameters (Å)		Raman modes (cm^{-1})		
	T_N	T_C, T_{cubic}	A	C	A^1_{1g}	E^2_g	A^2_{1g}
X=0	25		4.3298	40.9193	60.2	102.8	138.7
X=0.6		11.2, 158.3	4.3855	42.6452	59.4	99.6	132.3
X=0.65		11.3, 150.2	4.3838	42.6528	60.6	101.5	133.3
X=0.7		11.4, 160.4	4.3813	42.6303	60.3	101.3	132.9

Figure 2(a) depicts magnetization measurements on MnBi_2Te_4 performed with magnetic field, $H \parallel c$ and $H \perp c$. A clear antiferromagnetic transition at $T_N=25$ K is seen in magnetization performed with $H \parallel c$ indicating the Mn spins to be coupled antiferromagnetically along c-axis, while a ferromagnetic like ordering of the spins is noticed in measurements performed with $H \perp c$, in agreement with the literature [1]. For all the Se doped samples, we observe a completely different behavior firstly, the magnetization exhibits a broad hump between 130 – 170 K and a rise in magnetization below 25 K. Though the aim of this study was to modulate the spin structure, the observed behavior arises from the presence of magnetic phases in Se doped samples. The broad hump is due to the magnetic ordering of cubic phase of MnSe [2] and the ferromagnetic signal is coming from Mn doped Bi_2Te_3 phase [3].

Presence of Bi_2Te_3 type phase is also confirmed from the Raman spectroscopy measurements. The displacement of A^2_{1g} mode from 138.7 to 132.3 in the case of Se doped MBT match well with the phonon modes of Bi_2Te_3 [4].

CONCLUSION

We synthesized MnBi_2Te_4 and studied the effect of doping Selenium in it. MnBi_2Te_4 and Se doped MBT samples crystallizes in R-3m space group but the selenium doped samples prefer to form Mn doped Bi_2Te_3 as stable phase with MnSe as secondary phase. The antiferromagnetic ordering present in MnBi_2Te_4 is no longer preserved in Se doped samples rather they show a complex magnetic behavior coming from their two different phases.

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Influence of Loop Current in Kagomé Superconductors

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Abstract. Motivated by recent breakthroughs in superconductivity and a successive evolution of electronically ordered states in the vanadium-based kagomé-lattice metallic compounds AV_3Sb_5 ($A = K, Rb, Cs$), we perform a self-consistent theoretical study on the superconducting properties of the two-dimensional kagomé lattice. Using the Bogoliubov-de Gennes mean-field theory at very low temperatures, we investigate theoretically the impact of the orbital loop current on the superconducting properties. It is revealed that superconductivity in the kagomé lattice diminishes as the orbital loop current amplitude grows, due to its interplay with charge order and orbital loop current. In addition, when subjected to a Zeeman magnetic field, the presence of charge order intertwined with the time-reversal symmetry breaking orbital loop current can deform the U-shaped fully gapped density of states into a pseudo-gap V-shaped density of states.

INTRODUCTION

Recently, electronic instabilities including superconductivity and various competing electronic density wave-like orders such as charge density wave, pair density wave, spin-density wave have been discovered in the family of nonmagnetic kagomé metals AV_3Sb_5 ($A = K, Rb, Cs$) [1]. It is composed of corner-sharing triangles and large hexagonal voids with three sites in the unit cell, as shown in Fig. 1(a) & (b). It crystallizes in the space group: $P6/mmm$, No. 191, and the point group: C_{6v} , and has a stacking order of A-Sb2-VSb1-Sb2-A. Its unique electronic band structure features Dirac cones, two van Hove singularities ($E = 0, -2t$) and a dispersion-less flat band at an energy of $2t$, touching the top or the bottom of the dispersive band [Fig. 2(a)]. From high to low temperature, all three members first enter a charge-ordered state at a transition temperature T_{CDW} around 78 K and break the translational symmetry. It also exhibits an electronic nematic phase transition with a transition temperature T_{nem} ranging from 30 K to 50 K that destroys rotational symmetry C_6 . Experimentally, these kagomé metals undergo a superconducting (SC) phase transition at T_c ranging between 0.75 K and 2.3 K. Two types of charge-order states have been reported, the star of David and tri-Hexagonal (TrH) or inverse star of David patterns - both enlarge the unit cell size to a $2a \times 2a$ modulation [2,3]. Theoretical

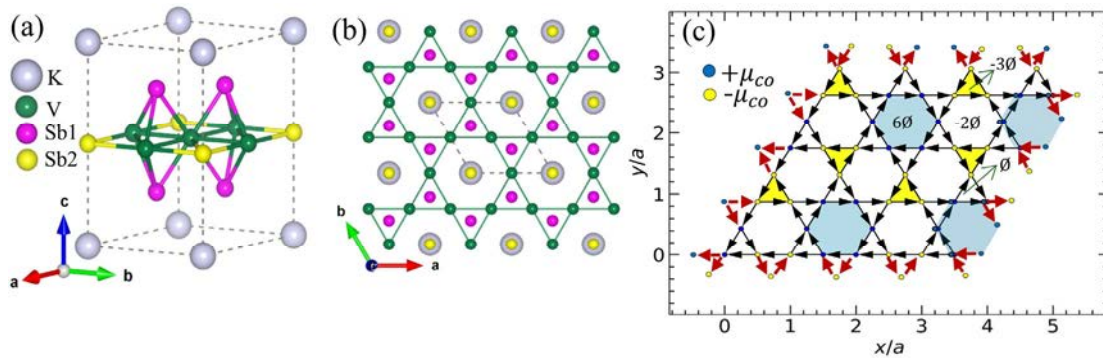


FIGURE 1. Crystal structure of the compound KV_3Sb_5 : (a) Top: Illustration of a 3D view of the unit cell: The V atoms form a structurally perfect 2D kagomé lattice. (b) Top view of the crystal structure along the c-axis. (c) Charge order configuration with intertwined orbital loop current on the $4a \times 4a$ lattice with positive and negative modulation of the chemical potential μ_{co} on the kagomé lattice. The arrows represent the loop current propagation direction, and θ is the associated flux.

studies suggest that the interplay of chiral charge order and superconductivity generates a “triple-Q” chiral pair density wave [4,5]. In particular, the TrH charge order is predominantly observed for all three compounds and is more energetically favored, as shown in Fig. 1(c), which is considered a theoretical model in this study.

MODEL AND METHOD

The electronic system in the kagomé lattice can be described by the nearest neighbor tight-binding Hamiltonian at the mean spin-singlet pairing field as:

$$H_{Tot} = -t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + H.c.) - \sum_{i, \sigma} (\mu_0 + \xi_i \mu_{co}) c_{i\sigma}^\dagger c_{i\sigma} + \sum_i (\Delta_i c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger + H.c.) - it_{lc} \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} - H.c.) \quad (1)$$

where t is the electron hopping amplitude, μ_0 is the global chemical potential, μ_{co} is the charge order amplitude, ξ_i is a local variable (± 1) that generates the TrH charge order pattern, and the complex nearest neighbor hopping it_{lc} incorporates the time-reversal symmetry breaking orbital loop current. The Hamiltonian is diagonalized using a unitary transformation, and the local spin-singlet pairing gap with the on-site attractive interaction strength U is obtained as

$$\Delta(r_i) = -U \langle c_{i\uparrow} c_{i\downarrow} \rangle = -U \sum_n [u_{ni\uparrow} v_{ni\downarrow}^* (1 - f(E_n)) + u_{ni\downarrow} v_{ni\uparrow}^* f(E_n)] \quad (2)$$

where $u_{ni\sigma}$ ($v_{ni\sigma}$) is the corresponding quasiparticle (quasi-hole) amplitude at site i and spin σ is obtained by solving Bogoliubov-de Gennes (BdG) equations, and $f(E_n)$ is the Fermi distribution function. The self-consistency iterations are performed until the pairing amplitudes reach convergence across the entire lattice.

RESULTS AND DISCUSSION

We have studied the density of states (DOS) of the kagomé lattice within only the nearest neighbor tight-binding approximation for a positive hopping integral $t = 1$ [Fig. 2(a), inset] and after introducing onsite SC order parameter Δ as well, shown in Fig. 2(b),

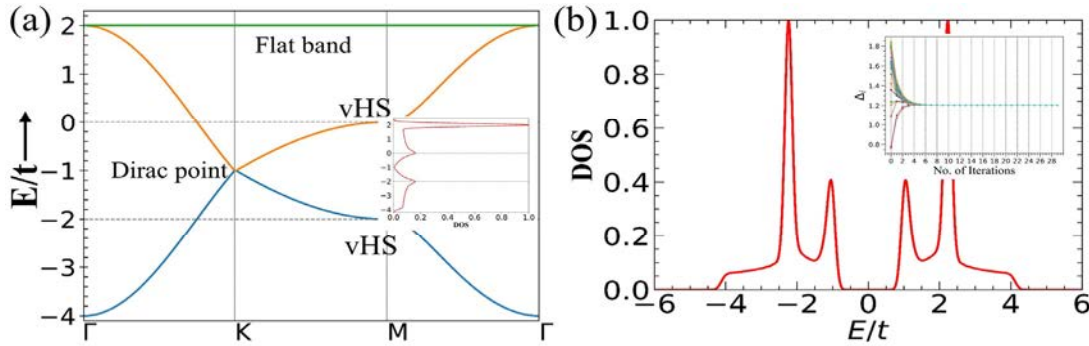
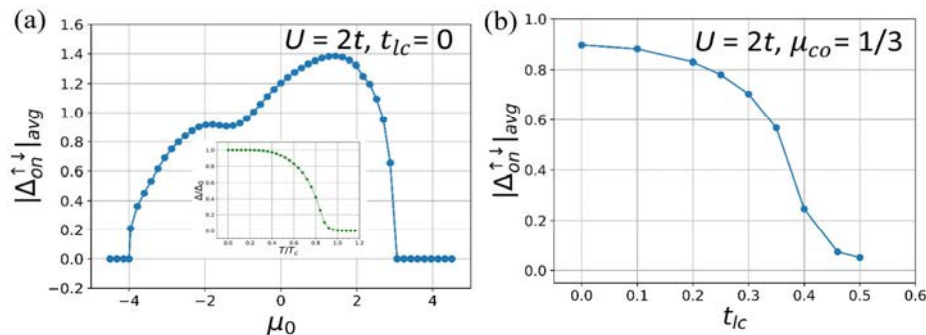


FIGURE 2. (a) Band structure for the nearest-neighbor tight-binding model on the kagomé lattice showing three distinct bands: two dispersive bands and a flat band. The inset shows the DOS of the kagomé lattice, (b) DOS of the kagomé lattice after introducing Δ , and the inset showing the convergence of SC order parameter with iterations.

which demonstrates the energy gap of 2Δ in the SC system. We iteratively solve the SC order parameter Δ_i (initially a random array of real values) using the above BdG self-consistent equations until self-consistency is achieved and it converges to just one value of SC order parameter for all lattice sites [Fig. 2(b), inset]. Fig. 3(a), the variation of the on-site SC order parameter with global chemical potential is shown. Inset qualitatively shows the occurrence of a phase transition from the normal state to the SC state. In Fig. 3(b), it shows the evolution of the average value of absolute SC pairing as a function of t_{lc} for a $6a \times 6a$ lattice with periodic boundary conditions. It has been observed that as the amplitude of the orbital loop current increases, the pairing amplitude decreases, and a further rise eventually suppresses the SC pairing amplitude. The energy dependence of the DOS for a $10a \times 10a$ kagomé lattice for different strengths of t_{lc} is shown. In Fig. 4(a), one can see a typical U-shaped fully gap structure DOS for $t_{lc} = 0$ for normal states. On the other hand, inclusion of a small value of t_{lc} , for example $t_{lc} = 0.2$ along with Zeeman magnetic field B_z , implies the presence of a pseudo-gap featuring a V-shaped DOS [shown in Fig. 4(b)] for the chiral flux state.



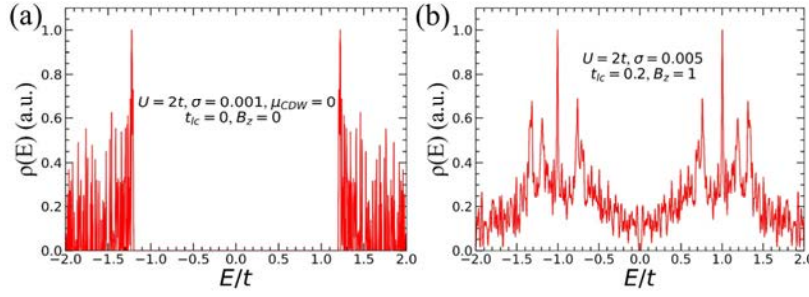


FIGURE 4. DOS plots of the kagomé lattice with open boundaries for different t_{IC} values, in the absence of chemical potential modulation μ_{co} , shown for magnetic fields $B_z = 0$ and $B_z = 1t$.

CONCLUSIONS

In summary, using a fully self-consistent theory, our results indicate that an increasing loop current amplitude leads to a suppression of the superconducting pairing amplitude. Furthermore, the inclusion of the Zeeman magnetic field transforms the DOS from a fully U-shaped gap to a V-shaped pseudo-gap.

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DFT+DMFT Study Of Magnetism In SrCoO₃

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Abstract. This work presents Density Functional Theory (DFT)-cum-Dynamical Mean Field Theory (DMFT) study of cubic perovskite SrCoO₃. We have used PBEsol exchange correlational functional which gives lattice constant quite close to the experimental values. The momentum-resolved spectral function plot suggests that electronic correlation among Co-d electrons has introduced incoherent states majorly contributed by t_{2g} - d_n states. We also investigated quasiparticle lifetime and $\text{Im}\Sigma(\omega)$ to confirm Fermi-Liquid behaviour. The Hubbard parameters $U_{full} = 4.80$ eV and $J_{crpa} = 0.72$ eV gave $T_c \sim 300$ K in fair agreement with the experimental results.

INTRODUCTION

The cubic perovskites ABO₃ showcase a variety of physical, chemical and structural properties viz. metal-insulator transition, spin-state transition, room temperature T_c , multiferrocity, liberty to introduce large oxygen vacancies, superconductivity¹, large thermopower², spin-glass behaviour etc. This makes them an interesting class of compounds for technological applications such as storage devices(dynamic RAM), energy conversion, actuators, sensors, tunable microwave devices, super-capacitors, spintronics, solid oxide fuel cells etc. Being the end member of Ruddlesden Popper (RP) series ABO₃ perovskites establish foundation of exotic electronic properties displayed by other RP members with reduced dimensionality. SrCoO₃ in particular, attracts attention because it remains stable in cubic structure. It shows ferromagnetic (FM) behaviour with a high curie temperature(T_c) of around 305 K and resides in negative charge transfer regime. The compounds, say BaCoO₃, a small-gap semiconductor has T_c 250 K⁴ and metallic CaCoO₃ has T_c 54 K⁵. The room temperature T_c of SrCoO₃ compared to these cobalt oxides belonging to same family, makes SrCoO₃ an interesting compound for investigation. But existing literature is very limited and that too mostly using static mean-field. Thus, in this work, our aim is to perform a consistent first-principle based beyond static -mean field study to understand effect of electronic correlations in determining magnetic properties of this compound.

COMPUTATIONAL DETAILS

SrCoO₃ crystallizes in simple cubic crystal with space group Pm-3m. DFT calculations were performed using full potential based WIEN2k⁶ code. The lattice parameter of 3.77 Å obtained through volume optimization. We employed GGA-PBEsol⁷ exchange-correlation functional. All calculations were performed over a mesh size of 12x12x12 keeping RMTKmax equal to 7. The RMT values for Sr, Co and O were taken as 2.30 au, 1.87 au and 1.61 au respectively. The convergence criteria was set for charge at 10⁻⁴ Coulomb/cell. DMFT calculations have been carried out using eDMFT⁸ code. Here impurity model of DMFT is solved using CTQMC (continuous-time Quantum Monte Carlo) impurity solver with *exactd* double counting scheme and *full* type of Coulomb potential. The value of Coulomb interaction parameters U and J were calculated using constrained Random Phase approximation as implemented in GAP2 code⁹.

RESULTS AND DISCUSSION

For calculating partially screened Coulomb interaction parameters U and J , all the bands having $3d$ character

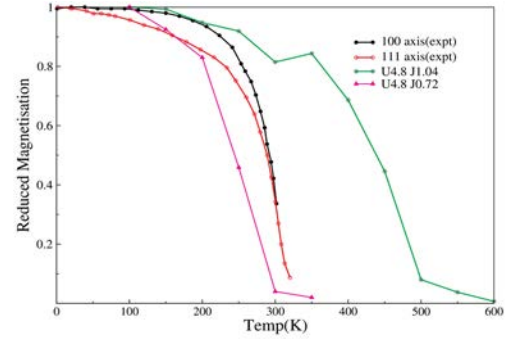
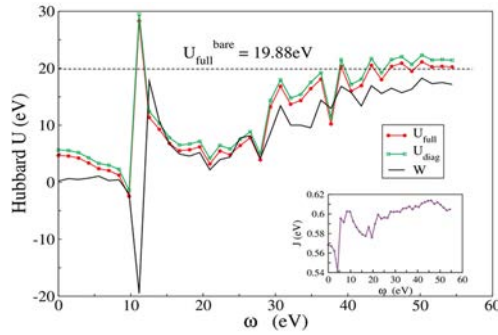


FIGURE 1. Coulomb Interaction parameters as a function of ω **FIGURE 2.** Temperature Dependence of Magnetisation

which spread across the energy window of -8 eV to 4 eV were selected for wannierization. The variation of U , J and fully screened Coulomb interaction W with ω has been plotted in Fig.1. $U_{full(diag)}$ is the average of all(/diagonal) elements of resulting U matrix. The difference in values of W and U signifies the need to eliminate $3d$ - $3d$ transition for calculating appropriate value of U to be used in DFT+DMFT calculations where intra- $3d$ orbital screening is already included. The large difference between the value of bare Coulomb interaction U_{bare} and screened Coulomb interaction at low frequencies shows the importance of screening effects in correlated systems. In the static limit i.e. at $\omega = 0$, $U_{full} = 4.80$ eV, $U_{diag} = 5.68$ eV and $J = 0.51$ eV. Around 12 eV, U shows a dip in value which could be attributed to plasmonic excitation. This plasmon excitation frequency agrees well with the typical range of 5 - 15 eV reported for metals. At very high frequencies, the polarization vanishes indicating minimized screening effects, therefore screened Coulomb interaction parameters W and U approach the value of bare Coulomb interaction $U_{full}^{bare} = 19.88$ eV and $U_{diag}^{bare} = 21.25$ eV. On the other hand, partially screened J shows a relatively constant value of 0.6 eV over entire frequency range. Miyake et al¹⁰ have shown that the dependency of Coulomb interaction parameters on the basis function is very small and thus using the cRPA calculated U and J for DFT+DMFT calculations should not affect results of this work. However, since T_c value is typically seen to be sensitive to J , we have applied a conversion factor of $7/5$ to the static value of $J = 0.51$ eV to account for difference in basis set of cRPA and eDMFT code. Henceforth, we have used value of $J_{crpa} = 0.72$ eV and $U_{full} = 4.80$ eV for DFT+DMFT calculations.

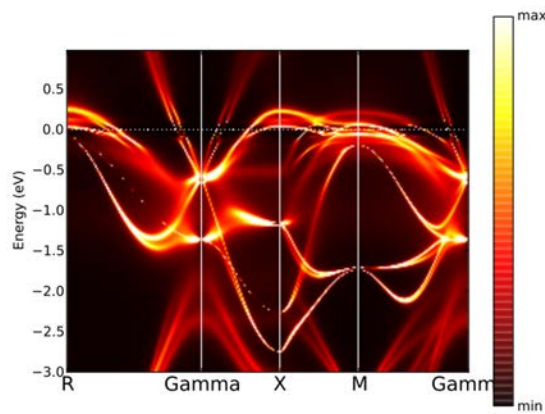


FIGURE 3. Momentum resolved spectral function at 200 K

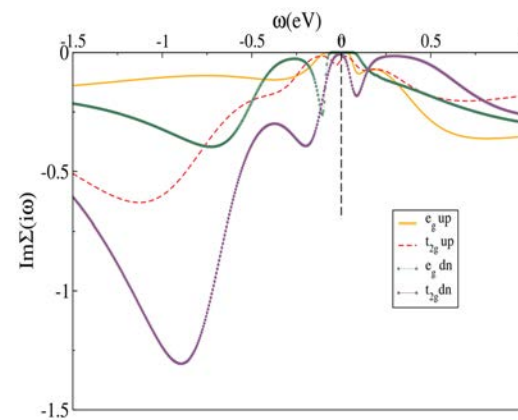


FIGURE 4. Imaginary part of self-energy at 200 K

In Fig.2 we have plotted reduced magnetization which is calculated by dividing magnetization at a particular temperature by the saturation magnetization ($0.92\mu\text{B}/\text{Co}$ at 100K). It was observed that $J_{\text{yukawa}} = 1.04$ calculated using Yukawa potential in eDMFT code, overestimated value of T_c to almost twice of the experimental value of 305K . Whereas, for J_{crpa} , the magnetization curve agrees qualitatively with experimental curve giving $T_c \sim 300\text{K}$, though it highly underestimates the saturation magnetization. Figure 3 shows momentum-resolved spectral function plot at temperature 200K . Here min and max denote the increasing order of the degree of coherency of the states. It is observed that in the energy window of -0.2eV to 0.2eV around Fermi level, there is a mix of coherent and incoherent features. Here t_{2g} - dn states are coherent while e_g - up states contribute to incoherence. Below -0.5eV , there is large incoherence majorly due to t_{2g} - dn states. The existence of these incoherent features can be verified from imaginary part of self energy $\text{Im}\Sigma(\omega)$ at 200K shown in Fig. 4. The value of $\text{Im}\Sigma(\omega)$ indicates inverse lifetime of quasiparticle. Hence, the small finite value of $\text{Im}\Sigma(\omega)$ at Fermi-level indicates quasiparticle of finite lifetime. Around Fermi level (-0.03eV to 0.02eV), $\text{Im}\Sigma(\omega)$ has small but finite value for both t_{2g} and e_g states. This implies that the states in the vicinity of Fermi level are nearly coherent. From 0.04eV to 0.16eV we observe peak like feature indicating small incoherence due to these states. Beyond $\pm 0.5\text{eV}$, the $\text{Im}\Sigma(\omega)$ starts gaining finite value for both the states. The incoherent features in valence band are contributed by t_{2g} states while incoherency in conduction band is due to e_g states. For a Fermi-liquid, inverse quasiparticle lifetime Γ shows quadratic variation with temperature. Therefore, we plotted Γ/T vs. T in Fig.5. Here we get almost linear variation validating the Fermi-liquid behaviour.

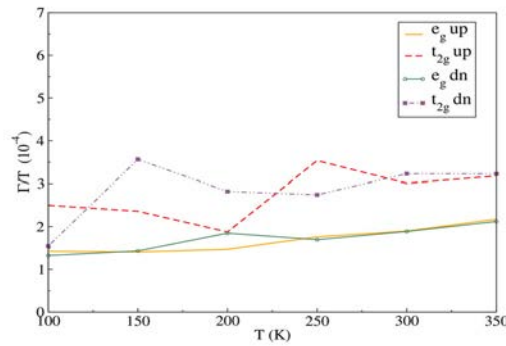


FIGURE 5. Variation of inverse quasiparticle lifetime with temperature

CONCLUSION

In summary, we have used DFT+DMFT approach to investigate electronic and magnetic properties of cubic the incoherent states. The temperature-dependent quasiparticle lifetime and $\text{Im}\Sigma(\omega)$ confirm Fermi-liquid behavior and moderate correlations. Our study emphasizes the key role of Hund's coupling in dictating the magnetism and electronic structure of this system.

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Length-Dependent Localization of Majorana Bound States in Rashba and Magnetically Textured Nanowires

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Abstract. We study the spatial localization of Majorana bound states in finite one-dimensional nanowires with effective p-wave superconductivity induced via Rashba spin-orbit coupling, Zeeman field, and proximity-induced s-wave pairing. Additionally, we explore an analogous system without any external magnetic fields by introducing engineered spin-spiral textures that replicate the effects of Rashba spin-orbit coupling and Zeeman field. By computing the local density of states of the two zero-energy quasiparticle eigenstates as a function of wire length, we identify two critical length scales, L_{c1} and L_{c2} , which mark the distinct regimes of localization of Majorana bound states. For $L < L_{c1}$, the states are strongly hybridized, contributing equally at both ends. For $L_{c2} < L$, each state is localized at a separate end, consistent with ideal end-localized Majorana bound states. The intermediate regime ($L_{c1} < L < L_{c2}$) exhibits partial localization with residual overlap. Notably, the crossover occurs at a shorter length in spin-textured nanowires, suggesting stronger Majorana bound states confinement than in Rashba-based systems. These findings provide insight into how finite-size effects govern the emergence and spatial separation of Majorana bound states in realistic platforms.

INTRODUCTION

Kitaev's seminal model of a one-dimensional spinless p-wave superconductor predicts the emergence of zero-energy Majorana bound states (MBS) strictly at the ends of a chain [1]. This elegant theoretical construction has inspired a variety of realistic platforms that emulate Kitaev's model using semiconductor nanowires. A prominent example involves a nanowire with strong Rashba spin-orbit coupling (RSOC), an induced s-wave superconducting pairing and a Zeeman field. In such systems, the interplay of RSOC and Zeeman field effectively yields p-wave pairing in a spin-polarized band, enabling a topological superconducting phase with MBS at the wire ends [3]. Also, the engineered magnetic textures (such as spin spirals or helical fields) can simulate the required RSOC and magnetic field, thereby enabling topological superconductivity even in the absence of an external magnetic field [4].

The realization of MBS is of great interest not only for their fundamental non-Abelian exchange statistics but also for their potential use in fault-tolerant topological quantum computing [2]. However, practical nanowires differ significantly from Kitaev's idealized chain. In realistic finite-length systems, the spatial separation of the MBS is limited, leading to overlap between the end-localized modes. This overlap lifts the exact zero-energy degeneracy and leads to a hybridization of the states. Consequently, the physical properties associated with isolated MBS, such as quantized zero-bias peaks and topologically protected qubits, are compromised [5]. It is therefore essential to understand how the wire length L affects the localization and hybridization of these zero-energy MBS.

In this work, we use Bogoliubov-de Gennes (BdG) technique to study finite-length nanowires with either RSOC and Zeeman field or spin-spiral textures. We compute the local density of states (LDOS) of the two zero-energy quasiparticle eigenstates as a function of the wire length and extract quantitative signatures of their spatial localization. Our analysis reveals two critical length scales, L_{c1} and L_{c2} , that mark a smooth crossover from hybridized to spatially separated MBS. The transition between these regimes captures the gradual suppression of MBS overlap and clarifies how finite-size effects mediate the emergence of ideal end-localized MBS. These results offer valuable insights for experimental efforts to engineer topological qubits in finite-length nanowires.

MODEL AND METHOD

We use the model Hamiltonian for the nanowire described below [6]

$$\begin{aligned}
H = & (4t - \mu) \sum_{i,\sigma} c_{i,\sigma}^\dagger c_{i,\sigma} - t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + H.c.) + \Delta \sum_i (c_{i,\uparrow}^\dagger c_{i,\downarrow}^\dagger + H.c.) \\
& - \left(\frac{g^* \mu_B}{2} \right) \sum_{i,\sigma,\sigma'} ([\mathbf{B}_{ext} + \mathbf{B}_i] \cdot \boldsymbol{\sigma})_{\sigma,\sigma'} c_{i,\sigma}^\dagger c_{i,\sigma'} - \left(\frac{i\alpha}{2a} \right) \sum_{\langle i,j \rangle, \sigma, \sigma'} (\boldsymbol{\sigma} \times \mathbf{d}_{ij})^z_{\sigma,\sigma'} c_{i,\sigma}^\dagger c_{j,\sigma'}
\end{aligned}$$

where $c_{i,\sigma}^\dagger$ ($c_{i,\sigma}$) is the fermionic creation (annihilation) operator at site i with spin σ , t is the hopping energy, a is the unit lattice spacing of the one-dimensional lattice, Δ is the proximity-induced superconducting gap, and μ is the chemical potential. Fourth term expresses both the external field $\mathbf{B}_{ext}$ and the spin spiral texture ($\mathbf{B}_i$ at site i) under the one-dimensional lattice. where g^* is the effective g -factor of electrons, μ_B is the Bohr magneton, and $\boldsymbol{\sigma}$ represents the Pauli spin matrices. The last term represents the Rashba SOC with strength α originating from the broken-structure inversion symmetry and $\mathbf{d}_{ij}$ is the unit vector between sites i and j . We use $m^* = 0.026 m_0$ (the effective mass for InAs), $a = 10$ nm, $\Delta = 0.2$ meV, $\alpha = 30$ meV-nm and $g^* = 10$, unless otherwise specified. We diagonalize the Hamiltonian using a unitary transformation of the fermionic operators $c_{i\sigma} = \sum_n (u_{i\sigma}^n \gamma_n + v_{i\sigma}^n \gamma_n^\dagger)$, where $u_{i\sigma}^n$ ($v_{i\sigma}^n$) represents quasiparticle (quasihole) amplitude, and γ_n ($\gamma_n^\dagger$) is a fermionic annihilation (creation) operator. The profile of the LDOS is obtained using $\rho_i = \sum_\sigma (|u_{i\sigma}|^2 + |v_{i\sigma}|^2)$, corresponding to the lowest-energy quasiparticle eigenstates at $\mu = 0.1$ meV for Rashba nanowire and $\mu = 0.25$ meV for spin spiral textured nanowire.

RESULTS

Our simulations reveal a clear length-dependent crossover in the localization behavior of zero-energy quasiparticle states in finite nanowires, both with RSOC coupling and engineered magnetic textures. We compute the LDOS in the topological regime, focusing on the two zero-energy eigenstates across varying nanowire lengths. Figure 1(a) presents the maximum LDOS within the left half of the Rashba nanowire, capturing the Majorana peak localized at one end. For short nanowires up to a critical length L_{c1} , both ρ_1 and ρ_2 (LDOS for the two quasiparticle energy eigenstates at zero) contribute equally to the Majorana peak at each end, indicating an equal-weight localization pattern. As the wire length increases beyond L_{c2} , this symmetric localization changes, either ρ_1 or ρ_2 exclusively localizes at a particular end, and the other at the opposite end, each with doubled intensity. In the intermediate regime $L_{c1} < L < L_{c2}$, the contributions are mixed, defining a distinct crossover from hybridized to spatially separated Majorana localization.

Figure 1(b) further highlights this crossover by quantifying the LDOS asymmetry between the two ends, showing that the peak-height difference remains negligible for $L < L_{c1}$, and then rises past $L > L_{c2}$. To assess the overlap of the zero-energy states in the bulk, we compute the maximum LDOS over the central 20 sites of the nanowire, shown in Fig. 1(c). The order of the LDOS in the middle of the nanowire is 10^{-5} , about three orders of magnitude lower than at the ends and becomes negligible as the wire length increases beyond L_{c2} , indicating vanishing overlap between the Majorana wavefunctions.

The same phenomenology holds for nanowires with a spiral magnetic texture [Figs. 1(d)–(f)]. Notably, the crossover in this case occurs at shorter lengths compared to the Rashba nanowire. Figures 1(g)–(j) show spatial LDOS distributions for zero-energy quasiparticle eigenstates at two different lengths. At $L = 800a$, both ρ_1 and ρ_2 contribute to both ends, while at $L = 1700a$, both ρ_1 and ρ_2 localize exclusively at opposite ends, each contributing fully and independently.

CONCLUSION

These findings carry direct implications for experimental platforms targeting Majorana bound states and topological quantum computation. Only nanowires longer than L_{c2} , which in our case came around $16 \mu m$ for Rashba nanowire and $13 \mu m$ for spin spiral textured nanowire, can host well-isolated MBS. In contrast, wires of length shorter than L_{c2} exhibit spectral overlap, split peaks, and diminished topological protection. Our work thus quantitatively establishes the critical lengths for pristine nanowires necessary to achieve robust Majorana localization and design fault-tolerant topological qubits in finite-size systems.

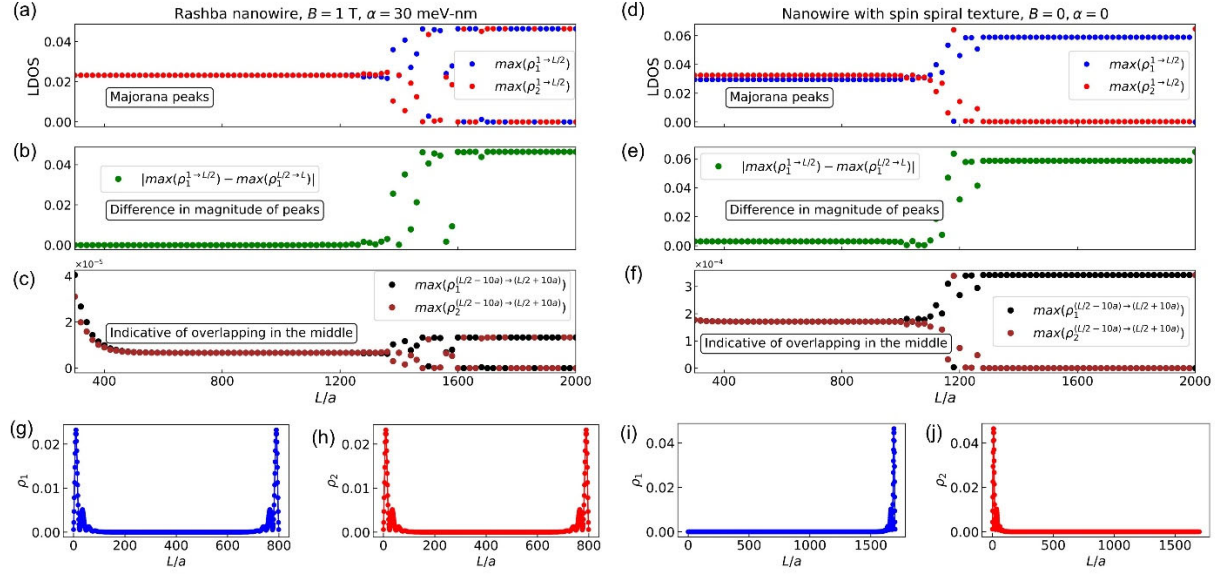


FIGURE 1. (a) shows the variation of maximum value of LDOS in the first half of the Rashba nanowire corresponding to the two quasiparticle energy eigenstates at zero energy as the length of the nanowire increases. (b) shows the variation of the magnitude of the difference between the maximum LDOS corresponding to the one quasiparticle energy eigenstates at zero energy in the first half and second half of the Rashba nanowire as the length of the nanowire increases. (c) shows the variation of the maximum value of the LDOS corresponding to the two quasiparticle energy eigenstates at zero energy in the middle of the nanowire spanning 20 sites as the length of the nanowire increases. (d), (e) and (f) show the same information as in (a) (b) and (c) but for nanowire proximitized with spin spiral magnetic texture and without any external magnetic field and RSOC. (g)-(j) ρ_1 and ρ_2 (LDOS for the two quasiparticle energy eigenstates at zero) for nanowire of lengths $L = 800a$ and $1700a$.

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Mn Doping Effects on Structural and Magnetic Properties of NiFe_2O_4 Nano-Ferrites

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Abstract. Mn-doped nickel ferrite nanoparticles with the formula $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) were synthesized using the sol-gel auto-combustion method. X-ray diffraction study confirmed a cubic spinel structure, with the lattice parameter increasing systematically with Mn^{2+} content. SEM images revealed spherical nano-sized particles with slight agglomeration. Saturation magnetization (Ms) measured by SQUID varied from 25.55 to 44.26 emu/g, and all samples showed low coercivity, confirming their soft magnetic nature. The composition-dependent variations in structural and magnetic properties make these ferrites attractive for soft magnetic applications.

INTRODUCTION

Nickel ferrite (NiFe_2O_4) is a soft ferrimagnetic material that crystallizes in an inverse spinel structure and is extensively utilized in transformer cores, inductors, magnetic recording media, and microwave devices due to its low eddy current losses, high electrical resistivity, and good chemical stability [1,2]. The properties of spinel ferrites can be effectively tailored through cation substitution, which alters the cation distribution between the tetrahedral (A) and octahedral (B) sites of the lattice. Partial substitution of divalent cations such as Mn^{2+} at the Ni^{2+} site in NiFe_2O_4 can significantly modify the superexchange interactions between magnetic ions, thereby enhancing or tuning the magnetic and electrical properties of the material [3,4].

At the nanoscale, additional factors such as finite particle size, surface effects, and increased surface-to-volume ratio further influence the magnetic behavior, often resulting in properties that differ markedly from their bulk counterparts [3]. Therefore, studying the combined effects of cation substitution and particle size reduction provides valuable insights into the design of ferrite materials with optimized properties for advanced technological applications.

In the present work, Mn-doped NiFe_2O_4 ($\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$) nano-ferrites were synthesized using the sol-gel auto-combustion method, a versatile low-temperature technique capable of producing homogeneous, fine-grained powders [5]. The influence of Mn substitution on structural parameters, and magnetic properties of the resulting nano-ferrites was investigated.

EXPERIMENTAL

Nickel nitrate, manganese nitrate, and ferric nitrate precursors (AR grade) were mixed in stoichiometric ratios with citric acid as the fuel and chelating agent. The solution was continuously stirred and heated at 80°C on a magnetic stirrer until it transformed into a viscous gel. The temperature was then raised to 200 °C to initiate auto-ignition of the gel to form ferrite powders and subsequently calcined at 500 °C for 5 hours. The phase formation and lattice parameters were determined using X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation. The surface morphology and particle size of the synthesized samples were examined using scanning electron microscopy (SEM), while the magnetic properties were studied by recording room-temperature M–H hysteresis loops with a SQUID magnetometer.

RESULTS AND DISCUSSION

XRD patterns (Fig. 1) confirmed the formation of a cubic spinel structure for all compositions with minor secondary phase consistent with previous reports [3]. The diffraction peaks were sharp and well defined, indicating good crystallinity. As indicated in Table 1, the lattice parameter increased with Mn doping due to the larger ionic radius of Mn^{2+} (0.83 Å) compared to Ni^{2+} (0.69 Å). SEM micrograph and the corresponding particle size distributions of the NiFe_2O_4 sample are shown in Fig. 2(a). Nearly spherical nanoparticles were observed with some degree of agglomeration, which is common in ferrite nanoparticles due to interparticle magnetic interactions. The average particle size ranged from 15.15 nm to 19.5 nm, confirming nanoscale dimensions. M-H hysteresis loops (Fig. 2b), along with plots of saturation magnetisation (Fig. 3a), retentivity and coercivity (Fig. 3b), confirmed that all compositions exhibit soft magnetic behaviour with low coercivity. The saturation magnetization (M_s) initially increased with Mn substitution up to $x = 0.4$, then decreased at higher Mn doping levels. The observed maximum in M_s at $x = 0.4$ is a result of the optimal balance between enhanced B-sublattice moment due to Mn^{2+} substitution and minimal occupation of Mn^{2+} ions at A sites. Beyond this composition, the disruption of sublattice alignment and reduced exchange interaction lead to lower M_s values [1,3].

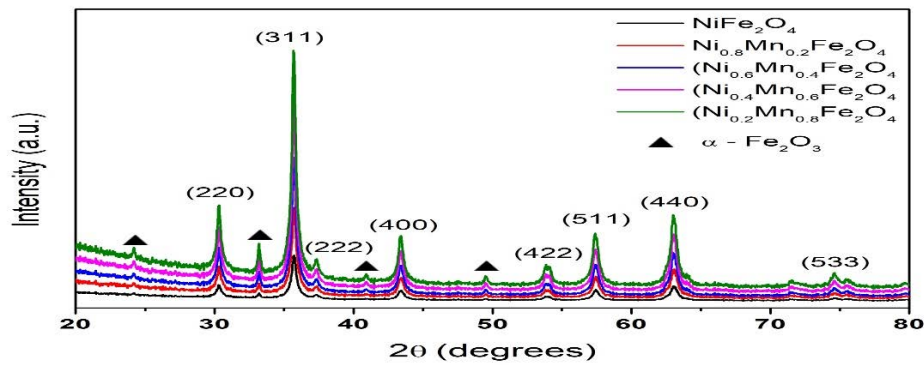


FIGURE 1. X-ray Diffraction patterns of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$)

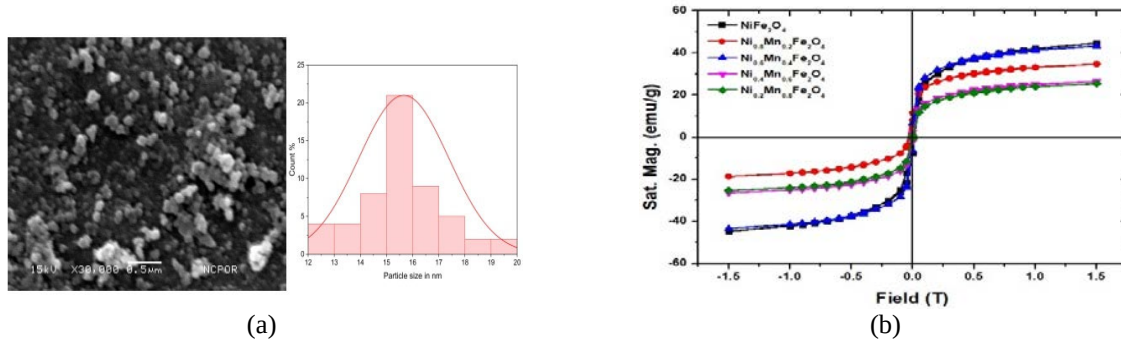


FIGURE 2. (a) SEM image and histogram of NiFe_2O_4 (b) Room temperature M-H hysteresis loops of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$)

TABLE 1. Lattice parameter, Average Particle Size estimated from SEM images, Saturation Magnetisation, Retentivity and Coercivity of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$)

Sample	Lattice Parameter a (Å)	Average Particle Size (nm)	Saturation Magnetisation M_s (emu/g)	Retentivity M_r (emu/g)	Coercivity H_c (T)
NiFe_2O_4	8.3360	15.66	44.26	6.25	0.016
$\text{Ni}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$	8.3376	15.15	34.69	3.37	0.012
$\text{Ni}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$	8.3381	19.50	43.35	4.74	0.011
$\text{Ni}_{0.4}\text{Mn}_{0.6}\text{Fe}_2\text{O}_4$	8.3423	17.02	26.51	1.02	0.0068
$\text{Ni}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$	8.3438	19.04	25.55	1.23	0.0026

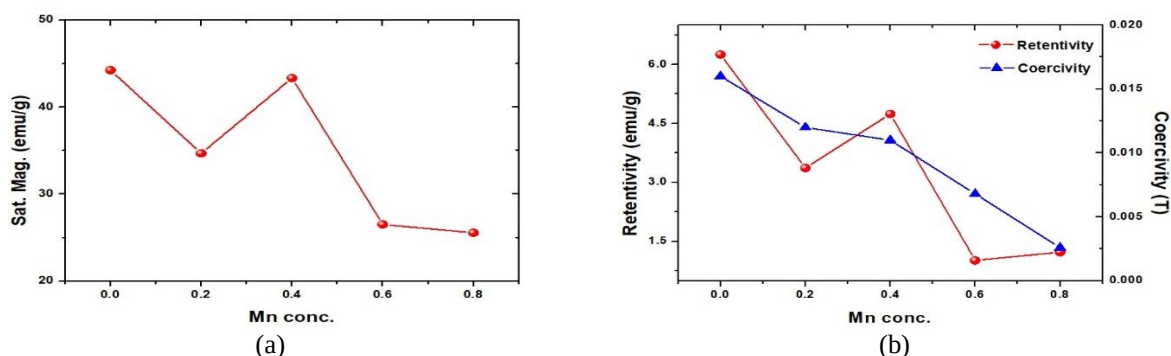


FIGURE 3. (a) Variation of saturation magnetisation with Mn concentration (b) Variation of retentivity and coercivity with Mn concentration of $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.2, 0.4, 0.6, 0.8$)

CONCLUSIONS

Mn-doped NiFe_2O_4 nano-ferrites were successfully synthesized by the sol-gel auto-combustion method. XRD confirmed a single-phase cubic spinel structure with increasing lattice parameter upon Mn doping. SEM revealed nearly spherical nano-sized particles. SQUID analysis showed that all compositions exhibited soft magnetic characteristics. The saturation magnetization (M_s) showed a composition-dependent variation, reaching a maximum at $x = 0.4$. This behavior is attributed to the optimal enhancement of the B-sublattice moment at moderate Mn substitution, whereas higher Mn levels lead to redistribution of Mn^{2+} ions and reduced super-exchange interactions, thereby lowering M_s . These tunable structural and magnetic properties make Mn-doped NiFe_2O_4 suitable for soft magnetic device applications.

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Field Induced Spin Dynamics and Schottky anomaly in $\text{Gd}_2\text{Hf}_2\text{O}_7$ Pyrochlore

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Abstract. In This study we investigate the structural and magnetic properties of disorder pyrochlore oxide $\text{Gd}_2\text{Hf}_2\text{O}_7$. polycrystalline sample of $\text{Gd}_2\text{Hf}_2\text{O}_7$ synthesized with solid state chemical method. we perform a comprehensive analysis magnetization, to understand the evaluation of spin dynamic under the effect of external magnetic field 0 - 70 Oe and temperature variation 1.8 K to 300 K. we observe the effective magnetic moment $\mu_B = 7.92 \mu_B$ for the free ion $^8S_{7/2}$ ground state of Gd^{3+} and isothermal magnetization measurements confirm the presence of weak single-ion anisotropy. No visible evidence of glassiness in magnetization.

INTRODUCTION

In magnetic materials, geometrical disorder creates many intrinsic complications, like geometrical frustration, competing magnetic interactions and constraints on spin's degree of freedom, which is dramatically impacts the ground state of material. The interplay between geometry of lattice structure and spin systems, are key to understand the competition of magnetic interaction. $\text{R}_2\text{M}_2\text{O}_7$ rare earth oxides have attracted significant interest due to their unique low temperature spin dynamics, it influenced a frustration in system. magnetic pyrochlore oxides exhibits strong frustration in case of antiferromagnetic exchange interaction between spins [1]. Well known spin ice material $\text{Dy}_2\text{Ti}_2\text{O}_7$ and $\text{Ho}_2\text{Ti}_2\text{O}_7$ possess a finite residual entropy skin to Pauling value of water ice[2]. Many experiments report a lack of long-range ordering down to very low temperature, along with it an unusual spin fluctuation spectrum indicate a significant density of low energy excitations. The numerous combinations of corner sharing tetrahedra configuration of R and M site ions in $\text{R}_2\text{M}_2\text{O}_7$, are utilized to substitute the current spin ice state and disrupt the symmetry of the crystal structure. Besides of titanium, Zirconate and hafnate pyrochlores offers the novel approach to discovering similar magnetic ground state. In case of $\text{R} = \text{Gd}^{3+}$ and Er^{3+} set of pyrochlore shows much convenient behavior to have a long-range antiferromagnetic order[3,4]. The Gadolinium pyrochlores, $\text{Gd}_2\text{M}_2\text{O}_7$ ($\text{M} = \text{Ti}, \text{Sn}, \text{Ge}, \text{Pt}, \text{and Zr etc.}$) contains the key features of Heisenberg antiferromagnet and demonstrate a long-range ordering down to dilution temperature[5]. Weaker interactions dipole-dipole, next-nearest-neighbor exchange, and single-ion anisotropy—collectively lift ground-state degeneracy, stabilizing a specific ordered phase.

EXPERIMENTAL DETAILS

The polycrystalline sample is synthesized by Solid State Reaction Method. the rare earth oxide Gd_2O_3 (99.99% purity) was pre-heated for several hours at 300°C and add HfO_2 (99.99% purity) in stoichiometric amount. The constituent mixture is heated at 1350°C for 50 hours with several intermediate grinding and the final heat treatment was given to pallet at the same temperature. The room temperature powder X-Ray Diffraction (XRD) was performed with Cu K_α Source of wavelength $1.54\text{\AA}$ in 2θ range $10^\circ - 90^\circ$ to examine the phase purity. We have use Rietveld Refinement on XRD Pattern with Fullprof software to know the Crystal Structure and VESTA program for Visualization of Structure. The magnetic measurements were carried out using Magnetic property Measurement System (MPMS-III Quantum Design Built) in the temperature range 1.8K – 300K.

RESULTS AND DISCUSSION

The Powder XRD Pattern of $\text{Gd}_2\text{Hf}_2\text{O}_7$ in single phase with cubic pyrochlore Structure shown in Fig. 1(a). The modeling of XRD pattern with space group Fd-3m (No. 227), the atomic position of Gd atom is at 16d ($1/2, 1/2, 1/2$), the Hf atom at 16c (0, 0, 0), the O_1 atom at 48f ($x, 1/8, 1/8$), and the O_2 atom at 8b ($3/8, 3/8, 3/8$) site. The obtained

crystallographic parameter is listed in table 1. The obtained lattice parameter is very close to $\text{Gd}_2\text{Zr}_2\text{O}_7$ ($a = 10.53 \text{ \AA}$) [3]. It shows the presence of superstructure pyrochlore peaks as (1, 1, 1) and (3, 1, 1) at 14.5° and 28° . According to the pyrochlore stability rule of $r_A/r_B = 1.12 \text{ \AA}$ value lies beyond the range of stable pyrochlore ($1.48 \text{ \AA}$ to $1.78 \text{ \AA}$) which is smaller than other Gadolinium based pyrochlore.

The structure (Fig. 1b), with bond lengths/angles from VESTA (Table 1), was extracted. The various bond length makes a unique tetrahedra with magnetic ion. the bond angle α between oxygen $\text{O}_2\text{-O}_2\text{-O}_2$ atoms and 48f oxygen site's x-axis are distortion parameter for structure differences, order fashion rather than a perfect cube around Gd^{3+} . Here, the $\alpha = 102.27^\circ$, indicate a large deformation from the fluorite structure.

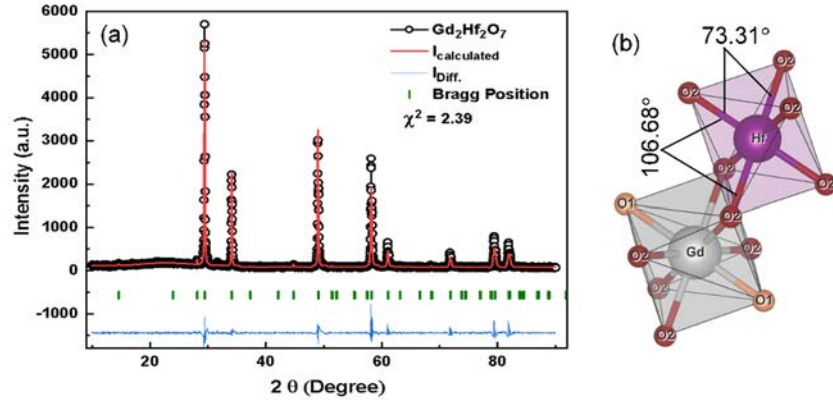


FIGURE 1 (a) Room-temperature X-ray diffraction (XRD) pattern of $\text{Gd}_2\text{Zr}_2\text{O}_7$ pyrochlore, confirming the expected cubic fluorite-related structure. (b) Local coordination environment of Gd^{3+} (rare-earth cation) surrounded by distorted GdO_8 octahedra and HfO_6 octahedra (not tetrahedra, per standard pyrochlore geometry), highlighting the $\text{O}_2\text{-Hf-O}_2$ bond angles. Two distinct oxygen sites, O_1 (light red) and O_2 (red), coordinate to Gd^{3+} with differing Gd-O bond lengths.

Illustrate the Temperature dependent DC Susceptibility χ_{DC} at 100 Oe is configured in Fig.2 (a). The data showing paramagnetic behavior under both Zero Field Cooling (ZFC) and Field Cooling (FC) with completely overlapped curve. There is no bifurcation between FC cooling and FC warming data, so it assures that there is no visual significance of glassiness. Inset - Fig.2 (a). represent fitting of inverse DC magnetic Susceptibility χ_{DC}^{-1} is collected above 50 K by Curie Weiss law as

$$\chi_{\text{DC}} = \chi_0 + \frac{C}{T - \theta_{\text{CW}}}$$

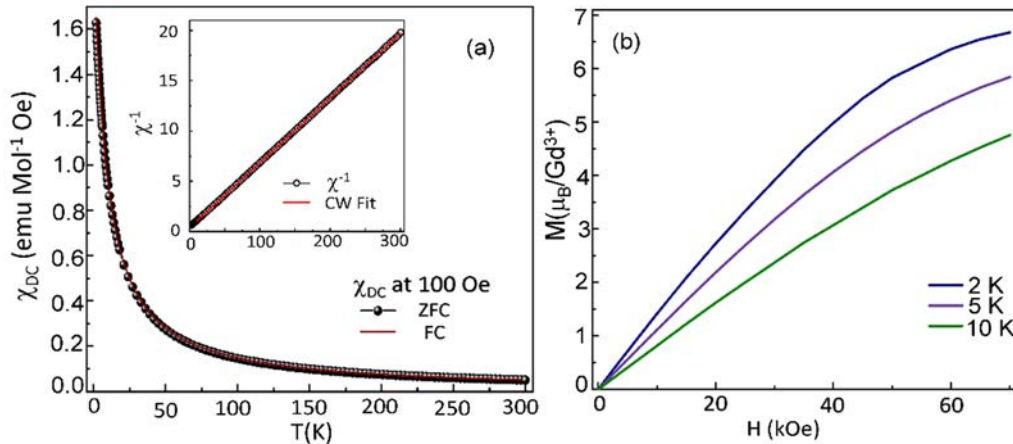


FIGURE 2. (a) The DC Susceptibility nature with temperature variation in the range of 1.8K to 300K. inset (a) shows the Curie Weiss fit to inverse Susceptibility data above 300K. (b) represent the Field dependent Magnetization at 2, 5 and, 10K. it shows a saturation moment of $\sim 7\mu_B/\text{Gd}^{3+}$ indicate a mixture of higher crystal Field Level.

Here, in this equation χ_0 is temperature independent variable represented the core diamagnetism or Pauli Paramagnetism. C is a Curie Weiss constant, θ_{CW} is CW temperature and, T used for Temperature. the CW fitting

yields $\chi_0 = 1.36 \times 10^{-4}$ Curie Weiss temperature $\theta_{CW} = -6.23$ K and $\mu_{eff.} = 7.92 \mu_B$ for free ion $^8S_{7/2}$ for ground state Gd^{3+} [6,7]. Further The validation of $g \sim 2$ value calculated by using expected $J = S = 7/2$, and $\mu_{eff.} = g\mu_B\sqrt{J(J+1)}$ is agreed with electron spin resonance (ESR) experimental value[8,9]. The isothermal magnetization as a function of applied magnetic field upto 70 KOe at 2 K is shown in Fig.2. (b). As shown the data is monotonically increases at low temperature and achieve a saturation phase at high temperature without showing any hysteresis nature. there is no evidence of long-range ordering upto 2 K low temperature and the saturation magnetization is approaches $\sim 7 \mu_B/Gd^{3+}$ [10].

Tables 1.

TABLE 1. Structural Parameter of $Gd_2Hf_2O_7$ obtained from refinement of Room Temperature XRD.

Parameter	$Gd_2Hf_2O_7$	Bond Length between atoms	Angstrom (Å)
a (Å)	10.51Å	O ₁ -Gd	2.27 Å
X (O1)	0.3630	O ₂ -Gd	2.46 Å
$\angle \alpha$ (O ₂ O ₂ O ₂)	102.27°	O ₁ -O ₂	2.93 Å
$\angle B$ (O ₁ O ₂ O ₂)	83.43°	O ₂ -O ₂	2.66Å

CONCLUSION

We have studied the structural and magnetic properties of $Gd_2Hf_2O_7$, confirming a single-phase cubic pyrochlore structure with local distortions. Magnetic measurements show paramagnetic behavior without glassiness or long-range order down to 2 K. The effective magnetic moment ($7.92 \mu_B$) matches the expected Gd^{3+} free-ion value. Negative Curie–Weiss temperature indicates weak antiferromagnetic interactions. These results suggest $Gd_2Hf_2O_7$ is a promising candidate for exploring frustrated magnetism.

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Heat Capacity of $\text{Ho}_2\text{Sn}_2\text{O}_7$ Pyrochlore at Low Temperatures

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Abstract: $\text{Ho}_2\text{Sn}_2\text{O}_7$ is a rare earth pyrochlore compound known for its geometrically frustrated magnetic interaction which gives rise to exotic ground states including spin ice. Sample is prepared using solid state method. Crystallographic Phase is confirmed by X-ray diffraction to that of pyrochlore structure. We have investigated the heat capacity of $\text{Ho}_2\text{Sn}_2\text{O}_7$ down to 2K and magnetic fields up to 3T. Debye contribution to heat capacity has been estimated and the Debye temperature is found to be 354K. The phonon contribution is subtracted to get magnetic contribution. This magnetic contribution is typical of Schottky anomaly as there is no tangible magnetic ordering seen down to 2K. This demands ultralow temperature investigation below 2K, which is being planned. Magnetization measurements (not shown here) performed from 2K up to 30K shows no ordering. Hence this sample shows all needy precursor state for a spin ice compound. Results will be discussed.

INTRODUCTION

Transition Ice has very complex structure and shows fascinating properties and shows many different phases with varying temperature and pressure. In 1933 Bernal-fowler has shown the first model of ice structure and ice rule viz 2in-2out where molecules are in tetrahedron arrangement[1]. In 1935 Linus Pauling given the concept the residual entropy of ice and has calculated it[2]. In 1956 P.W. Anderson has connected this to proton disorder to spin systems which gives to idea of frustration in magnetic system[3]. Many spin ice compounds have been discovered such as $\text{Dy}_2\text{Ti}_2\text{O}_7$, $\text{Ho}_2\text{Ti}_2\text{O}_7$, $\text{Ho}_2\text{Sn}_2\text{O}_7$, $\text{Dy}_2\text{Sn}_2\text{O}_7$ spin liquids like $\text{Tb}_2\text{Ti}_2\text{O}_7$, $\text{Gd}_2\text{Ti}_2\text{O}_7$ [4]. Ice become a model for spin ice, quantum materials and magnetic monopoles. $\text{Ho}_2\text{Sn}_2\text{O}_7$ has geometrically frustrated system and in $\text{Ho}_2\text{Sn}_2\text{O}_7$ over all magnetic moment is of Ho^{3+} and Ti^{4+} is nonmagnetic [5] in low temperature range the $\theta_{\text{CW}} = 1.8\text{K}$ [6]. It belongs to $\text{Fd-}3\text{m}$ space group. Magnetization below 1K shows slow dynamics of magnetic moment in low temperature region with some small ferromagnetic cluster[7]. In the manuscript we have investigate polycrystalline sample $\text{Ho}_2\text{Sn}_2\text{O}_7$ thermal and magnetic properties.

EXPERIMENTAL DETAILS

The Polycrystalline $\text{Ho}_2\text{Sn}_2\text{O}_7$ sample has been prepared using solid-state reaction. Constituent oxides were used in 1:2 stoichiometric ratio and mixed thoroughly ($\text{Ho}_2\text{O}_3 + 2\text{SnO}_2 = \text{Ho}_2\text{Sn}_2\text{O}_7$). Calcination of the powders was done at 1200°C for 24 hours for the reaction to be proper between precursors. Pellets were made from grounded materials and were kept in furnace for 24 hours at 1200°C for sintering. XRD (X-ray Diffraction) were carried out to study the crystallographic phase as well as its details. QD 14T-PPMS at UGC- DAE CSR Indore has been used to measure heat capacity and specific heat has been estimated from 2-30K and in magnetic fields 0-3 Tesla.

RESULT AND DISCUSSION

X-ray diffraction

The structural XRD has been used to study the crystal structure of $\text{Ho}_2\text{Sn}_2\text{O}_7$. **Figure 1** shows the XRD and its analysis reveal crystallographic purity and homogeneity. Lattice parameter is $10.3778(2) \text{ \AA}$ and a structural refinement using Rietveld technique is carried out for $\text{Ho}_2\text{Sn}_2\text{O}_7$. Results are shown in **Figure 1**.

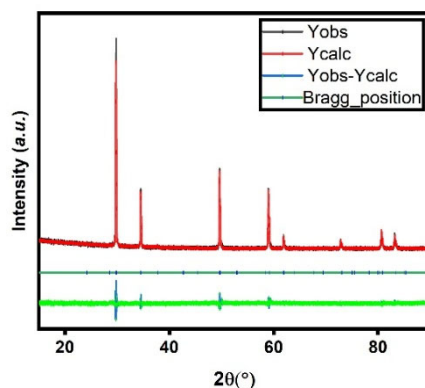


Figure. 1 XRD patterns of $\text{Ho}_2\text{Sn}_2\text{O}_7$. Black color shows observed data and red shows calculated pattern from Rietveld refinement. Blue line shows difference of calculated & observed patterns. Vertical lines are indicative of Bragg peaks.

Heat Capacity

The heat capacity measurements for $\text{Ho}_2\text{Sn}_2\text{O}_7$ have been made in the temperature range of 30-2K with different applied magnetic fields up to 3T with a PPMS system at UGC-DAE CSR Indore using relaxation calorimetry. Since the heat capacity measured is down to 2K only (Figure 2a), it shows no signatures of ordering except a rise at low temperatures. This demonstrates the need to perform measurements of heat capacity below 2K, which will be reserved for future.

Zero Field Specific heat

Zero field specific heat reveals a featureless monotonic trend with a rise at low temperature. This indicates absence of long range ordering. The specific heat of $\text{Ho}_2\text{Sn}_2\text{O}_7$ has a lattice heat capacity (C_L) and a magnetic contribution (C_m) as could be seen by the low temperature rise. To extract more information, we have also shown a graph of C/T versus T^2 as an insert in **Figure 2a**. It reveals a very low lattice contribution. βT^3 is the lattice contribution expected and the same is calculated. Magnetic contribution is C_m is estimated by an analysis of subtracting Lattice Contribution from the total heat capacity. This is done in the region of low temperatures. Estimate of the β is $4.8022 \times 10^{-4} \text{ JK}^{-4}\text{mol}^{-1}$ Ho. Calculated Debye temperature is 354K. These are as per the expectation.

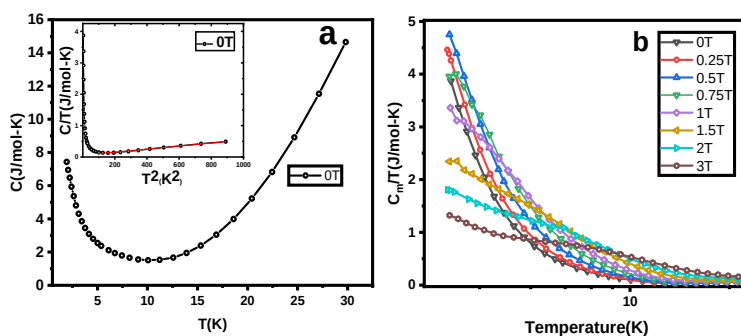


Figure.2. a) Specific heat measurements down to 2K in zero field. Lattice contribution is calculated as $C = \beta T^3$ with $\beta = 4.8022 \times 10^{-4} \text{ JK}^{-4} \text{ mol}^{-1}$. C/T versus T^2 plot is also shown for clarity. **b)** Magnetic heat capacity C_m/T vs Temperature $T(\text{K})$ for $\text{Ho}_2\text{Sn}_2\text{O}_7$. Magnetic fields of 0-3T have been used. Peaks shift to high temperatures and gets broadened upon increasing magnetic fields.

. **Figure b** shows magnetic contribution which is typical of Schottky anomaly as there is no tangible magnetic ordering seen down to 2K. Only partial high temperature portion of Schottky peak is seen. A careful look will reveal that it shifts to high temperature when the field is increased. This is a typical variation of Schottky anomaly. Recently we have reported on the spin-ice observation in $\text{Dy}_2\text{Ti}_2\text{O}_7$ pyrochlore [8] where-in one could see a similar characteristic down to 2K. However, the scenario changes drastically when the measurements are extended below 2K down to 100mk using a dilution refrigerator. This work is reserved for future studies. However, the similarity of the present data with the reported one indicates that $\text{Ho}_2\text{Sn}_2\text{O}_7$ is a suitable candidate to explore spin-ice characters in a different system of interest.

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First-Principles Study of The Intrinsic Characteristics of 2D NaReN₂ Monolayer

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Abstract: The current assessment evaluates the structural, electronic, optical and transport properties of a monolayer of sodium rhenium nitride (NaReN₂). The monolayer crystallizes in trigonal symmetry and possesses metallic behaviour as unveiled by its band structure exhibiting zero band gap. In depth analysis of its optical response, comprising absorption coefficient, reflectivity and refractive index has been performed to highlight its possibility for optoelectronic and photonic applications.

INTRODUCTION

The unfolding of two-dimensional materials in research endeavour can be attributed to the discovery of graphene, from its three-dimensional counterpart graphite, which exhibits a hexagonal crystalline structure[1]. Following that 2D materials have modernized the field of nanotechnology by virtue of their distinguished physical properties and their ability to facilitate device miniaturization with enhanced performance.[2-4] Three-dimensional NaReN₂ is having hexagonal symmetry with space group of P6₃/mmc whereas two-dimensional NaReN₂ monolayer crystallizing in trigonal structure having space group P3m1. No previous studies have published on the NaReN₂ monolayer by means of first principles study. In the present study, nature of material, electronic and optical properties are simulated and interpreted

COMPUTATIONAL STRATEGIES

The Density Functional Theory computations were executed for the quaternary compound NaReN₂ to investigate its ground state structural stability and optical response. simulations were implemented utilizing WIEN2K package, grounded in the Full-potential Linearized Augmented plane wave method[5]. The self-consistent field cycle was regarded as converged when the total energy difference between consecutive iterations was less than 10⁻³ Ry. 10 x 10 x 1k point grid were utilized under the Monkhorst – pack scheme for Brillouin zone integrations.

RESULTS AND DISCUSSION

STRUCTURAL PROPERTY

Two-dimensional monolayer structure of NaReN₂ with trigonal symmetry with the space group of P3m1, inferred from the bulk phase was developed to investigate its structural and electronic properties. Initiated from the experimentally reported 3D lattice parameters, 2D structure was acquired by slicing along the appropriate crystallographic plane and inserting reasonable vacuum spacing, 15Å [6].

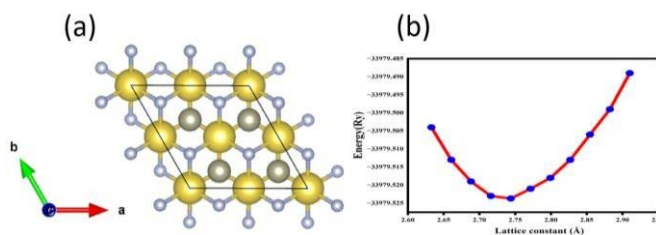
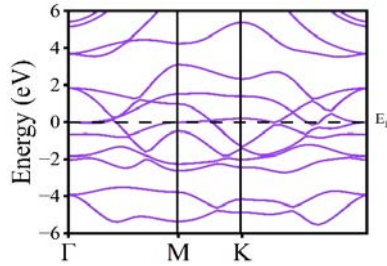


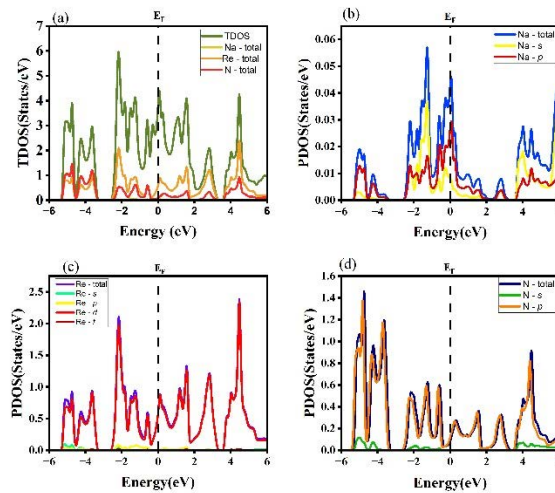
FIGURE 1. (a) Structure of NaReN₂ monolayer, (b) optimization curve of NaReN₂ monolayer

ELECTRONIC PROPERTY

The electronic band structure calculation utilizing GGA exchange–correlation was performed within the WIEN2K framework. The outcome unveil that the NaReN₂ monolayer depicts metallic behavior, since the conduction and valence bands intersect at the fermi level, featuring no band gap. The band structure was graphed along high-symmetry directions in the Brillouin zone, employing the k-path assigned Γ M K Γ . The schematic structure of the trigonal NaReN₂ monolayer and lattice constant versus the energy plot is displayed in the Fig.1 and band structure in Fig.2.

**FIGURE 2.** Band structure of NaReN₂ monolayer.

The total and partial density of states of the NaReN₂ monolayer were computed to reaffirm its metallic nature and to specify the orbital contributions around the fermi level. The DOS results evidently indicates a finite density of states at the fermi energy, which is a distinctive trait of metallic systems. This validates the inexistence of a band gap and justifies the results acquired from the band structure analysis. As depicted in the Fig.3 partial DOS , it is apparent that the Na-s, Re-d, and N-p orbitals make a significant contribution near Fermi level.

**FIGURE 3.** TDOS and PDOS of NaReN₂ monolayer

OPTICAL PROPERTIES

The optical properties of the NaReN₂ monolayer were analysed by computing the absorption coefficient, reflectivity and refractive index. From Fig the absorption initiates from 0 eV and the highest peak at 85.991 with 9.34 eV photon energy ,signifying that the material can absorb photons of low energy. Reflectivity and refractive index have the maximum peak at infra-red region and as the energy increases peaks gradually decreases.

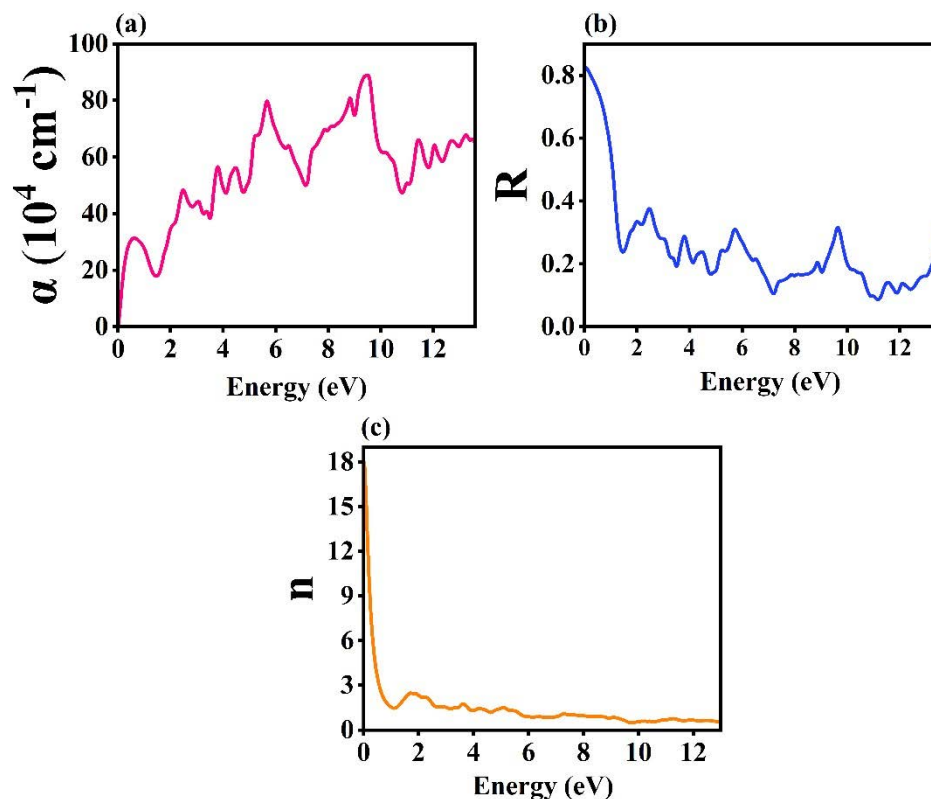


FIGURE 4.(a) is the absorption coefficient, (b) and (d) are reflectivity and refractive index of 2D-NaReN₂.

CONCLUSION

In summary, the structural , electronic and optical properties of the theoretically predicted NaReN₂ monolayer is obtained by way of first principles study in WIEN2K software. The NaReN₂ monolayer has a trigonal structure and has metallic nature.

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Influence of Strontium Doping on the Heat Capacity Properties of CuCrO₂ Delafossite

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Abstract: CuCrO₂ is a delafossite oxide. It has a layered rhombohedral crystal structure (R-3m). As such, it demonstrates exceptional thermodynamic performance and has great potential as an electronic material. In this paper we present an analysis of the structural and thermal properties of 5% strontium (Sr) doped CuCrO₂, focusing on how this modification affects the material. X-ray diffraction analysis confirmed that Sr was successfully incorporated into the lattice (i.e., rhombohedral structure), and also exhibited a shift in the antiferromagnetic transition temperature (~24.5 K) of the undoped CuCrO₂ to ~23.5 K upon incorporation of 5% Sr. It provides valuable information regarding the impact of Sr on the thermodynamic behavior of CuCrO₂ and can be used to modify the functional properties of this material.

INTRODUCTION

Delafossite oxides have a crystal structure with alternating monovalent A-site cations (typically Cu⁺), which are coordinated linearly, and BO₆ octahedra that are edge-sharing. The B-site is occupied by trivalent metals (Cr³⁺ is common), giving delafossite oxides an anisotropic structure. This layer structure is important to their transparency, and it also affects their electrical, magnetic, and thermal characteristics^{1,2}. CuCrO₂ has received significant attention for its dual properties of being intrinsic p-type conductivity and exhibiting antiferromagnetism at low temperatures³. These dual properties are rare for TCOs. Doping is an effective way to modify TCO properties; therefore, this research project focuses on Sr²⁺ doping of CuCrO₂, which has been synthesized via solid-state methods, to study how cation doping alters the structural and thermodynamic properties of CuCrO₂.

EXPERIMENTAL DETAILS

The conventional solid state reaction method was used to prepare pure CuCrO₂ and Sr-doped CuCrO₂ (CuCr_{0.95}Sr_{0.05}O₂) samples. Bruker D8 Advance X-ray diffractometer using Cu K- α radiation was used to study phase purity. Specific heat measurements using a relaxation calorimetry were performed in a Physical Property Measurement System (QD-PPMS) at UGC-DAE CSR Indore.

X-ray Diffraction Analysis

The XRD is performed at room temperature. Both patterns exhibit sharp diffraction peaks, confirming the crystalline nature of the samples. All the prominent peaks are of the rhombohedral crystal structure with R-3m space group, consistent with the standard pattern of CuCrO₂ (JCPDS No. 01-089-6744), indicating that the delafossite phase is maintained even after Sr doping. No secondary phases are detected, suggesting that the 5% doping of Sr²⁺ at the Cr³⁺ site does not cause significant phase transformation. The Sr doped sample shows a minor peak shift towards lower values relative to the pure sample. This shift is indicative of a lattice expansion, which may be due to the slightly larger ionic radius of Sr²⁺ (1.18 Å) compared to Cr³⁺ (0.615 Å). The peak broadening remains minimal, implying that the crystallinity is preserved. This size difference leads to increment of crystallite size and decrement of microstrain⁴.

Sr doping in CuCrO ₂ (%)	Crystallite size D (nm)	Micro strain (ε)
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0%	55.26	0.0021
5%	58.73	0.00196

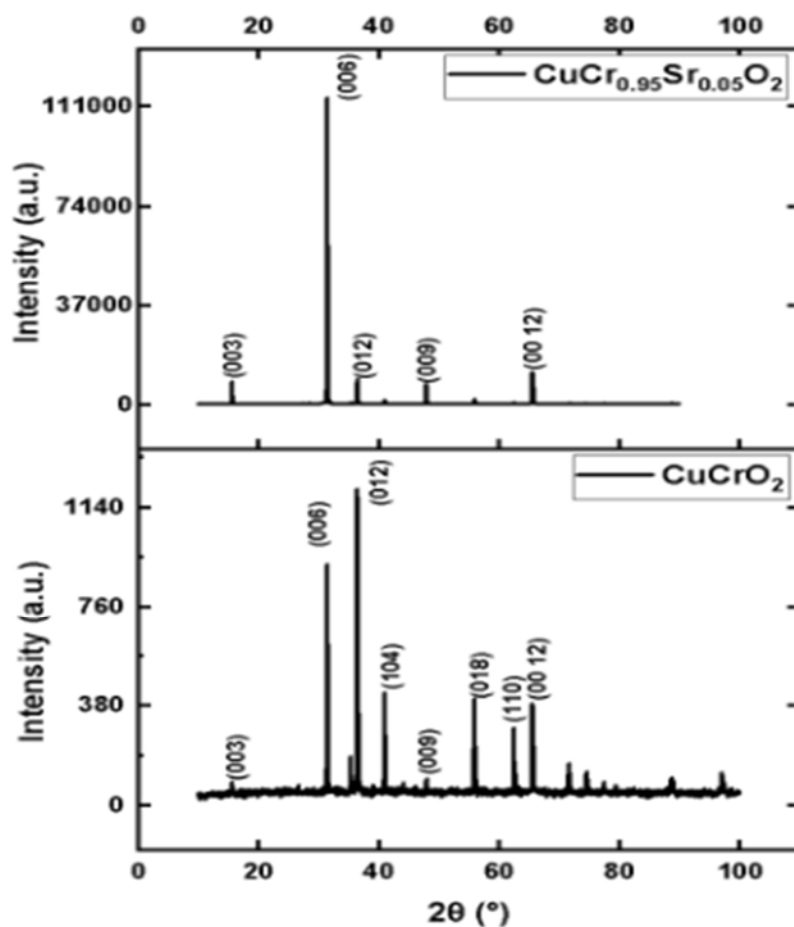


FIGURE 1: XRD pattern of CuCrO_2 and 5% Sr doped CuCrO_2 .

Heat Capacity Analysis

The specific heat (C_p) vs. temperature (T) plot at 0T for CuCrO_2 and $\text{CuCr}_{0.95}\text{Sr}_{0.05}\text{O}_2$ shows a clear λ -type anomaly, indicative of an antiferromagnetic (AFM) transition. For the undoped CuCrO_2 , the peak appears around 24.5 K similar value reported in literature⁵, corresponding to the Néel temperature (T_N). Upon 5% Sr doping, the transition shifts slightly to a lower temperature (~ 23.5 K) and becomes broader, suggesting suppression and weakening of long-range AFM order.

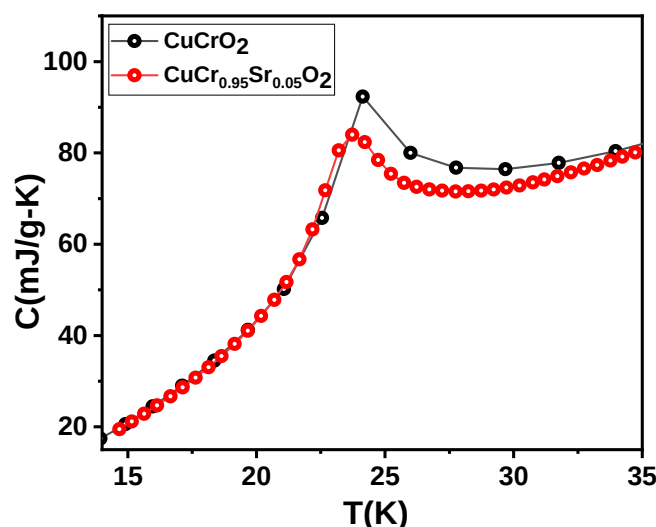


FIGURE 2: Heat Capacity of CuCrO₂ and 5% Sr doped CuCrO₂

CONCLUSION

The detailed investigation of Sr-doped CuCrO₂ (CuCr_{0.95}Sr_{0.05}O₂) shows that substitution of strontium greatly influences the properties and hence the applications of CuCrO₂. X-ray diffraction confirms the delafossite phase, while the observed peak shift toward lower 2θ values indicates an expansion in lattice because of the larger ionic radius of Sr²⁺, leading to increased crystallite size. This helps in reduction of strain. Reduction in the band gap is seen through Optical studies (not shown here) from 3.39 eV (undoped) to 3.09 eV (Sr-doped). This is an indication that supports enhanced p-type conductivity. This in turn assist visible light absorption improvement. Slight shift of T_N of AFM transition of about 1K is seen in heat capacity measurements. This AFM is antiferromagnetic transition, shift seen is in the Néel temperature, for pure it is 24.5 K and for the 5% Sr doped CuCrO₂ it is now 23.5 K. Further support for these findings of heat capacity and the associated anomalies seen near the AFM transition comes from Magnetization measurement (not shown). In essence, Sr doping in CuCrO₂ is seen to tune effectively the structural and functional properties while modifies its potential for optoelectronic and magnetic applications.

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Magnetization and Heat Capacity of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Cr}_2\text{O}_4$

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Abstract: Non-magnetic substitution of Zn ion on the magnetic Co ion in CoCr_2O_4 significantly modifies the thermodynamic and magnetic properties of the system. In this research we are focusing on its low temperature heat capacity measurements and temperature dependent magnetic measurement to explain the phase transitions. Specifically, we study the doping effect in magnetic and thermal changes in $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Cr}_2\text{O}_4$. Heat capacity measurements displayed characteristics anomalies at, $T_c=26\text{K}$. The study highlights the complex thermodynamical behaviour of zinc-doped cobalt chromite and a role of A-site nonmagnetic ion substitutions in tuning their thermodynamical properties.

INTRODUCTION

Transition metal chromite (CoCr_2O_4) is an interesting compound whose magnetic characteristics have an attraction among researchers in the fields of materials science and condensed matter physics. CoCr_2O_4 , a member of the spinel oxide family, exhibits unique properties that have led to much investigation. Magnetic ordering and spin frustration are two unique phenomena that result from the complex interactions between electron spins within the crystal lattice of the substance^{1,2}. Along with providing insight into the basic properties of magnetic materials, an understanding of CoCr_2O_4 's magnetism holds promise for future uses in fields like spintronics and magnetic storage systems. In this investigation, we explore the interesting state of CoCr_2O_4 magnetism, studying the key principles driving its magnetic behaviors and considering the implications for the advancement of science and technology.

The structure of Cobalt chromite has a general formula CoCr_2O_4 (AB_2O_4), in this Co^{2+} is a bivalent cation and Cr^{3+} is a trivalent cation situated on tetrahedral and octahedral sites respectively and oxygen is an anion. Cobalt chromite has a paramagnetic (PM) to ferrimagnetic (FIM) transition with a Curie temperature ($T_c=94\text{K}$). CoCr_2O_4 also shows spin reorientation transition (T_s) at 27K and lock-in transition (T_l) at 13K . So it will be very useful to study the magnetic properties of CoCr_2O_4 ³.

EXPERIMENTAL DETAILS

The sample of 50% Zn-substituted Cobalt Chromite ($\text{Co}_{0.5}\text{Zn}_{0.5}\text{Cr}_2\text{O}_4$) has been synthesized by solid-state reaction route (SSRR). Sample was denoted by CZCO. Cobalt oxide (Co_3O_4), Chromium oxide (Cr_2O_3), and Zinc oxide (ZnO) powder were used in a stoichiometric ratio as a basic precursor. These oxide powders were grounded using an agate mortar and pestle for 10 hours. The powder obtained after grinding was calcined for the first time at 1000°C for 12 hours, After the first calcination it was ground again for 2 hrs and then calcinated for the second time at 1050°C for 12 hours and then re-ground for 4 hours. This powder was subsequently formed into pellets by applying pressure of 5 tons and sintering was done at 1100°C . Using the Advanced D8 Bruker X-Ray Diffractometer, XRD pattern was recorded in 2θ (10 to 80°) with step size 0.02° at a wavelength of $1.5406\text{\AA}$ to get the phase confirmation and refinement by the Rietveld refinement in fullprof suite 64bit software. A QD-PPMS was used to determine magnetic field and temperature-dependent magnetization. Heat Capacity measurement was done by a Physical property measurement system (14T/2K PPMS from Quantum Design) for resistivity and heat capacity.

RESULT AND DISCUSSION

Structural Analysis

The structural properties of 50% doped CoCr_2O_4 ($\text{Co}_{0.5}\text{Zn}_{0.5}\text{Cr}_2\text{O}_4$) spinels were initially characterized by an X-ray diffractometer. The diffraction measurements were performed in a range of 2θ (20 to 80) at 300K. CZCO diffraction pattern has been studied with Rietveld refinement using Fullprof software is shown in Figure 1⁴. A black solid line reflects the pattern established by the structural model, and red symbols highlight the observed data. Using the Rietveld refinement, a good agreement exists between the estimated and observed profiles (as seen by the blue solid line) is established. The XRD pattern for 50% substituted CoCr_2O_4 (CZCO) is shown in **Figure. 1**, it was found that the value of the lattice parameter is 0.83392 nm. XRD pattern confirms that CZCO is a cubic spinel. Its structure is with a space group of Fd-3m . The refinement shows a good fit between the calculated and observed patterns⁵.

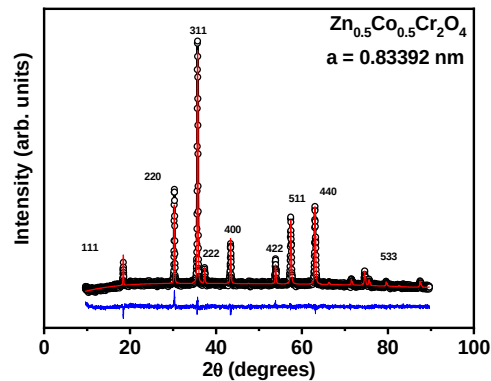


Figure. 1 Diffraction pattern of 50% Zn doped Cobalt chromite

Temperature-Dependent and Field Dependent Magnetization

Temperature-dependent magnetization is the most important technique to understand the temperature-dependent magnetic property, phase transition at different temperatures, magnetic interaction, and stability of any material^{6,7}. **Figure 2 (a)** shows the temperature-dependent magnetization of the 50% Zn doped cobalt chromite were measured in both ZFC (Zero field cooled) and FC (Field cooled) in the range of temperature, 5 to 300 K at the applied magnetic field 500Oe respectively.

The transition occurs at 26K and is the Curie temperature T_c ⁹. A spin reorientation temperature T_s is also mildly observed at 10K, when 50% of non-magnetic Zn ions are doped. 75K is the Curie temperature in CoCr_2O_4 . But the Curie temperature drops dramatically to 26K when the Zn ions are added. This substantial decrease depicts the impact on cobalt chromite's magnetic characteristics of replacing magnetic Co ions with non-magnetic Zn ions¹⁰.

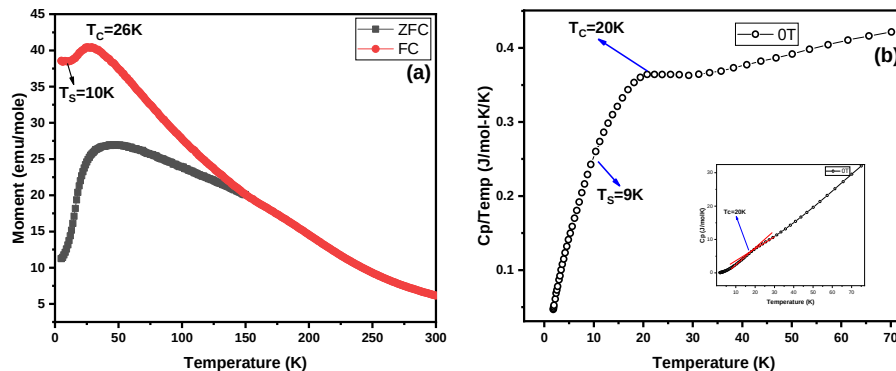


Figure. 2 (a) Temperature Dependent Magnetization curve for 50% Zn Substituted Cobalt chromite. (b) The temperature-dependent Heat Capacity of 50% Zn-substituted CoCr_2O_4 at an applied magnetic field of 0T. Ferrimagnetic T_c is shown, while the spin reorientation at T_s is speculated.

Heat Capacity Measurement

Heat capacity measurement was performed out in the range of 2K to 75K in 0T and shown in **Figure 2(b)**. The graph of heat capacity versus temperature of $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Cr}_2\text{O}_4$ has a small hump at around 20 K, where the material enters to the curie temperature which is the transition from paramagnetic to ferrimagnetic state. The most noticeable hump at $T_s=21$ K is normally observed due to the spin spiral transition in pure CoCr_2O_4 ^{11,12}. This feature is broadened upon 50% of Zn doping. With the increasing doping of Zn ion the T_c shifted towards the lower temperature $T_c=26$ K. Spin reorientation (T_s) is at ~ 10 K as compared to the Cobalt Chromite, may be due to the disordered spin interaction^{11,13}.

CONCLUSION

We report the effect of doping of non-magnetic Zn^{2+} ion on the magnetic ion Co^{2+} on the tetrahedral site A of spinel CoCr_2O_4 . Magnetization studies revealed a significant change in magnetic characteristics, as the Curie temperature dropped with increased Zn ion doping. These results show that Zn doping has a significant impact in magnetic interactions in the CoCr_2O_4 spinel. The heat capacity measurement observed substantial anomalies at $T_c=26$ K, relating to phase transitions, showing changes in the specific heat capacity due to Zn doping.

ACKNOWLEDGEMENT

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Low Temperature Heat Capacity of NiCr_2O_4

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Abstract. Nickel chromite (NiCr_2O_4) synthesized via the sol-gel method, exhibits a complex interplay of structural and magnetic transitions. The material undergoes a series of structural changes, viz cubic to tetragonal around 310 K, followed by a second transition from tetragonal to orthorhombic near 65 K, and a third distortion inside orthorhombic structure near 30 K. This complex structural behavior is coupled with magnetic transitions. At 75 K, the sample transitions to a ferrimagnetic state. A further spin re-orientation is observed at 30 K. To understand the low temperature thermal behavior of the material we perform the heat capacity measurements that confirm these transitions, showing anomalies at these specific temperatures.

INTRODUCTION

Nickel chromite (NiCr_2O_4) is a fascinating example of a multiferroic spinel compound with the general formula AB_2X_4 ¹. Its unique structural and magnetic properties have made it a subject of extensive research, particularly for its potential applications in catalysis, gas sensing, and high-temperature alloys. As a normal spinel, NiCr_2O_4 features Ni^{2+} ions occupying the tetrahedral A-sites and Cr^{3+} ions residing in the octahedral B-sites^{2, 3, 4}. This specific cationic arrangement results in a rich set of physical phenomena, inclusive of multiple structural and magnetic phase transitions. The most notable characteristic of nickel chromite is its temperature-dependent phase transitions. At approximately 300-310 K, system undergoes transition from a cubic in to a tetragonal phase. This transition is widely attributed to the Jahn-Teller (JT) effect, a phenomenon that lowers the symmetry of a system to remove orbital degeneracy. Furthermore, a second magnetic and structural transition is seen at a lower temperature, typically between 60K and 80 K. This transition is from a paramagnetic to a ferrimagnetic state, marked by the spontaneous alignment of magnetic moments from the Ni and Cr ions^{5,6,7}.

EXPERIMENTAL PROCEDURES

Sol-Gel Method

Nickel chromite (NiCr_2O_4) synthesis the sol-gel method involves a precise procedure. The process begins with preparing two solutions. To create solution A, add citric acid to distilled water and stir continuously. Solution B is made by mixing $(\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ nickel nitrate and chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) in distilled water. These two solutions are then combined, and a magnetic stirrer is used to mix them thoroughly. Ammonia is added in this solution to maintain the pH to 7, which facilitates the formation of a gel. The resulting gel is then heated in an oven at 70 °C to form ash. The ash is ground for five hours in an agate mortar and subsequently calcined (heated) at 750 °C, 800 °C, and 850 °C for 12 hours. Heating rate used is 5 °C per minute to obtain the final crystalline NiCr_2O_4 product^{8,9,10}.

Characterizations

We obtained X-ray diffraction pattern with the help of a X-ray diffractometer (Bruker D8 advance) in the 2θ range (10° to 80°) using Cu $K\alpha$ radiation of $\lambda = 1.5406 \text{ \AA}$. Temperature-dependent magnetization measurement (M vs T) was performed in the temperature range ($5 \text{ K} \leq T \leq 300 \text{ K}$), using PPMS (physical properties measurement system). Additionally, (FC) field cooling and (ZFC) zero field magnetic measurements were performed. Heat capacity measurements were employed to confirm the magnetic transition using the PPMS-14 tesla (Quantum Design).

RESULT AND DISCUSSION

X-ray Diffraction (XRD)

To analyze the crystal structure of the NiCr_2O_4 sample we XRD technique. The XRD pattern is matching well with the JCPDS card No. 01-088-0109 which confirms the formation of single phased NiCr_2O_4 with cubic crystal structure and space group no. 227 (space group $Fd-3m$). lattice parameter values obtained after refinement are as follows: $a=b=c = 8.307 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$ ¹¹

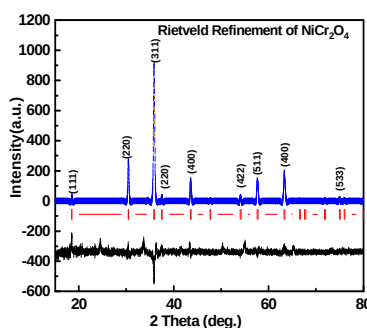


FIGURE 1. Rietveld refinement pattern of NiCr_2O_4 .

Magnetic Measurement

Zero Field Cooled (ZFC) and Field Cooled (FC) techniques were applied to understand magnetic properties of NiCr_2O_4 . In ZFC measurement, the sample is cooled from 300K to 5K without applying the magnetic field. For FC magnetic measurement, the sample is cooled from 300K to 5K by applying a magnetic field of 500 Oe. **FIGURE 2(a):** depicts the FC/ZFC curves for NiCr_2O_4 . Bottom panel is the ZFC curve of NiCr_2O_4 . They show phase changes from paramagnetic to ferrimagnetic state, at a Curie Temperature denoted by $T_C \sim 75 \text{ K}$ and a Spin reorientation transition T_s at 30K for NiCr_2O_4 . Results are very close to previous reported data.^{8,12}

Heat Capacity

Heat capacity measurement is a fundamental technique. It is an important technique used for identification of phase transitions. **FIGURE 2:(b)** shows the heat capacity of NiCr_2O_4 with temperature at 0T. The transition at 75K is due to the paramagnetic to ferrimagnetic ordering in the system reported. The sharp peak at $\sim 30 \text{ K}$ is due to the second magneto-structural transition, which is in line with literature referred above¹³. It is important to note that at a field of 10T the peak has totally vanished (data not shown). This could be due to the fact that the spin system is sensitive to magnetic fields and a more detailed study is needed to understand.

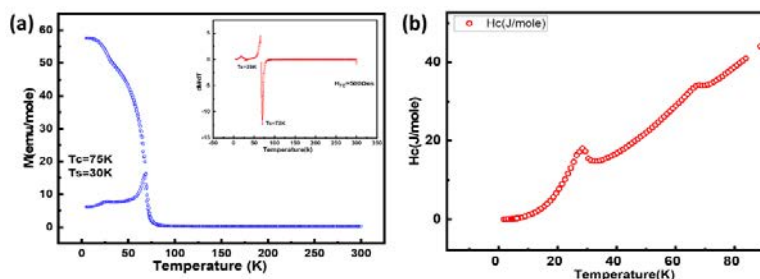


FIGURE 2(a): ZFC and FC Magnetization and the inset shows the plot of FC data in an expanded scale.
(b): Heat capacity of NiCr_2O_4 as the function of temperature.

CONCLUSIONS

Nickel Chromite materials are used in many magnetic applications, including sensors, memories, magnets, and magnetic recording devices. NiCr_2O_4 is one such well-known, Exchange Bias material whose functionality ranges from magnetism to dye degradation. The sample is made through a sol-gel route and characterized by XRD. It has been investigated for its low-temperature magnetic and thermal properties. Magnetization shows this system to have a Ferri-magnetic transition with $T_c \sim 75\text{K}$ while there is a clear anomaly due to a spin re-orientation transition at $T_s \sim 30\text{K}$. The Heat capacity shows clear anomalies around the said transitions and can be used to confirm these phase transitions.

ACKNOWLEDGEMENT

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Exploring the Effect of Twist Angle in Nb₁₅S₃₀ Biflake Structure via Ab-initio Calculations

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Abstract. Twistronics explores how the relative twist between stacked layers influences the properties of low-dimensional materials. While this concept has been widely applied to infinite 2D systems, its effect on finite-sized flakes remains less studied. In this work, we investigate monolayer, bilayer, flake, and biflake forms of NbS₂ using first-principles calculations. Monolayer and bilayer structures show metallic and non-magnetic behaviour, whereas Nb₁₅S₃₀ flake and Nb₁₅S₃₀ biflake exhibits semiconducting feature. The magnetic moment of twisted Nb₁₅S₃₀ biflake increases when angle ranging from 1° to 15° which arises due to its edge-effect and Nb₁₅S₃₀ biflake get stabilized at an angle of 14° which suggests a possible magic angle. Hence, these results indicates the potential application of twisted biflakes for spintronic and nanoscale device applications.

INTRODUCTION

Two-dimensional (2D) and lower-dimensional flakes have been studied widely due to their tunable magnetic and electronic properties; these properties arise due to edge effects as a consequence of reduced dimensionality [1]. Changing the relative twist angle between staked layers also affects the electronic properties and makes them tunable [2]. Twistronics was first explored in twisted bilayer graphene when it was twisted at a $\sim 1.1^\circ$ angle; the twist resulted in superconductivity and correlated insulating states [3], in the present world known as the "magic angle." After the study in graphene, the idea quickly escalated to other 2D materials, i.e., transition metal dichalcogenides (TMDs) such as MoS₂, WSe₂, and NbSe₂ [4–6]. NbS₂, a metallic TMD with a structure similar to NbSe₂, is a good choice for these kinds of studies. Previous research indicates that the 4×4 supercell of a 2D NbS₂ monolayer demonstrates magnetic instability, implying edge-induced magnetism [7]. In this work, we investigate NbS₂ in monolayer and bilayer forms, as well as in 0D Nb₁₅S₃₀ flake and biflake configurations, to study size and edge effects. Then we studied the effect of twist in biflake structure. Computational details are presented in Section 2, results and discussion in Section 3, and conclusions in Section 4.

COMPUTATIONAL DETAILS

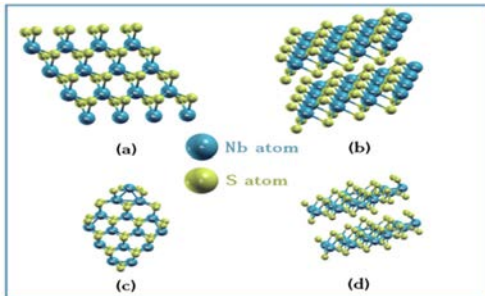


FIGURE 1. Structures of different NbS₂ configurations (a) An extended view of monolayer (ML) NbS₂ (b) The structure of bilayer (BL) NbS₂ (c) The atomic arrangement of a Nb₁₅S₃₀ flake (d) The atomic arrangement of a Nb₁₅S₃₀ biflake.

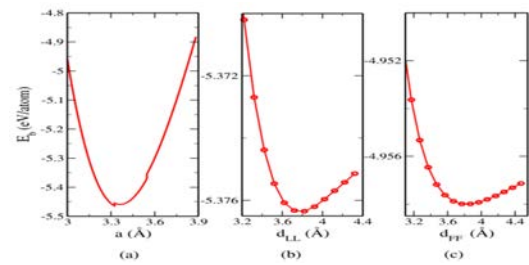


FIGURE 2. Binding energy curves for: (a) NbS₂ monolayer as a function of lattice parameter 'a', (b) NbS₂ bilayer as a function of interlayer distance d_{LL} and (c) Nb₁₅S₃₀ biflake as a function of interflake distance d_{FF} .

For the structural optimization of 2D NbS₂ systems (monolayer and bilayer) and 0D Nb₁₅S₃₀ flake and bilake, first-principles simulations were performed using Density Functional Theory (DFT) with the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code [9]. The GGA-PBE functional was employed to account for exchange-correlation effects. A double-zeta polarized (DZP) basis set with 20meV confinement energy and a mesh cutoff of 300 Ry were used. A 15×15×1 Monkhorst-Pack k-point grid was used for 2D structures, while a 1×1×1 grid was used for the 0D systems. Norm-conserving relativistic pseudopotentials were used to describe core–valence interactions.

RESULTS AND DISCUSSION

Structural characteristics of NbS₂ monolayer (NbS₂ ML), NbS₂ bilayer (NbS₂ BL), NbS₂ monoflake (Nb₁₅S₃₀) and twisted NbS₂ bilake (Nb₁₅S₃₀) with atoms Nb = 15 and S = 30 have been computed. Relaxed structures are shown in Figure 1. We computed the twisted properties of bilake at angles ranging from 1° to 15°, and as seen in Figure 4, they stabilize at an angle of 14° since the formation energy is at its lowest at that angle. NbS₂ monolayers and bilayers have no magnetic moment, whereas both untwisted and twisted flakes have some magnetic moment which is caused by the edge effects of the flakes in Figure 6. This magnetic moments in twisted bilake (Nb₁₅S₃₀) increases sharply when twisted angle ranges from 1° to 15° as shown in Figure 5(b). Also, based on binding energies, we discovered that the NbS₂ bilayer (NbS₂BL) is the most stable structure (-5.480 eV/atom) shown in Table 1, the graphical representation was shown in Figure 2.

TABLE 3. Calculated structural parameters of lattice constant (*a*), inter-layer and interflake distance (*d_{LL/dFF}*), binding energy (*E_b*), formation energy (*E_f*), homo-lomo gap (*E_{HL}*) and magnetic moment (*μ*).

System	<i>a</i> (Å)	<i>d_{LL/dFF}</i> (Å)	<i>E_b</i> (eV/atom)	<i>E_f</i> (meV)	<i>E_{HL}</i> (eV)	<i>μ</i> (μ _B)
NbS ₂ ML	3.324(3.362)[10]	---	-5.37	---	---	0.00
NbS ₂ BL	3.324	3.80	-5.480	-327.490	---	0.00
Nb ₁₅ S ₃₀ flake	---	---	-4.955	---	0.546(↑) 0.109(↓)	0.678
Nb ₁₅ S ₃₀ bilake	---	3.870	-4.958	-217.155	0.031(↑) 0.528(↓)	1.204

Figure 3 displays the electrical band structures for both 2D and 0D systems. Based on these band structures, we found that NbS₂ monolayers and bilayers have no band gap, indicating that they are metallic in nature, whereas monoflakes and bilake exhibit semiconducting nature for alternative spin channels i.e. up spin and down spin respectively.

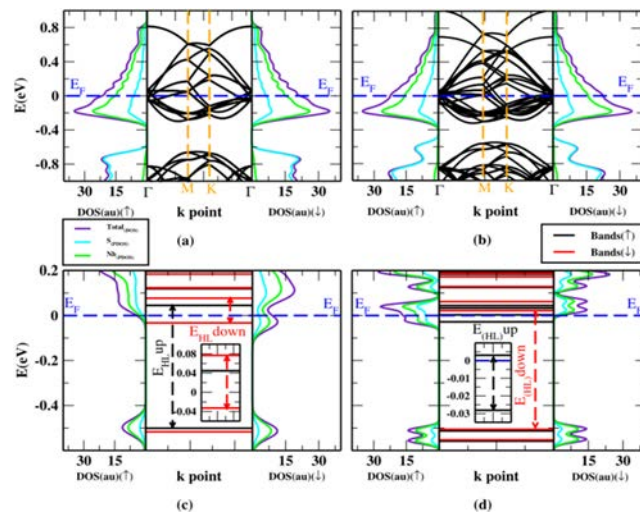


FIGURE 3. Electronic band structures and density of states for (a)NbS₂monolayer (b)NbS₂bilayer (c)Nb₁₅S₃₀ flake (d)Nb₁₅S₃₀ bilake.

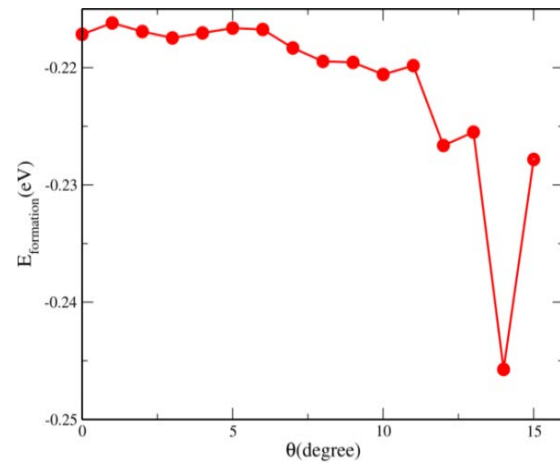


FIGURE 4. Variation of formation energy of Nb₁₅S₃₀ bilake with twist angle.

Additionally, we computed the HOMO-LUMO gap for spin up and spin down channels with twisted angle as shown in Figure 5(a) and found that for spin up channel, as we goes on increasing the twisting angle, HOMO-LUMO gap decreases in biflakes while it increase for spin down as twisted angle increases. Thus these materials are highly recommended for the applications in spintronics.

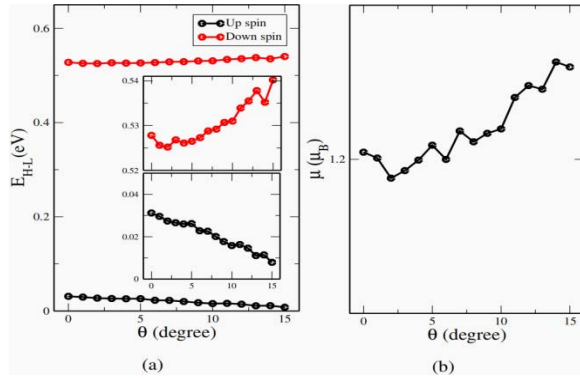


FIGURE 5. (a) HOMO-LUMO gap variation for spin-up and spin-down channels with twist angle for $Nb_{15}S_{30}$ biflake. (b) Total magnetic moment of $Nb_{15}S_{30}$ biflake as a function of twist angle.

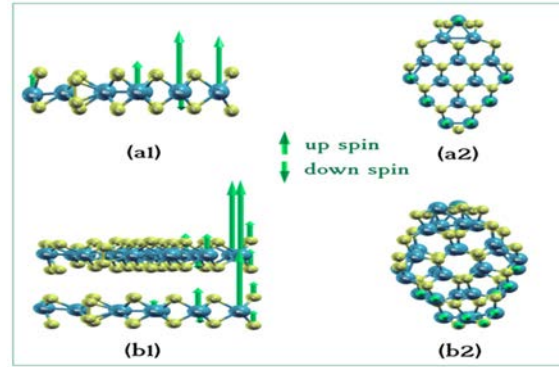


FIGURE 6. (a1) side view of spin vector of $Nb_{15}S_{30}$ flake (a2) top view of spin vector $Nb_{15}S_{30}$ flake and (b1) side view of spin vector rotated(14°) biflake (b2) Top view of spin vector rotated(14°) biflake.

CONCLUSIONS

Twisting $Nb_{15}S_{30}$ biflake we can tune their electronic and magnetic properties. At 14° twist angle we were able to get formation energy minima and enhanced magnetic response, suggesting a possible magic angle. Based on these results $Nb_{15}S_{30}$ biflake can be used for nanoscale device applications and spintronic.

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Observation of Magnetic Anomalies in vdW Antiferromagnet MnPSe₃

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Abstract. This work reports the structural and magnetic characterization of antiferromagnetic semiconductor MnPSe₃ crystals. X-ray diffraction (XRD) was employed to investigate the structural properties of the material. Distinct magnetic anomalies and phase transitions are revealed through temperature and field-dependent magnetization measurements.

INTRODUCTION

The discovery of two-dimensional (2D) magnetism in van der Waals (vdW) materials has opened new avenues for exploring magnetism in lower dimensions. These materials exhibit remarkable quantum effects and offer unique physical properties that are highly attractive for use in advanced nanoelectronic and spintronic devices [1, 2]. Transition metal phosphorus trichalcogenides (MPX₃, where M is a transition metal and X is a chalcogen) are an interesting group of 2D magnetic van der Waals materials because of their unique layered structure [3]. MnPSe₃, a member of this family, is an antiferromagnetic semiconductor with exceptional properties. It has an energy band gap of 2.27 eV and can be exfoliated into atomically thin layers. In this study, we present a systematic investigation of the magnetic properties of bulk MnPSe₃. Magnetic measurements conducted at various field strengths reveal distinctive anomalies in the system. Structural characterization was carried out using X-ray diffraction (XRD).

RESULTS AND DISCUSSION

MnPSe₃ has a layered crystal structure and crystallizes in trigonal R-3 space group. Each unit cell of MnPSe₃ consists of Mn²⁺ ions arranged in a hexagonal honeycomb lattice. In the center of each honeycomb, there is a P-P dimer, which is covalently bonded to six selenium (Se) atoms. Figure 1 (a) shows the schematic of the crystal structure of MnPSe₃ [4]. MnPSe₃ exhibits a pronounced paramagnetic to antiferromagnetic phase transition at the Neel temperature T_N. Below the transition temperature, the magnetic ions in the crystal align oppositely to their nearest neighbors forming an antiferromagnetic structure. Evidence from neutron diffraction confirms that the magnetic moments in MnPSe₃ are aligned parallel to the basal (*ab*) plane [5].

The crystal structure of exfoliated MnPSe₃ flakes was characterized by XRD using Bruker D8 Advance diffractometer with Cu K_α radiation $\lambda = 1.54 \text{ \AA}$. The XRD pattern shows sharp peaks indicating the high crystallinity of the sample. The characteristic peaks are (0 0 3), (0 0 6), (0 0 9), (0 0 12) and (0 0 18). Figure 1 (b) represents the XRD pattern of bulk MnPSe₃.

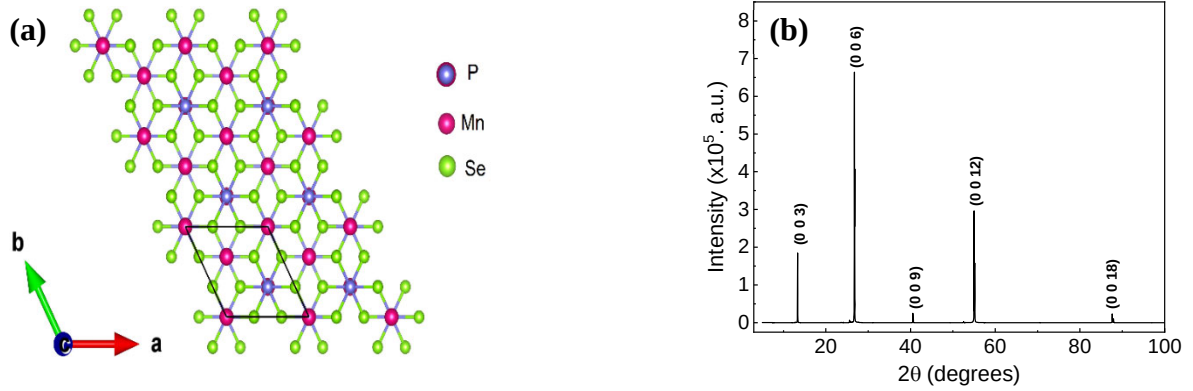


FIGURE 1. (a). Schematic of the crystal structure of MnPSe₃. (b) XRD of bulk MnPSe₃ crystal

The magnetic characterizations of bulk MnPSe₃ were performed using Physical Property Measurement System (Quantum design PPMS Evercool II). Figure 2 represents the temperature dependence of magnetic susceptibility of bulk MnPSe₃ with the different magnetic fields applied parallel to the *ab* plane.

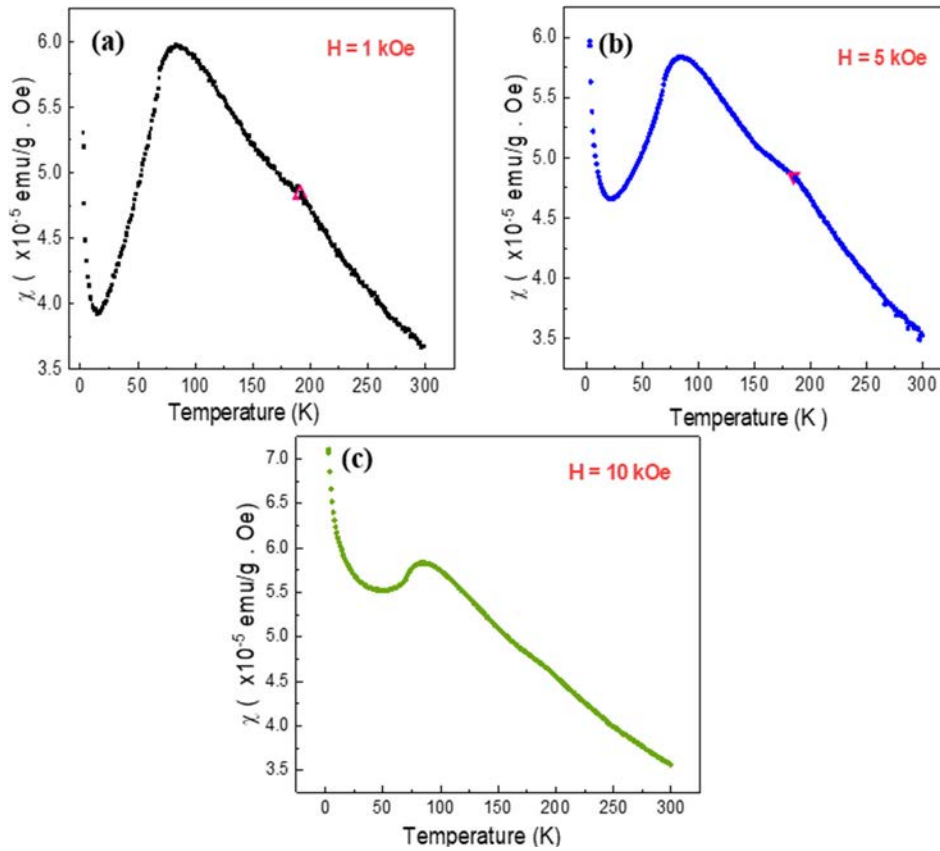


FIGURE 2. Temperature dependence of magnetic susceptibility for magnetic field (H) applied parallel to *ab* plane (a) $H = 1$ kOe, (b) $H = 5$ kOe, (c) $H = 10$ kOe (Bumps observed in the graph are represented by triangular markings).

All the figures represent the zero field cooled measurements taken in the temperature range 5-300 K. The Neel temperature (T_N) is calculated from the minima of derivative of χ (T) curve is 70 ± 2 K. The sharp decrease in magnetization above T_N , marks the transition from the antiferromagnetic to the paramagnetic phase. An additional bump is observed in the susceptibility curve around $T \sim 192$ K when the applied field $H = 1$ kOe. Interestingly this bump shifts to a slightly lower temperature $T \sim 186$ K, when the magnetic field strength is increased to 5 kOe, as shown in Fig. 2(b). However, the bump disappears entirely when the field strength is further increased to 10 kOe. These anomalies might be due to magnetic exchange interactions happening in the system.

CONCLUSIONS

The structural and magnetic properties of the antiferromagnetic MnPSe_3 crystal were systematically investigated. Field and temperature-dependent magnetization measurements reveal unique features in the system. Our findings provide a foundation for exploring fundamental magnetic interactions in 2D van der Waals crystals.

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Phase Evolution and Magnetic Frustration in Tunnel-Structured $\text{Ba}_{1.3}\text{Mn}_8\text{O}_{16}$

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Abstract. Synthesis, crystal structure and magnetic behaviour of $\text{Ba}_{1.3}\text{Mn}_8\text{O}_{16}$ (BMO) is presented here. BMO crystallizes in monoclinic structure at room temperature, confirmed via X-ray diffraction and scanning electron microscopy (SEM) equipped with energy dispersive analysis of X-ray (EDX). Small, needle-shaped single crystals were crushed to confirm the crystal structure at room temperature using powder X-ray diffraction. Magnetic susceptibility measurements performed on the bulk sample reveal long range antiferromagnetic (AFM) ordering of Mn ions at low temperatures in BMO.

INTRODUCTION

With various distinct chemical and structural changes, the hollandite family offers numerous possibilities to tailor its properties for targeted applications like crystalline host matrices for the immobilization of radioactive caesium [1], electrode material of Li-ion batteries [2] or ferro- or antiferromagnetic materials [3]. The crystal structures of hollandite $\text{A}_{2-x}\text{B}_8\text{O}_{16}$ (A: large cations such as Cs, K or Ba and B: small and medium-sized cations including transition metal) have tetragonal or monoclinic symmetry. The A cations reside in 1D tunnels separated by a framework of B-O octahedra [1]. The large cations (Ba and K), occupy the channels inside the tunnel structure as shown in figure 1.

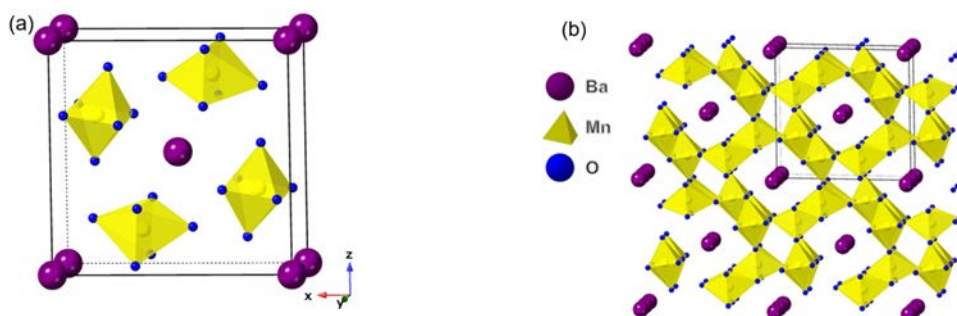


FIGURE 1. Crystal structure of $\text{Ba}_{1.3}\text{Mn}_8\text{O}_{16}$. (a) A single unit cell showing MnO_6 octahedra (yellow), with Ba (purple) and O (blue) atoms. (b) Extended view illustrating the tunnel-type framework formed by corner-sharing MnO_6 octahedra and the arrangement of Ba ions within the tunnels.

In addition to the structural flexibility, many hollandites of the $\text{A}_x\text{M}_8\text{O}_{16}$ (A = Ba, Sr, Pb, Cs, K, Na, Rb; M = transition metal ion) chemical composition exhibits interesting magnetic and electronic properties, sensitive to the content of A site ion and oxidation state of transition metal ion at B site which forms octahedra with oxygen. In general, the magnetic ordering depend on the transition metal cation, such as Mn in the present case. For example, $\text{KMn}_8\text{O}_{16}$ exhibits spin glass freezing whereas $\text{K}_2\text{Cr}_8\text{O}_{16}$, orders ferromagnetically below 180 K [4,5].

In the present study, the compound $\text{Ba}_{1.3}\text{Mn}_8\text{O}_{16}$ (BMO) has been systematically investigated using temperature-dependent X-ray diffraction, scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy and

magnetization measurements. The primary objective is to examine its structural and magnetic characteristics, with particular emphasis on understanding how these properties can be tuned through possible structural modifications.

EXPERIMENTAL

The BMO compound was synthesized using the salt-flux method. [6]. The respective mixture BaNO_3 , MnO and KCl with molar ratio of 1.3:8:12 were grounded and heated in a tightly covered alumina crucible at 100°C/h until 850°C that temperature was maintained at this value for 72h then slow cooled to room temperature. The resulting product was thoroughly washed with deionized (DI) water to remove residual KCl and subsequently dried at 100°C for 1h. Temperature dependent XRD has been done using Anton Paar's diffractometer with $\text{Cu-K}\alpha$ radiation. Magnetic measurements were performed using a commercial SQUID magnetometer.

RESULTS AND DISCUSSION

Rietveld refinement of room temperature XRD pattern of BMO reveals striking features which were missed in $\text{Ba}_{1.2}\text{Mn}_8\text{O}_{16}$. A monoclinic $I2/m$ structure was reported for $\text{Ba}_{1.2}\text{Mn}_8\text{O}_{16}$ [6,7] whereas our XRD data reveal a structural phase transition from high temperature $I2/m$ to $P2/n$ (200°C) for BMO. At room temperature, a coexistence of two monoclinic phases exist, with pure $I2/m$ stabilizing only above 200°C . A minute impurity of manganese dioxide was present in the sample which is included in the refinement as a third phase. The refined XRD pattern at RT is given in figure 2a. Figure 2b shows the XRD patterns at few selected temperatures between 75°C to 200°C for a 2θ range of 16° to 44° with highlighting few selected peaks showing change in profile shape as a result of structural phase transition. A peak near 24° remains unindexed which is supposed to be originating from Ba ordering inside the tunnel. The occurrence of superstructure reflections is commonly observed in other members of this family, and high-resolution data is essential to resolve the superstructure in these compounds. The refined lattice parameters for the $P2/n$ phase are: $a = 9.944(1) \text{ \AA}$, $b = 2.8546(3) \text{ \AA}$, $c = 9.790(1) \text{ \AA}$, with $\beta = 90.50(1)^\circ$, while for the $I2/m$ model the parameters were $a = 9.986(1) \text{ \AA}$, $b = 2.8618(4) \text{ \AA}$, $c = 9.702(2) \text{ \AA}$, with $\beta = 91.40(1)^\circ$.

To confirm the phase homogeneity, (SEM) and (EDS) have been performed on the sample. The SEM micrograph, given in figure 2c shows the needle shape micro-size crystals with few micrometer length. The size of crystals was not enough for anisotropic magnetic studies and therefore, the crystals were crushed and pressed into pellet form for sintering at 850°C . EDS spectra on pellet sample confirms the Ba:Mn ratio = 1.3:8.5 which is very close to the desired stoichiometry. A minute impurity of MnO_2 was also confirmed in the EDX analysis.

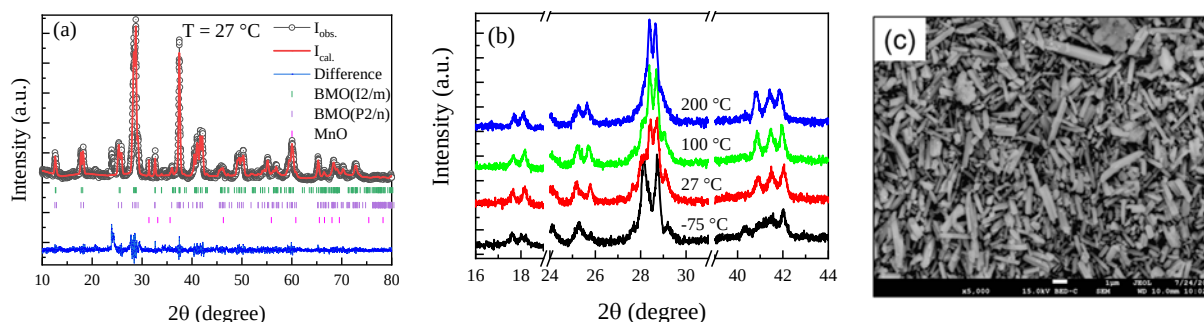


FIGURE 2. (a) Rietveld refinement of $\text{Ba}_{1.3}\text{Mn}_8\text{O}_{16}$ XRD data using a three-phase model. The goodness of fit parameter is 1.43. (b) Temperature-dependent XRD patterns showing peak evolution during the phase transition. (c) SEM image revealing the needle-like morphology of BMO particles.

Magnetic susceptibility $\chi(T)$ measurements have been performed on pellets samples and given in figure 3. The Zero Field Cooled (ZFC) and Field Cooled (FC) $\chi(T)$ increases with decreasing temperature followed by a sharp peak at Néel temperature (T_N) = 21 K. The T_N in the present case is slightly lower than that of $\text{Ba}_{1.2}\text{Mn}_8\text{O}_{16}$, which

orders at 25 K [7]. The increased Ba content at the A-site is expected to influence the Mn–Mn bond distances, potentially leading to the reduced ordering temperature, as observed in the present case. The ZFC and FC curve bifurcate below T_N . This suggests the presence of magnetic frustration or competing exchange interactions, likely originating from the mixed valent nature of Mn ions and the tunnel-based framework typical of hollandite-type structures. The CW fit of the data, given in the inset of figure 2a gives a negative Weiss constant of -570 K and effective paramagnetic moment value of $5.1 \mu_B$ which is close to the expected value of $4.46 \mu_B$. The isothermal magnetization (M - H) curves shown in figure 3(b), recorded at 2 K, 40 K, and 100 K. All curves are linear, symmetric, and exhibit no hysteresis, consistent with antiferromagnetic behavior.

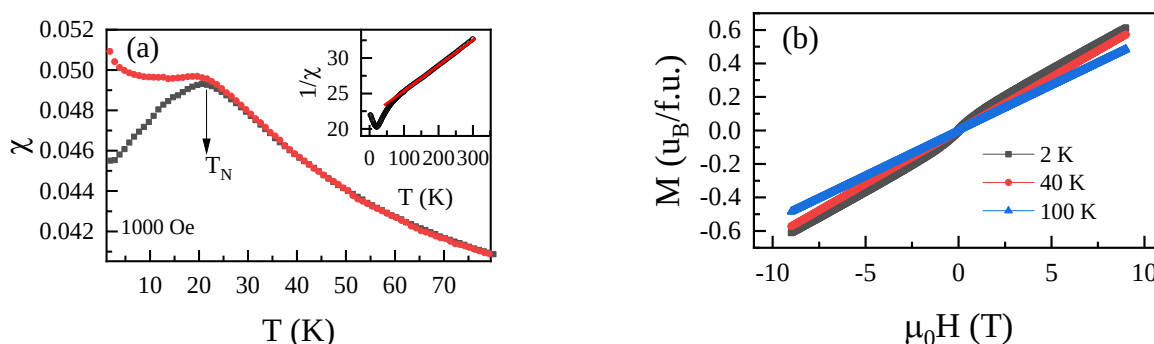


FIGURE 3. (a) M -vs- T behavior of $Ba_{1.3}Mn_8O_{16}$. The inset presents the Curie-Weiss fit. (b) Isothermal magnetization curves measured at different temperatures.

CONCLUSION

$Ba_{1.3}Mn_8O_{16}$ exhibits a complex phase behavior, having coexistence of monoclinic $I2/m$ and $P2/n$ phases at room temperature, with a complete transition to $I2/m$ above 200 °C. SEM-EDS analysis confirms phase homogeneity with near-ideal stoichiometry. Magnetic susceptibility measurements indicate antiferromagnetic ordering at 21 K. The observed bifurcation in ZFC/FC curves and a high negative Weiss constant point toward magnetic frustration associated with the mixed-valent Mn ions in the tunnel framework.

ACKNOWLEDGMENTS

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Boosting OER Kinetics Through Cobalt Doping in SrMnO₃ Perovskite Oxides

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ABSTRACT: The oxygen evolution reaction (OER) plays a significant role in water splitting, and addressing its sluggish kinetics necessitates the development of highly efficient and stable electrocatalysts. Perovskite oxides have gained significant attention as cost-effective alternatives to noble-metal catalysts due to their tunable electronic structures and abundant active sites. In this study, cobalt-doped SrMn_{1-x}Co_xO₃ ($x = 0, 0.25, 0.50, 0.75, 1$) was synthesized via a sol-gel method to enhance its OER activity. Co substitution at the Mn site introduces mixed-valence states (Mn³⁺/Mn⁴⁺ and Co²⁺/Co³⁺), improving electronic conductivity and facilitating faster charge transfer. X-ray diffraction confirmed the retention of the perovskite structure, while FE-SEM and EDX show the morphology and elemental composition of the sample. Electrochemical measurements in 1 M KOH demonstrated that 50 % Co-substituted exhibited the lowest overpotential of 337 mV at 10 mA cm⁻², smallest Tafel slope of 101 mV/dec, and an electrochemical active surface area (ECSA) of 24.6 cm². This work demonstrates that 50 % Co doping is an effective strategy to boost the intrinsic OER activity as compared to pristine SrMnO₃, making it a promising non-noble-metal electrocatalyst for OER.

INTRODUCTION

Developing efficient and stable electrocatalysts for the oxygen evolution reaction (OER) is crucial for improving water splitting technologies and renewable energy conversion. Noble metal-based catalysts such as RuO₂ and IrO₂ exhibit excellent OER activity but suffer from high cost and limited abundance, prompting the search for earth-abundant alternatives [1-2]. Perovskite oxides with the general formula ABO₃ have emerged as promising candidates due to their tunable electronic structures, high stability, and rich surface redox chemistry [3]. Among them, SrMnO₃ is attractive because of its mixed-valence manganese states, which provide active sites for oxygen electrocatalysis. However, its intrinsic electronic conductivity and moderate catalytic activity limit its practical performance. Cobalt doping at the B-site of SrMnO₃ offers a rational strategy to enhance OER efficiency by modulating the electronic structure and creating oxygen vacancies. The incorporation of Co introduces additional redox couples (Co²⁺/Co³⁺/Co⁴⁺), improving charge transfer kinetics and optimizing the adsorption energy of oxygen intermediates. Furthermore, Co doping induces lattice distortions and promotes oxygen vacancy formation, facilitating a more favorable lattice oxygen-mediated mechanism. This work focuses on the synthesis, characterization, and electrochemical evaluation of Co-doped SrMn_{1-x}Co_xO₃ ($x = 0, 0.25, 0.50, 0.75, 1$), aiming to establish a cost-effective, durable, and highly active perovskite catalyst for sustainable OER applications.

METHODOLOGY

SrMn_{1-x}Co_xO₃ was synthesized via a sol-gel method [4]. The starting precursors included strontium nitrate (Sr(NO₃)₂, 99.995%), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99% AR), and manganese (II) chloride tetrahydrate (MnCl₂·4H₂O, 99%), all sourced and purchased from Sigma-Aldrich. Additional reagents such as potassium hydroxide (KOH), anhydrous citric acid (99.5%, Sigma-Aldrich), double-distilled water (H₂O), ethanol (C₂H₅OH, 99.9% AR), and a D520 Nafion dispersion solution were used. All chemicals were stored in a moisture-free environment and used directly without further purification. SrMn_{1-x}Co_xO₃ was synthesized using a sol-gel method. Sr(NO₃)₂ and Co(NO₃)₂·6H₂O were dissolved in 20 mL of distilled water and stirred for 35 minutes. The metal to citric acid ratio used was 1:1.5, with the citric acid also being dissolved in 20 mL of distilled water. The solutions were stirred until a gel formed, after which the gel was dried in an oven at 100°C. Subsequently, it was calcined at 850°C for 6 hours.

RESULTS AND DISCUSSIONS

XRD Analysis, EDX, and FESEM analysis of $\text{SrMn}_{1-x}\text{Co}_x\text{O}_3$

X-ray diffraction (XRD) was employed to verify the phase composition, purity, and crystallographic structure of the synthesized samples. Intense peaks observed at 27.41° , 32.98° , 35.32° , 39.6° , 43.37° , 49.09° , 60.37° , and 64.89° correspond to the (102), (110), (103), (004), (202), (203), (213), and (205) planes, respectively. The formation of a hexagonal phase of SrMnO_3 , as referenced in JCPDS card 00-084-1612. Additionally, intense peaks at 18.9° , 28.6° , 32.68° , 43.7° , 47.5° , 55.7° , 58.4° , and 68.5° correspond to the (100), (101), (110), (201), (102), (112), (300), and (220) planes, respectively, indicating a hexagonal phase of SrCoO_3 , as noted in JCPDS card 00-040-1018. $\text{SrMn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0.25, 0.5, 0.75$) matches with JCPDS of both SrMnO_3 and SrCoO_3 . The substitution of Co resulted in a slight peak shift due to lattice distortion caused by the differing atomic radii of Co and Mn. Energy-dispersive X-ray (EDX) spectra confirm that all elemental compositions, such as Sr, Mn, Co, and O, are present in the sample as shown in Fig. 1. (B). The field-emission scanning electron microscope (FE-SEM) provides a morphological of the synthesis sample.

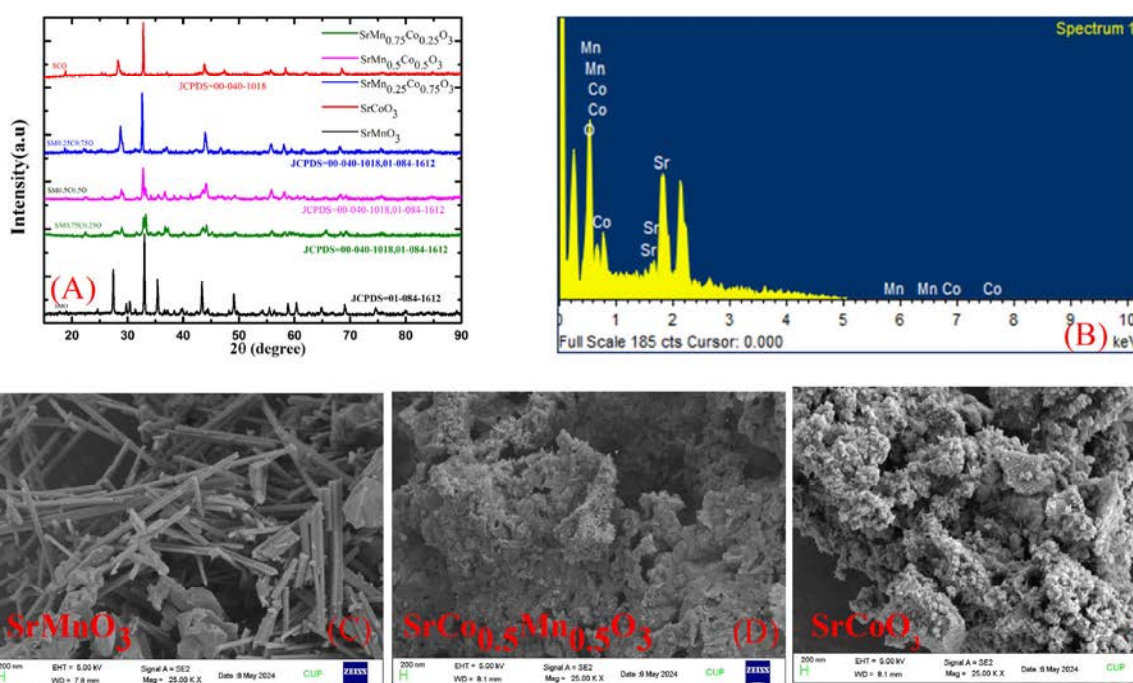


FIGURE 1. (a) XRD pattern of synthesised material $\text{SrMn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0, 0.25, 0.5, 0.75, 1$) (b) EDX spectrum of 50 % Co substituted (c) FE-SEM image of SrMnO_3 (d) 50 % Co Substitution (e) SrCoO_3

All electrochemical experiments were performed at room temperature using an Origalys (Model- OGF01) potentiostat equipped with a standard three-electrode setup. To prepare the catalyst ink, 10 mg of the synthesized sample was placed in a centrifuge tube, followed by the addition of 200 μL of distilled water and 200 μL of ethanol. The mixture was ultrasonicated for 10–15 minutes to ensure proper dispersion. Subsequently, a small amount of Nafion binder was added, and the suspension was ultrasonicated for an additional 15 minutes. Prior to each electrochemical test, a 1 M KOH electrolyte was freshly prepared using double-distilled water. OER measurements were conducted in 1 M KOH solution (pH 13.8), representing a highly alkaline environment. The three-electrode configuration consisted of a nickel foam working electrode (WE), a platinum counter electrode (CE), and an Ag/AgCl reference electrode (RE). The prepared catalyst ink was drop-cast onto the nickel foam and dried in a desiccator overnight. During OER measurements, all three electrodes were immersed in the electrolyte. The potentiostat applied a potential between the reference and working electrodes, while the resulting current was recorded between the working and counter electrodes.

The electrocatalytic performance of the as-prepared $\text{SrMn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0, 0.25, 0.5, 0.75, 1$) toward (OER) was systematically evaluated in a 1 M potassium hydroxide (KOH) electrolyte. As shown in the Linear Sweep Voltammetry (LSV) curve of $\text{SrMn}_{1-x}\text{Co}_x\text{O}_3$ ($x = 0, 0.25, 0.5, 0.75, 1$) in Fig. 2(a), the overpotential required to achieve a current density of 10 mA cm^{-2} at a scan rate of 100 mV/s^{-1} was determined to be 337 mV for the 50 % Co substituted sample. The corresponding Tafel plot, presented in Fig. 2(B), was used to analyze the OER reaction kinetics, yielding a Tafel slope of 101 mV dec^{-1} . The intrinsic electrocatalytic activity of the material was further assessed by estimating the electrochemical double-layer capacitance (C_{dl}), obtained from the slope of the linear fit of anodic and cathodic current densities, as shown in Fig. 2(C). The electrochemically active surface area (ECSA) was subsequently calculated using the equation $\text{ECSA} = C_{dl} / C_s$, where C_s represents the specific capacitance of a smooth planar electrode, taken as 0.040 mF cm^{-2} [5].

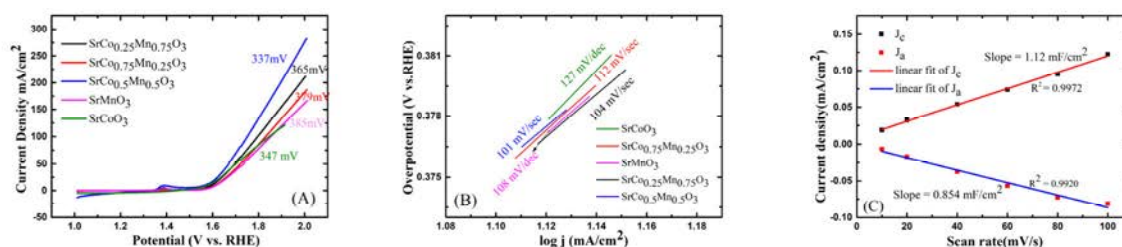


FIGURE 2. (A) Polarization curve $\text{SrMn}_x\text{Co}_{1-x}\text{O}_3$, (B) Tafel plot, (C) corresponding plot of j_c and j_a , (where j_c and j_a are cathodic and anodic current density) vs. scan rate

CONCLUSIONS

We have successfully grown different substitutions of Co in $\text{SrMn}_{1-x}\text{Co}_x\text{O}_3$ perovskite by the sol-gel approach. SrMnO_3 and different substitution of Co, such as 25%, 50%, 75%, 100 % shows the overpotentials 385, 365, 337, 379, 347 mV and Tafel slopes 108, 104, 101, 112, 127 mV/dec. ECSA values of SrMnO_3 , 25%, 50%, and 75% cobalt substitutions are 5.07, 24.2, 24.6, and 3.528 cm^2 , respectively. The 50% Co-substituted sample shows a small value of Tafel slope 101 mV/dec, and a low overpotential 337 mV as compared to pristine SrMnO_3 and calculated ECSA of 24.6 cm^2 . The enhanced performance is attributed to the improved optimized adsorption energies of oxygen intermediates and enhanced surface redox activity. Hence, an optimum substitution of Co improves the OER activity of SrMnO_3 .

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Magnetocaloric Properties of Colossal Magnetoresistive Manganites ($\text{Re}_{1-x}\text{A}_x\text{MnO}_3$): A Variational Treatment

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Abstract. Using the variational method, we analyzed the significance of magnetic fields on the change in magnetic entropy ($-\Delta S_M$) at various temperatures of rare earth manganites that have been doped with alkaline earth, specifically $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{Re} = \text{La}, \text{Pr}$ & $\text{A} = \text{Ca}, \text{Sr}$, etc.), which demonstrate colossal magnetoresistance (CMR) anomalies. In the Jahn-Teller (JT) coupling domain of the strong lattice, a two-band (l-b) Anderson lattice model Hamiltonian has been implemented, which can be viewed as equivalent to the two-fluid models. For specific values of magnetic field parameters “h” and “m,” our results suggest that the change of the magnetic entropy ($-\Delta S_M$) increases with temperature. This change exhibits a low temperature sharp peak and decreases at high temperatures. The peak becomes sharper with increasing values of “h” and “m.” In this study, the parameters of the magnetic field “h = 0.05” and “m = 0.5,” with doping “x = 0.3, V = 0.1, and JH = 1.0,” produce a maximum of about “1.4 J/Kg K” for temperatures of about $T_c \sim 200$ K. It is apparent that our results are qualitatively in agreement with the results of the experiment. The principal factors that describe the magnetic and transport properties of these magnetic materials are spin-lattice coupling and double exchange interaction.

INTRODUCTION

Magnetocaloric effect (MCE) based magnetic refrigeration (MR) is an innovative form of cooling technology that possesses numerous benefits, including increased efficiency, scalability, and ecological protection, in comparison to the traditional vapor-compression refrigeration technique [1]. MCE is the fundamental concept of MR, which focuses on the isothermal magnetic entropy change (ΔS_M) and the adiabatic temperature change (ΔT_{ad}) of a magnetic material under the influence of a variable external magnetic field [2]. We are currently conducting research to identify suitable magnetic materials that are also cost-effective and have a substantial refrigerant capacity (RC). The three principal variables that characterize high-quality magnetocaloric materials are magnetic entropy change, adiabatic temperature change, and refrigerant capacity [3]. Refrigeration cycles typically use RC to quantify the amount of heat that is exchanged across the cold and hot sinks. Both the magnitude and the temperature width of ΔS_M (i.e., the full width at half maximum of the ΔS_M (T) peak) determine the value of RC. Because of their complicated magnetic phase transition, perovskite manganites have also been thought of as promising materials for magnetic cooling [4, 5].

In a recent examination, Ramakrishnan et. al [6] introduced a novel theoretical model of coexisting localized JT polarons and broadband electrons for doped rare earth manganites $\text{Re}_{1-x}\text{A}_x\text{MnO}_3$. They contended that this model is inevitable in the presence of orbital degeneracy and strong JT coupling. They asserted that it elucidates a diverse array of manganite's characteristic properties.

Using the Anderson lattice model, Panwar et al. [7] had previously proposed a variational approach to studying the ground state and thermodynamic characteristics of systems including heavy fermions. Panwar et al. have recently employed this variational method to investigate the magneto-transport properties of doped CMR manganites, including electrical resistivity and thermoelectric power, across a broad temperature range at zero and various magnetic fields [8, 9]. Implementing this variational approach, we continue to examine how the magnetic field affects the magnetic entropy change ($-\Delta S_M$) of alkaline-doped rare earth manganites at various temperature ranges in this study.

BASIC FORMULATION

In the Jahn-Teller (JT) coupling domain of the strong electron-lattice, we have employed the two-band (ℓ -b) Anderson lattice model Hamiltonian ' H_{lb} ' for manganites. This technique is comparable to the two-fluid models with (ℓ -b) hybridization. It is presented by.

$$H_{lb} = - \sum_{\langle ij \rangle \sigma} \bar{t}_{ij} (b_{i\sigma}^+ b_{j\sigma}) - \sum_{i\sigma} E_{jt} l_{i\sigma}^+ l_{i\sigma} + U \sum_{i\sigma} n_{i\sigma}^l n_{i\sigma}^b - J_H \sum_i \mathbf{s}_i \cdot \mathbf{S}_i - J_F \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - \sum_{k\sigma} V_K (l_{k\sigma}^+ b_{k\sigma} + h.c.) - \mu_B \sum_i \mathbf{s}_i \cdot \mathbf{h} \quad (1)$$

Our previous work, as cited in Ref. [8, 9], provides the specifics of the symbols employed. We refer to the electronic specific heat formulation that we have employed in prior research [7].

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \frac{\partial}{\partial T} \sum_{k\sigma} (E_{k\sigma}^- - \mu) f_{k\sigma}^- \quad (2)$$

The change in magnetic entropy $\Delta S_M(T, H)$ is related to the magnetization-related change of the specific heat $\Delta C(T, H)$ according to the fundamentals of thermodynamics [10].

$$\Delta C(T, H) = T \frac{\partial \Delta S_M(T, H)}{\partial T} \quad (3)$$

This is expressed as the change in magnetic entropy $\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0)$. Likewise, the change in magnetic specific heat $\Delta C(T, H) = C(T, H) - C(T, 0)$.

RESULTS AND DISCUSSION

In these computations, we have taken into account the unperturbed conduction band of simple semicircular density of states $N_\sigma(\epsilon_k) = (2/\pi) \sqrt{(1 - \epsilon_k^2)}$, which centers around zero energy. The bandwidth is $W=2.0$ eV, $U=5.0$, $E_{jt}=0.5$, $V=0.1$ & 0.2 , $\epsilon_F = -0.238$ eV (for $x=0.3$), and $J_H = 1.0$ & 2.0 eV. The doping value x is adjusted between 0.1 and 0.5.

Figures

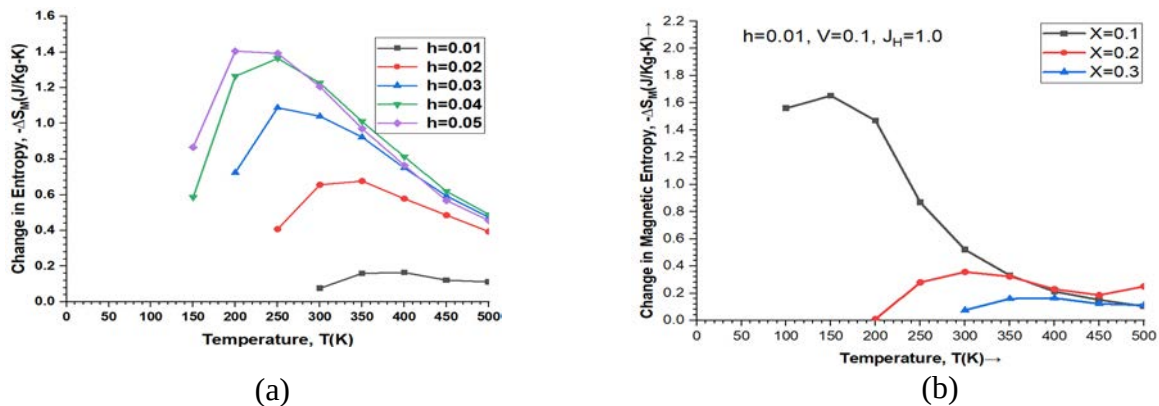


FIGURE 1. Variation of change in magnetic entropy ($-\Delta S_M$) as a function of temperature T (K) with [a] different magnetic parameter ' h ' at $x=0.3$; [b] different doping ' x ' at $h=0.01$ for a fixed value of $V=0.1$ & $J_H=1.0$. [See Ref. 11]

In Fig. 1, we demonstrated the variation in the magnetic entropy ($-\Delta S_M$) vs. temperature for a variety of the magnetic field parameters (' h ', ' m ') and dopings ' x '. The physical magnetic field H is related to the magnetic parameter h by the equation $h = g S_c \mu_B H_{\text{phys}} / t$. Using " $g=2$, $t=0.6$ eV, and $S_c=3/2$," we determine that $h=0.01$ corresponds

with $H_{\text{phys}} = 15\text{T}$, while the parameter m represents magnetization per site.

For a particular combination of magnetic field parameters 'h' and 'm', the magnetic entropy change ($-\Delta S_M$) increases with a rise in temperature in Fig. 1(a). The change reaches a maximum at temperature $T_c \sim 200\text{ K}$ and then decreases at higher temperatures. The ferromagnetic character is confirmed by the fact that ΔS_M is positive across the entire temperature range for all magnetic fields. Our outcomes are qualitatively aligned with the experimental results for the La-samples $\text{La}_{0.75}\text{Sr}_{0.1}\text{Ca}_{0.15}\text{MnO}_3$ [12] and $\text{La}_{0.7}\text{Ba}_{0.15}\text{Ag}_{0.15}\text{MnO}_3$ [13].

Additionally, we observe in Fig.1(a) that the peak's sharpness increases as the 'h' and 'm' values increase, and the variation in magnetic entropy is also substantial at moderate magnetic fields. A substantial magnetocaloric effect occurs across a wide spectrum of temperatures at the PM-FM transition temperature T_c . For magnetic field parameters "h = 0.05" and "m = 0.5," with doping "x = 0.3, V = 0.1, and $J_H = 1.0$," we achieve a moderate value of 1.4 J/Kg-K for $-\Delta S_M^{\text{max}}$ at $T_c \sim 200\text{K}$.

Although in Figs. 1(b), the maximum entropy change ($-\Delta S_M$) decreases as doping 'x' increases, the height of the curve's peaks at $T_c \sim 200\text{ K}$ decreases, and the peak shifts towards the higher temperatures.

The Zener double exchange model has been firmly suggested to provide insight into the significant magnetic entropy change ($-\Delta S_M$) in perovskite manganites [14]. The alteration in the Mn^{3+} & Mn^{4+} ratio during the doping process would be closely correlated with the impact of the double-exchange interaction between Mn^{3+} and Mn^{4+} ions. Furthermore, Guo et al. [15] propose that the substantial magnetic entropy change in perovskite manganites may be the result of spin-lattice coupling during the magnetic ordering process.

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Gamma Radiation Induced Synthesis of Cu and Ag Decorated Polyaniline for Thermoelectric Applications

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Abstract. In this study, we have successfully synthesized gamma radiation induced polyaniline (PANI) and copper/silver-decorated polyaniline samples. The single-pot in-situ synthesis approach allows the polymer and its composite to be synthesized in a pure form, without the need for any initiators or complex procedures. Gamma irradiation of the solution mixture produces both oxidizing and reducing species. In this environment, the Cu and Ag ions and aniline undergoes reaction simultaneously in a single pot, resulting in the formation of Cu/Ag-decorated PANI. The oxidizing species initiate the in-situ polymerization of aniline without the need for an external oxidizing agent, while the reducing species convert metal ions into neutral metal atoms, which become incorporated into the polymer matrix. The resulting samples were subjected to structural characterization using X-ray diffraction and thermoelectric property measurements. The Cu/Ag-decorated polyaniline sample exhibited the highest power factor of $\sim 4.48 \times 10^{-2} \mu\text{W}/\text{m}\cdot\text{K}^2$ at 300 K, which is nearly 13 times higher than that of pristine polyaniline.

INTRODUCTION

More than 60% of energy is lost as waste heat globally with a significant portion dissipated at or near room temperature. Thermoelectric (TE) materials can convert waste heat directly into electricity. The TE performance of a material is decided by figure of merit [$ZT=(S^2\sigma/\kappa)*T$], where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity of the material.¹ Inorganic materials such as Bi_2Te_3 and PbTe are commercially available TE materials due to their great performance. However, these materials are mostly toxic, brittle in nature, and have fabrication problems, limiting their applicability, particularly in flexible and wearable electronic devices. Organic TE materials, such as conducting polymers, provide several appealing benefits, including low thermal conductivity, tunable electrical conductivity, earth abundance, ease of synthesis, mechanical flexibility, low cost, light weight nature, and environmental friendliness and thus finds application in wearable electronics.² Polyaniline (PANI), an organic semiconductor has been widely investigated for thermoelectric applications and has been synthesized from its monomer, aniline. Polyaniline nanoparticles and nanocomposites have been synthesized using various techniques, including interfacial, chemical, electrochemical, and gamma irradiation polymerization methods. Among these, gamma irradiation induced synthesis offers a distinct advantage by enabling the single-pot synthesis of pure PANI and its nanocomposites, without the need for any additional initiators or complex processing steps. Gamma hydrolysis of the solution mixture generates reactive species which are both reducing (e.g., e_{aq}^- , H^*) and oxidizing (OH^* , H_2O^* , H_2O_2 , O_2^*) in nature, these are crucial for initiating and propagating the polymerization reaction. The oxidising species react with the monomers, initiating the polymerisation reaction without an external oxidising agent.^{2,3} Similarly, the reducing species can reduce metal ions (M^+) in solution to generate metal atoms (M) which gets incorporated in the polymer. Polyaniline occurs in three redox forms i.e, leucoemeraldine, emeraldine, and pernigraniline depending on the level of oxidation. Only the emeraldine salt (ES) form of polyaniline, which is the half-oxidized state, is both stable and electrically conductive and has applications in electronic industry (particularly in wearable thermoelectrics). The thermal conductivity of PANI is very low ($< 1 \text{ W/mK}$) and therefore, researchers desire to improve the power factor ($\text{PF}= S^2\sigma$) of PANI by using strategies like nanostructuring, doping or

making nanocomposites.^{3,4} In the present study, emeraldine salt (ES) form of PANI and Cu/Ag-decorated PANI samples were successfully synthesized via single-pot in-situ polymerization using gamma hydrolysis and their TE properties were systematically evaluated.

EXPERIMENTAL DETAILS

Polyaniline has been synthesized via gamma radiation-induced polymerization using aniline monomer (99% purity). A solution was prepared by dissolving 8 mL of distilled aniline in 200 mL of 1 M HNO₃ solution. The prepared solution was transferred into clean glass ampoules, which were then sealed to prevent contamination. To synthesize Cu/Ag-decorated PANI nanocomposites, copper (II) nitrate [Cu(NO₃)₂] and silver nitrate (AgNO₃) were used as metal precursors. A solution containing 10 mmol each of copper nitrate and silver nitrate was prepared by dissolving the salts in 250 mL of deionized water. Separately, 8 mL of aniline was dissolved in 200 mL of 1 M HNO₃ as described above. The two solutions were combined and stirred vigorously using a magnetic stirrer for 30 minutes to ensure uniform dispersion of metal ions. The resulting mixture was then transferred into a clean glass ampoule and then sealed it. These sealed ampoules were gamma irradiated with a dose of 3kGy (optimized dose) using a Co-60 gamma source under ambient conditions. Both the samples were then subjected to filtration and washed to obtain powders. The synthesized powder material obtained are then cold compacted into thin cylindrical shaped disc (10*1.5 mm²) and then characterized by XRD. Temperature dependent electrical conductivity and Seebeck coefficient was obtained from room temperature to 473 K using nano-voltmeter and current source meter (Keithley make). The Seebeck coefficient was measured using a homemade setup with a ΔT of 10K between the hot and cold ends under 10⁻³ mbar. The electrical conductivity was measured using the four probe method in the same setup.

RESULTS AND DISCUSSIONS

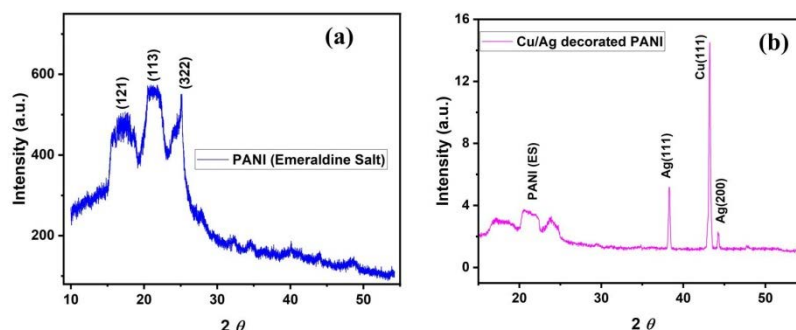


FIGURE 1. XRD pattern of gamma irradiation induced synthesis of (a) PANI (b) Ag and Cu decorated PANI.

Figure 1 (a) shows the XRD pattern of the emeraldine salt (ES) form of polyaniline which has three broad characteristic peaks corresponding to (121), (113) and (322) planes at the 2θ value ranges from ~ 15.5 – 25.1° and these peaks match with the PCPDF file 72-0634. This indicates that the polymer chain formed has orientation along these crystalline planes. The average crystallite size calculated by the Scherrer formula are 2.48 nm, 3.37 nm and 6.39 nm for (121), (113) and (322) planes respectively. Figure 1(b) presents the XRD pattern of Ag/Cu-decorated PANI, displaying characteristic peaks of copper (Cu) at 43.18° corresponding to the (111) plane, and silver (Ag) at 38.30° and 44.30° , corresponding to the (111) and (200) planes, respectively. Additionally, the Ag/Cu-decorated sample exhibits three broad peaks at lower 2θ values, attributed to the emeraldine salt (ES) form of PANI. The electrical conductivity for both the samples increases with increase in temperature and thus behaving like a semiconductor as shown in Figure 2 (a). From Figure 2 (b), it can be seen that the Seebeck coefficient is positive for both the samples, indicates holes are the majority charge carriers and the value of S , decreases with the increase in temperature. The highest value of the PF is obtained for Ag/Cu decorated PANI sample $\sim 4.48 \times 10^{-2} \mu\text{W}/\text{m}\cdot\text{K}^2$ at 300K and is shown in Figure 2 (c). The PF is compared with the reported work and is shown in Figure 2 (d).^{5,6}

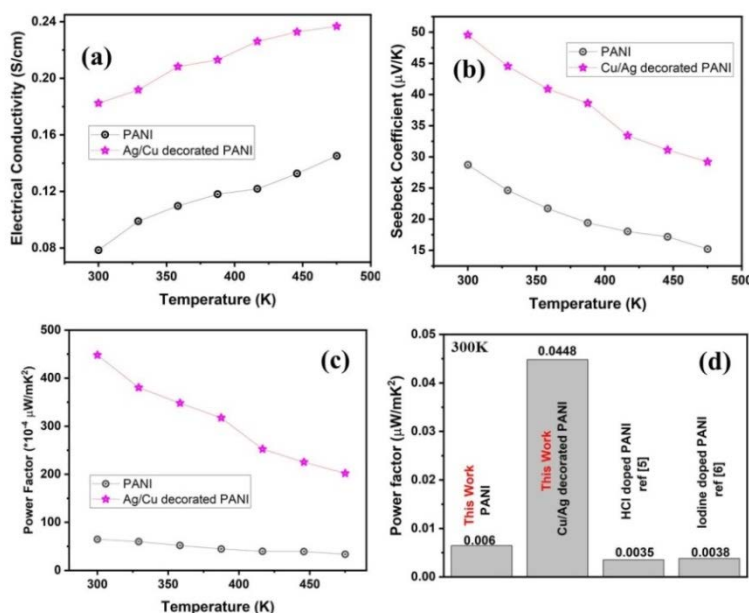


FIGURE 2. Temperature dependent (a) Electrical conductivity, σ (b) Seebeck coefficient, S (c) power factor, $\sigma^2 S$ (d) current work compared with the reported work [ref. 5 and 6]

CONCLUSIONS

In summary, we successfully synthesized polyaniline (PANI) and Cu/Ag-decorated PANI nanocomposites using gamma irradiation treatment. The single-pot in-situ polymerization method enables the formation of pure polymer and composite materials without the need for any additional initiators. The Cu/Ag-decorated PANI sample exhibited the highest power factor of approximately $4.48 \times 10^{-2} \mu\text{W/m} \cdot \text{K}^2$ at 300 K.

ACKNOWLEDGMENTS

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An Investigation of the Photoluminescence Properties of Europium Doped $\text{MgSr}_2(\text{PO}_4)_2$ Phosphor

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Abstract. This study investigates the photoluminescence characteristics of Eu^{3+} -doped $\text{MgSr}_2(\text{PO}_4)_2$ phosphors synthesized by a high-temperature solid-state reaction. X-ray diffraction (XRD) analysis and Fourier transform infrared (FTIR) spectroscopy of the phosphor were done to get an understanding of the phosphor's crystalline structure and the bonding of its functional groups. Photoluminescence measurements showed a red emission under UV light, mainly because of the electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu^{3+} ions. The spectral properties of Eu^{3+} ions are in sites of the host lattice that lack an inversion center. The results show that this phosphor is structurally stable as well as optically active could be a strong candidate as a red phosphor in display and lighting applications.

INTRODUCTION

Phosphate-based phosphors have gained substantial interest in recent years because of their chemical stability, low toxicity, high temperature resistance, and adaptable structure as host lattices for luminescent materials in lighting, display, and radiation dosimetry applications [1-2]. Among the different phosphates, orthophosphates having isolated PO_4^{3-} tetrahedra, such as alkaline and alkaline-earth types, are particularly important. They offer excellent thermal stability and hydrolytic stability and are potential hosts for the rare-earth ions that have been fairly extensively studied in terms of their crystal structure and luminescent properties [3]. Eu^{3+} ion, among the various rare-earth ions, finds the most use as an activator for red emission due to its particular 4f-4f transitions. These 4f-4f transitions are generally forbidden for free ions, but they become partially allowed in solid-state hosts due to the crystal field effect or the mixing with higher orbitals [4,5]. Phosphates such as LiMgPO_4 , $\text{Na}_3\text{Gd}(\text{PO}_4)_2$, $\text{MgZn}_2(\text{PO}_4)_2$, and $\text{Sr}_8\text{MgLa}(\text{PO}_4)_7$ are efficient luminescent materials under ionizing and UV radiations when doped with rare-earth ions such as Eu^{3+} , Tb^{3+} , Dy^{3+} , Tm^{3+} , and Cr^{3+} [6-9]. These host matrices are employed in various research studies for their photoluminescence (PL) characteristics useful in solid-state lighting.

This study provides a comprehensive overview of the synthesis, structural, and optical properties of Eu^{3+} doped $\text{MgSr}_2(\text{PO}_4)_2$ (MSP). And also based on the novel luminescent properties, these are used in commercial-based white LEDs. The color coordinates, color purity index, and CCT (K) values of the produced phosphor were calculated using the standards established by the International Commission on Luminescent Energy (Commission Internationale de l'Eclairage, 1932 (CIE) [10].

EXPERIMENTAL

Eu^{3+} doped MSP phosphor was synthesized by the conventional solid-state reaction method. Initially, high-purity MgO , SrCO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$, and Eu_2O_3 powders were weighed as per stoichiometry. The weighed amounts of MgO , SrCO_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$, together with mol % Eu_2O_3 , were mixed thoroughly in an agate mortar to ensure a homogeneous mixture. Next, the mixture was kept in a muffle furnace at 1000°C for 4 h. After it had cooled down under natural conditions, the sample was ground to obtain a fine powder. Eu^{3+} doped MSP sample was analysed using XRD to understand the purity and crystal structure. Then, FTIR spectroscopy was used to examine functional groups and bonds, whereas PL excitation and emission were recorded.

RESULTS AND DISCUSSIONS

Phase Purity Analysis and FTIR Analysis

The XRD pattern for Eu^{3+} doped MSP with a 2θ ranges from 10°C to 80°C is shown in Figure 1(a). The intense diffraction peaks clearly suggest that the sample contains a crystalline phase. As there exists no standard JCPDS data for MSP, the pattern data were compared with $[(\text{Sr}_{0.86}\text{Mg}_{0.14})_3(\text{PO}_4)_2]$ Magnesium strontium Phosphate with standard PDF no (00-047-1895). It can be deduced from the diffraction data that the structure of the powder sample closely agrees with $[(\text{Sr}_{0.86}\text{Mg}_{0.14})_3(\text{PO}_4)_2]$, the proposed structure of $\text{MgSr}_2(\text{PO}_4)_2$ from the intended synthesis, thus verifying the success of the synthesis and high phase purity. A FTIR spectrum of MSP showed characteristic bands of the PO_4^{3-} group. The spectrum reflects the vibrational stretching and bending of various functional groups in the sample. The broad absorption around $3720, 3412\text{ cm}^{-1}$ was assigned to the O–H stretching of adsorbed water (moisture present) in the sample. Sharp peaks near 1309 cm^{-1} , 1568 cm^{-1} , 698 cm^{-1} , 2362 cm^{-1} , and 2021 cm^{-1} were due to asymmetric and symmetric stretching vibrations of PO_4^{3-} , stretching vibrations of Sr–O, P=O, and Mg–O, respectively. The band lying between 568 cm^{-1} corresponded to the bending modes of phosphate groups, thereby confirming the formation of the orthophosphate structure.

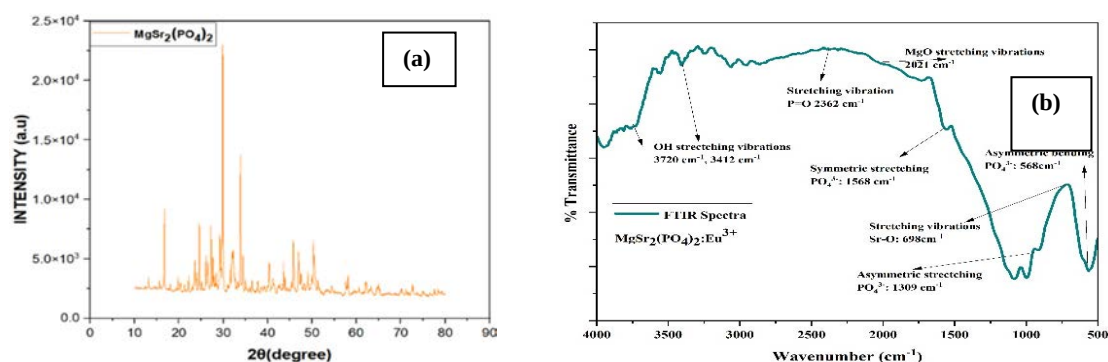


FIGURE1. (a) XRD pattern of MSP and (b) FTIR spectrum of Eu^{3+} doped MSP

Photoluminescence Analysis

The excitation and emission spectra for the MSP phosphor, which has been doped with Eu^{3+} , are illustrated in Figure 2. In Fig. 2(a), PL excitation spectra for the MSP doped with Eu^{3+} at 613 nm emission wavelength due to the $^5\text{D}_0$ to $^7\text{F}_2$ transition are shown. This spectrum shows several peaks within the $360\text{--}540\text{ nm}$ range, due to electronic transitions between the $4f\text{--}4f$ ($^5\text{D}_0$ to $^7\text{F}_j$) transitions and narrow lines in the red region of the Eu^{3+} ions. The excitation peaks appear at wavelengths of 362 nm , 382 nm , 394 nm , 414 nm , 465 nm , and 534 nm , corresponding to transitions from the ground state, $^7\text{F}_0$, to various excited states, including $^5\text{D}_4$, $^5\text{L}_7$, $^5\text{L}_6$, $^5\text{D}_3$, $^5\text{D}_2$, and $^5\text{D}_1$ of the Eu^{3+} ions. The most intense excitation peak occurs at 394 nm , linked to the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition of the Eu^{3+} ions. In Fig. 2(b), the emission spectrum of the MSP phosphor doped with Eu^{3+} ions is shown, with the excitation wavelength of 394 nm . The emission peaks at 592 nm , 613 nm , 653 nm , and 700 nm in the host sample are attributed to electronic transitions from $^5\text{D}_0$ to $^7\text{F}_1$, $^7\text{F}_2$, $^7\text{F}_3$, and $^7\text{F}_4$, respectively, of the Eu^{3+} ions. The emission peak with the highest intensity, found at 613 nm , is linked to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition.

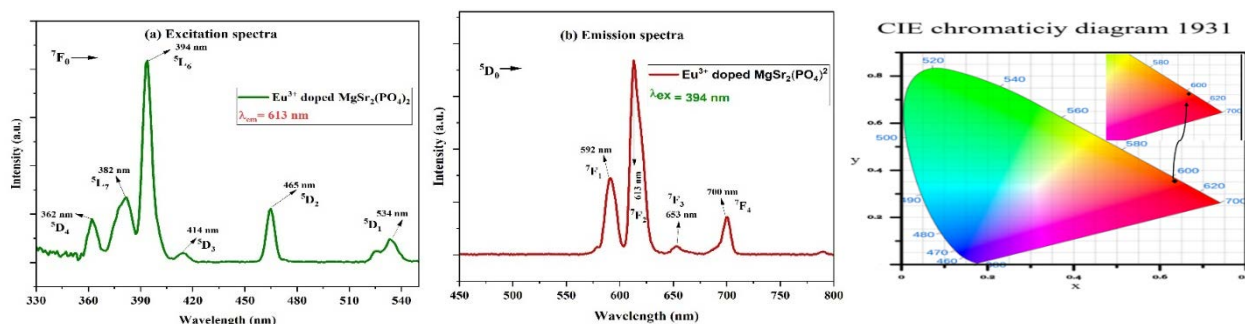


FIGURE 2. Photoluminescence Spectra of (a) Excitation and (b) Emission of Eu^{3+} doped MSP phosphor (c) CIE chromaticity diagram of Eu^{3+} doped MSP phosphor

The PL behaviour of Eu^{3+} -activated MSP phosphors can be interpreted on the basis of the $4f\text{--}4f$ intra-configurational electronic transitions of the Eu^{3+} ion, which are highly sensitive to the surrounding crystal structure. The absorption

of UV or near-UV photons induces transitions in the Eu^{3+} ion from the ground state ${}^7\text{F}_0$ to excited states, preferably ${}^5\text{L}_6$. The excited electrons undergo a non-radiative relaxation to the lower metastable ${}^5\text{D}_0$ level, from which they return radiatively to the ${}^7\text{F}_J$ manifold of the ground state (where $J = 0, 1, 2, 3, 4$), rendering sharp emission lines. The dominant emission usually arises from the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition (about 608–620 nm), an electric dipole transition that is allowed in a non-centrosymmetric environment. The intensity ratio of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions provides information about the symmetry around the Eu^{3+} ions; a higher ratio implies a less symmetric site and hence higher asymmetry of the crystal field. Eu^{3+} ions mainly substitute Sr^{2+} ions in the host lattice of MSP due to similar ionic sizes, and any local charge disparity is compensated by vacancies or interstitial ions. PO_4^{3-} groups provide very stable and thermally resilient conditions that forbid non-radiative losses and encourage PL emission. Hence, photoluminescence involves good energy absorption, non-radiative energy conversion, and sharp-line emissions caused by Eu^{3+} transitions in the crystal field of the MSP host.

Photometric Analysis

A CIE chromaticity diagram showing MSP phosphor doped with Eu^{3+} is shown in Fig. 2 (c). The Color Calculator v7.77 software was used in determining the photometric characteristics of the sample based on parameters such as CIE, CCT, and Color purity. Its CIE color was found to be $x=0.635$ and $y=0.353$, placing it in the red-orange region. The calculated CCT and color purity were 2320K and 87.58%, respectively. These findings may prove useful in the synthesis of materials that act as warm emitters in photo sensor devices such as LEDs. Such devices might have extremely bright applications in color-display systems and tall optical storage units.

CONCLUSION

In this study, we prepared Eu^{3+} doped MSP via solid-state reaction. XRD analysis revealed the sample to be well-crystallized. FT-IR analysis indicated the presence of P=O bonds, Mg-O, Sr-O, and OH stretching vibrations along with $(\text{PO}_4)^{3-}$ ion stretching and bending modes in the sample. The observed photoluminescence is due to the 4f-4f transitions of Eu^{3+} ions and is intensified by the phosphate host matrix. Upon excitation by 394 nm light, the MSP: Eu^{3+} emitted peak intensities at 592, 613, and 700 nm, with Eu^{3+} ion transitions of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^7\text{F}_2$, and ${}^7\text{F}_4$, respectively, corresponding to the red-orange region. From the CIE chromaticity plot, the coordinates of the orange color are established to be $x = 0.635$ and $y = 0.353$; and the CCT value and color purity of the sample are established to be 2320 K and 87.58%, respectively. All these characteristics, along with sharp emission lines, make it a potential candidate for display devices, solid-state lighting, and warm-emitting LEDs.

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Theoretical Exploration of Structural, Mechanical and Electronic Properties of MgScO_3 : A Full Potential Approach

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Abstract. In this communication, we have investigated structural, mechanical and electronic properties of Perovskite MgScO_3 . We have used full potential linearized augmented plane wave method as implemented in Wien2k code. From our study we have been observed that MgScO_3 is mechanically ductile having anisotropic nature. From electronic band structure, we found that the given compound is 100% spin polarized and exhibit half-metallic behavior. The structural, mechanical and electronic properties have been reported for the first time. No experimental and theoretical data is available for comparison.

INTRODUCTION

Few years ago, the world's energy consumption was rising daily. Electricity is now produced using non-renewable energy sources. However, burning these sources depletes precious energy resources and puts our surroundings at risk [1]. In order to get out of this problem, researchers are searching for other potential and economically viable energy sources. Hydro, wind, biogas, tidal, and solar radiation are examples of renewable energy sources that offer an appropriate substitute to non-sustainable energy sources [2]. Due to its abundance and sustainable nature, solar energy is the best alternative among all renewable energy sources [3]. Perovskite materials are found suitable for this purpose which is used for solar cell applications. MTO (M-alkaline earth metal, T-transition metal, O-oxide) has previously found new uses in photocatalysis due to its band gap (~ 3.4 - 3.7 eV), which is inconsistent with the photocatalytic property [4]. MTO has a special place in this regard because of its excellent dielectric qualities and well-known material for the production of electric devices like microwaves [5]. Numerous investigations of various MTO combinations have been conducted. Some physical properties of MgTiO_3 were studied using DFT, as reported by Nazeer et al. [6]. From the survey of available literature it is evident that no experimental or theoretical data on MgScO_3 compound are available till now. Thus, we hereby study for the first time the structural, mechanical and electronic properties of given compound theoretically.

COMPUTATIONAL DETAILS

To investigate structural and electronic properties we have been employed full potential linearized augmented plane wave method (FP-LAPW) as embedded in Wien2k [7] software. For exchange correlation energy solids PBEsol-GGA [8] have been used. $R_{\text{MT}} \cdot K_{\text{max}} = 7$ is used as the cut-off parameter. The Monkhorst Pack approach [9] has been applied to Brillouin zone integration using a mesh of 1000 k-points. The convergence criteria for charge and energy are chosen at $10^{-3}e$ and 10^{-4} Ry, respectively.

RESULTS AND DISCUSSIONS

Structural and Mechanical Properties

The crystal structure of the Perovskite oxide MgScO_3 is simple cubic, belonging to space group $Pm3m$ (number 221). In MgScO_3 structure, Mg atom located at (0, 0, 0) site, Sc atom at (0.5, 0.5, 0.5) and O atom resided at (0, 0.5, 0.5) site, respectively. The unit cell structure of MgScO_3 is shown in **Figure 1(a)**. The energy versus volume curve is depicted in **Figure 1(b)**. The obtained equilibrium lattice constant (a_0), unit cell volume (V_0) and total energy (E_0) are also listed in **Table 1**.

For the investigation of mechanical properties, we have calculated elastic constants and derived parameters which are tabulated in **Table 2**. Firstly we have checked mechanical stability. Obtained elastic constants satisfied stability conditions meaning thereby that MgScO_3 is mechanically stable. From the table, we observed that Pugh's ratio B/G is more than 1.75 which reveals that MgScO_3 is ductile in nature which also confirms from Cauchy pressure ($C_{12} - C_{44}$), positive magnitude of Cauchy pressure indicates ductile nature. From anisotropy parameter (A), it is evident that the deviation in the value of A from 1 shows anisotropic behavior of given compound.

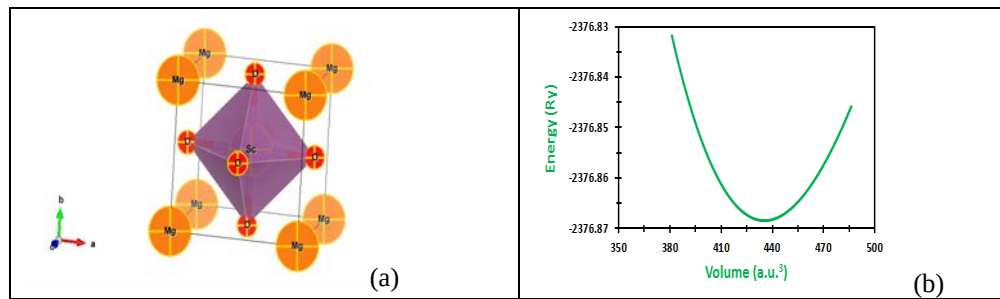


FIGURE 1.(a) The unit cell structure of MgScO_3 , (b) The energy versus volume optimization curve for MgScO_3 .

TABLE 1. Optimized lattice constant a_0 (Å), equilibrium unit cell volume V_0 (Å³) and the equilibrium energy E_0 (Ry) for MgScO_3 .

a_0 (Å)	V_0 (a.u. ³)	E_0 (Ry)
3.79	368.17	-2380.92

TABLE 2. Calculated independent elastic constants C_{11} , C_{12} and C_{44} (in GPa) and derived elastic parameters isotropic shear modulus 'G' (in GPa), Young's modulus 'Y' (in GPa), anisotropy factor 'A' for MgScO_3 .

C_{11}	C_{12}	C_{44}	B	G	Y	B/G	A
269.81	52.03	36.17	124.62	65.25	166.67	1.90	0.33

Electronic Properties

We have used the PBEsol-GGA approximation to calculate the electronic band structure (BS) and density of states (DOS) while considering a spin-polarization in order to study the electronic properties of MgScO_3 . Obtained band structure and DOS plot in spin up ($\uparrow$) as well as in spin down ($\downarrow$) channel along high symmetry directions in first Brillouin Zone are represented in **Figure 2(a) and (b)**. From BS plot, we found that the bands from valence band (VB) cross the fermi level and goes into conduction band (CB) in spin up channel indicates metallic nature and in spin down channel VB and CB are separated by an energy gap indicates semiconducting behaviour. Overall behavior of MgScO_3 is half-metallic and 100% spin polarized which also confirms from DOS plot. Similar characteristics

observed from DOS plot. BS studies reveals that the MgScO_3 is useful for spintronics applications due to its half-metallic behaviour.

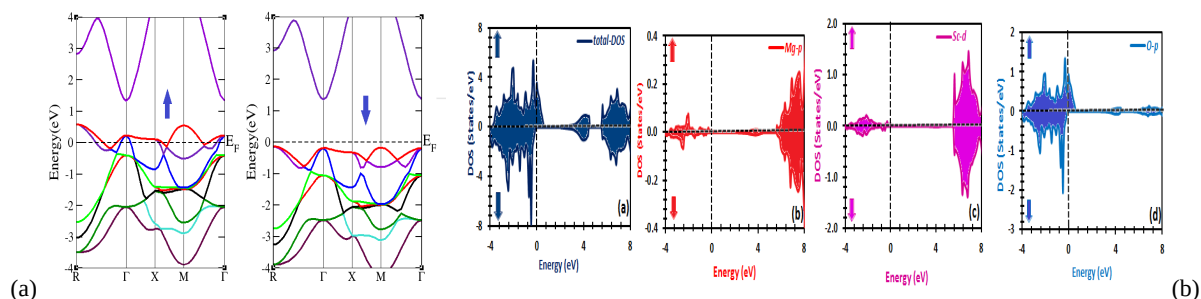


FIGURE 2. (a) Spin-polarized band structure of MgScO_3 , (b) Total and resolved partial density of states plots for MgScO_3 .

CONCLUSIONS

In this work, we have studied structural, mechanical and electronic properties of MgScO_3 using FP-LAPW approach. We have used Wien2k software to calculate these properties. Firstly, we have obtained structural parameters. Using these parameters we have obtained elastic constants and derived elastic parameters. Elastic constants shows that MgScO_3 is mechanically stable and exhibit ductile nature. From band structure and DOS plots we found that given compound is half-metallic and 100% spin-polarized. It is useful for spintronics applications. These results are reported for the first time. No experimental or theoretical results are present.

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Conductive Double Network Hydrogel for Functional Applications

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Abstract. This study reports the successful development of a double-network (DN) hydrogel using polyvinyl alcohol (PVA), sodium alginate (SA), and montmorillonite (MMT) for potential use in smart agriculture. The hydrogel was fabricated via physical and chemical crosslinking methods. Structural and crystallinity changes resulting from MMT incorporation were confirmed using X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). The hydrogel's performance was assessed through measurements of electrical conductivity, tensile strength, and water retention capacity. The DN hydrogel demonstrated improved tensile strength, electrical conductivity, and moderate water retention property, indicating enhanced mechanical stability and facilitated ionic transport due to the uniform dispersion of MMT.

INTRODUCTION

Hydrogels, as three-dimensional polymer networks, can retain large amounts of water without losing structural integrity [1]. This network is created by hydrophilic polymer chains through chemical or physical interactions. Because of their flexibility, water retention, and adjustable properties, hydrogels have been extensively studied for use in biomedicine, soft robotics, and wearable electronics [2]. However, traditional single-network hydrogels often face issues with poor mechanical strength and limited biodegradability, which limit their wider use [3].

To overcome these issues, double-network (DN) hydrogels are gaining interest as a promising alternative. DN hydrogels consist of two interpenetrating networks: one rigid and brittle, the other soft and ductile. This combination provides superior toughness and energy dissipation capabilities, addressing the mechanical limitations of conventional hydrogels. Typically prepared via a two-step process, DN hydrogels show improved stretchability, strength, and durability [4]. The selection of polymer components is crucial in determining their final properties.

Sodium alginate (SA), an eco-friendly polysaccharide of natural origin, typically extracted from the cells of brown algae, is known for its excellent biocompatibility, biodegradability, and high-water affinity [5]. Polyvinyl alcohol (PVA), though synthetic, is recognized for its water solubility, flexibility, and potential biodegradability under suitable conditions. When blended, SA and PVA complement each other by forming a more stable and reinforced network.

Incorporating nanomaterials like montmorillonite (MMT) clay further enhances hydrogel properties. MMT introduces ionic and hydrogen bonding with the polymer matrix, improving crosslinking density, mechanical strength, and thermal stability [6]. It is an abundant, cost-effective, and eco-friendly additive that strengthens the network and improves stress transfer across the matrix.

In this study, sodium alginate (SA), polyvinyl alcohol (PVA), and montmorillonite (MMT) were selected due to their biodegradability and cost-effectiveness compared to conventional synthetic polymers. The development of a double-network hydrogel combining natural and synthetic polymers with nanoclay reinforcement, aiming to achieve a balance of high mechanical strength, water retention, and environmental sustainability for potential use in smart agricultural applications.

EXPERIMENTAL SECTION

Methods

First, a 10 wt% PVA solution was prepared by mixing 30 mL of deionized water with 3 g of PVA at 115 °C for 1 hour, and cooled naturally. Separately, 0.6 g of SA was dissolved in 20 mL of water at 85 °C, followed by the addition of MMT, and the mixture was stirred for 1 hour. This SA–MMT mix was then combined with the cooled PVA and stirred for 1.5–2 hours to get a uniform hydrogel mixture. A 20 mL portion of the mixture was poured into a petri dish and ultrasonicated to remove air bubbles. It then underwent three freeze–thaw cycles to cross-link PVA. The formed hydrogel was then soaked in 2 wt% CaCl₂ for 6 hours to cross-link the sodium alginate, followed by rinsing with

deionized water to remove excess ions. The hydrogel samples were designated as PS, PSM1, PSM2, and PSM3, corresponding to MMT contents of 0 g, 0.05 g, 0.10 g, and 0.15 g, respectively, while keeping the amounts of PVA (3 g) and SA (0.6 g) constant for a total solution of 60 mL.

Characterization

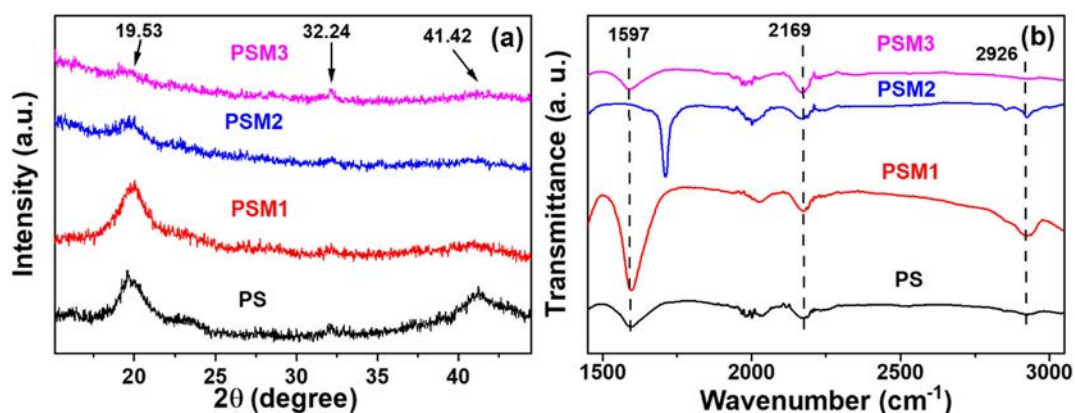
X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) were performed for the structural and functional analysis of hydrogels. Patterns were recorded utilizing Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) with a scanning speed of 2° per minute and a step interval of 0.02° using a Rigaku Miniflex 600 (Japan), and a PerkinElmer Spectrum 400 spectrometer used for functional study of the hydrogels. For tensile testing, the hydrogels were cut into strips measuring $40 \text{ mm} \times 10 \text{ mm}$, with thicknesses between 1 and 1.5 mm. The specimens were tested using a 500 N Zwick Roell Z010 Universal Testing Machine (UTM) to calculate the tensile strength at a crosshead speed of 50 mm/min. Each hydrogel formulation was tested in triplicate. To determine the moisture content, the specimens were first weighed in their swollen state, then oven-dried at a constant temperature of 50°C until a stable weight was achieved. The water content (wt%) was calculated gravimetrically based on the mass difference between the swollen and dry states, expressed as a percentage of the swollen weight.

RESULTS AND DISCUSSION

XRD analysis, as shown in Fig. 1(a), was carried out to investigate changes in the crystallinity of the PVA/SA/MMT DN hydrogels. The diffraction pattern showed a peak at 19.5° , corresponding to the semi-crystalline domains of the polymer matrix, likely associated with hydrogen bonding that stabilizes the internal structure [7]. Another peak observed at 41.4° is attributed to the ordered packing of PVA chains. The progressive decrease in peak intensity with increasing MMT content suggests that the addition of MMT disrupts the ordered arrangement of polymer chains, thereby enhancing the composite's amorphous nature.

The presence of functional groups in the hydrogel was identified using FTIR spectra, as shown in Fig. 1(b). A distinct peak at 2926 cm^{-1} appears in all hydrogel samples, originating from the stretching vibrations of C-H bonds within the methylene units of the PVA backbone [8]. Additionally, stretching modes associated with the carboxylate (COO^-) groups from sodium alginate are evident at 1597 cm^{-1} and 1415 cm^{-1} , suggesting the formation of ionically crosslinked networks and interactions with the layered structure of MMT [9].

Tensile strength values of the hydrogels are presented in Fig. 2(a). As evident from the Fig., increasing the amount of MMT in the hydrogel formulation leads to a corresponding increase in tensile strength. This enhancement is



attributed to the layered structure of MMT, which provides strong interfacial interactions with the hydroxyl and carboxyl groups of PVA and SA. These interactions contribute to the development of a denser and more mechanically

FIGURE 14: (a) XRD, and (b) FTIR of PVA/SA/MMT hydrogels

stable polymer network. Additionally, the presence of MMT facilitates effective stress transfer and functions as a physical crosslinker, further reinforcing the hydrogel structure.

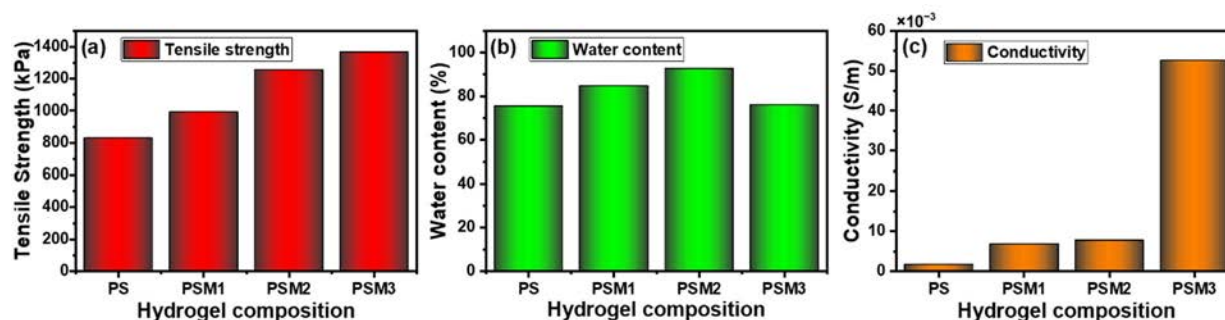


FIGURE 15: (a) Tensile strength, (b) Water content, and (c) Conductivity of the PVA/SA/MMT

The water content of the PVA/SA/MMT DN hydrogel increased with the addition of MMT, reaching a maximum up to the PSM2 sample, [Fig. 2(b)]. This is due to the hydrophilic nature of MMT, which facilitates greater water absorption within the polymer matrix through hydrogen bonding and electrostatic interactions. However, beyond this composition, a decline in water content was observed. The presence of excess MMT may reduce the availability of free hydrophilic sites due to particle agglomeration, which can disrupt the uniformity of the network and hinder water diffusion pathways. Figure 2(c) illustrates the conductivity behavior of the hydrogels, which gradually increases with the rising content of MMT. This enhancement is primarily attributed to the presence of MMT, which introduces additional ionic pathways and promotes the mobility of charge carriers within the hydrogel network. The observed improvement in conductivity reflects a better dispersion of MMT and stronger interactions between the MMT layers and the polymer chains.

CONCLUSION

The PVA/SA/MMT DN hydrogel was synthesized using physical crosslinking of PVA and chemical crosslinking of SA. The incorporation of MMT into the DN hydrogel enhanced both its tensile strength and electrical conductivity. XRD and FTIR analyses confirmed structural interactions between the components and a reduction in crystallinity as a result of MMT addition. However, an excessive amount of MMT reduced the water retention capacity, likely due to particle agglomeration and disruption of the hydrogel's porous structure.

ACKNOWLEDGEMENT

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Thin Film CuO and MnO₂/CuO On Cu Foil For Supercapacitor Electrode Application

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Abstract. The selection and design of electrode materials are critical in defining the performance of supercapacitors. The surface area, film thickness, number of oxidation states, and stability are all important factors responsible for good results. In this study, CuO nanoneedles and layered heterostructure of MnO₂ and CuO were electrochemically prepared on a Cu foil. The structure, and morphology was determined by Raman Spectroscopy and Scanning Electron Microscopy respectively. A mixed stoichiometric form of MnO₂ and Mn₂O₃ was observed for the heterostructure. Cyclic Voltammetry and Galvanostatic charge Discharge was performed to understand the electrochemical nature of the samples. The CuO_Cu exhibited a specific capacitance of 218 F g⁻¹, while the MnO₂/Mn₂O₃_Cu electrode achieved a higher value of 454 F g⁻¹ at a scan rate of 20 mV s⁻¹ in 1 M KOH electrolyte.

INTRODUCTION

The rising global energy demand has driven the development of advanced energy storage technologies for sustainable systems. To meet power needs, supercapacitors are a promising candidate. Transition metal oxides as electrodes fill the gaps of cost-effectiveness, efficiency and sustainability, alongwith the scope of nanoscale engineering. The theoretical specific capacitance of CuO is reported as 1783 F g⁻¹ within a voltage window of 0.68 V. Various morphologies of CuO, such as nanoplates, bud-like structures, flower-shaped forms, and have been explored to enhance its electrochemical performance.. Manganese oxide possesses a theoretical capacitance of 1370 F g⁻¹. Different crystalline phases of MnO₂—characterized by chain-like frameworks, layered structures, and spinel configurations—contribute to efficient electron transport, enhanced ion intercalation, and an abundance of electroactive sites, respectively[1,2]. In this work CuO and MnO₂ are studied to explore their individual and synergistic effects. CuO is a promising candidate due to its non-toxicity, abundance and its morphological tunability. Manganese oxides have received special attention due to their multiple oxidation state properties, morphology, crystalline structure, and surface nanoarchitectures.

EXPERIMENTAL

Cu foil of thickness 0.127mm was anodized galvanostatically using a two-step method to grow nanoneedles. A bluish colour was observed on conversion of the Cu to Cu(OH)₂ (Sample Cu(OH)₂_Cu). This was then heat treated at 170°C to form CuO (Sample CuO_Cu). 0.1M Manganese nitrate precursor was used for the electrodeposition of MnO₂ on the prepared Cu-CO. A three-electrode set up was used, with a working electrode as the CuO_Cu, reference electrode Ag/AgCl and the counter electrode used was a Cu foil to prevent stripping reaction. The prepared sample (Sample MnO₂/Mn₂O₃_Cu) was then heat treated at 450°C at a 5^o/min heating and cooling rate for 30mins.

RESULTS AND DISCUSSION

The Raman spectra of the Cu(OH)₂_Cu and CuO_Cu samples are presented in Figure 1. (A) and (B). The presence of copper hydroxide is confirmed by the characteristic peaks observed at 288 cm⁻¹ and 486 cm⁻¹, while the peak at 614 cm⁻¹ corresponds to the formation of CuO. The Raman-active modes of CuO are reported to include one A_g mode and two B_g modes [3]. Differences in grain size are responsible for the slight shift in the Raman bands that is observed.

The $\text{MnO}_2/\text{Mn}_2\text{O}_3\text{-Cu}$ Raman spectroscopy shows a prominent peak at 651 cm^{-1} , which is characteristic of MnO_2 , along with another peak at 476 cm^{-1} , which is usually associated with Mn_2O_3 nanostructures. These spectral features indicate that the $\text{MnO}_2/\text{Mn}_2\text{O}_3\text{-Cu}$ sample comprises a mixed stoichiometry of MnO_2 and Mn_2O_3 [4]. The SEM image of the $\text{Cu}(\text{OH})_2\text{-Cu}$ sample showed a uniform and well-distributed nanoneedle morphology densely packed on the substrate surface. The nanostructured networks of electrodes lead to a dramatically enlarged surface area, which is beneficial for electrochemical performance. The $\text{MnO}_2/\text{Mn}_2\text{O}_3\text{-Cu}$ layer was then grown on this high-surface-area nanoneedle architecture.

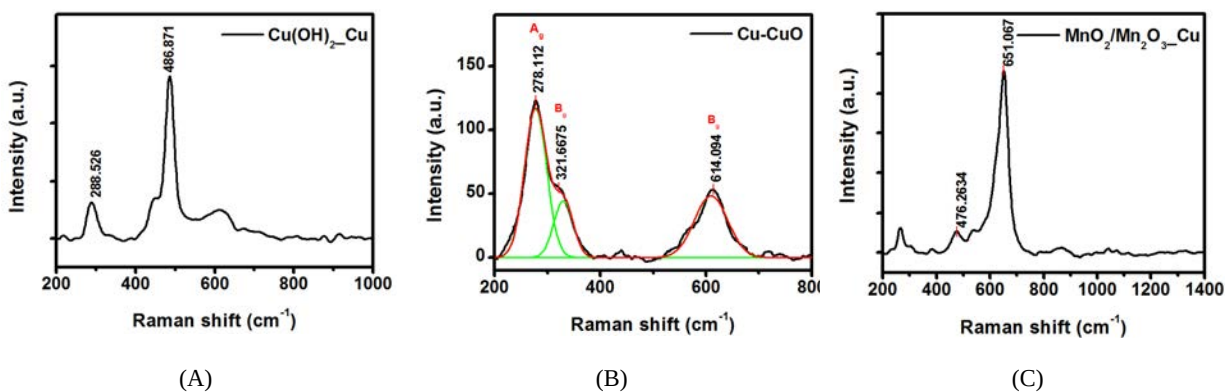


FIGURE 1. Raman spectra of (A) Cu-CH, (B) Cu-O and (C) Cu-MOx.

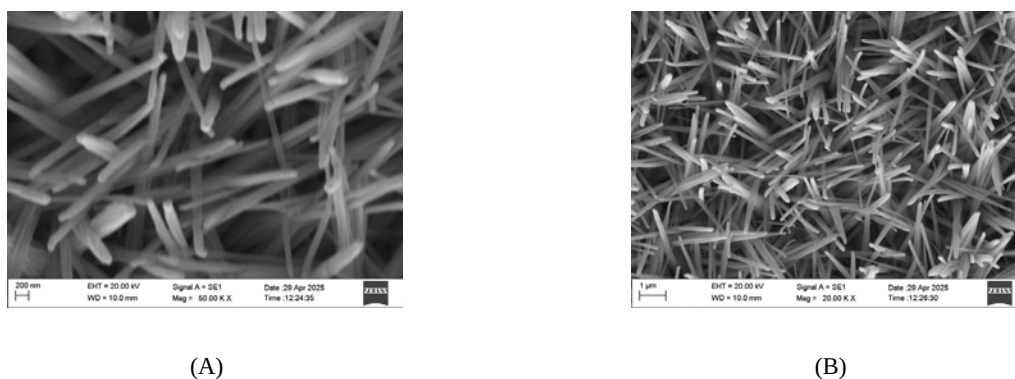


FIGURE 2. SEM images of (A) $\text{Cu}(\text{OH})_2\text{-Cu}$ 50KX magnification and (B) 20KX magnification showing uniform and densely packed nanoneedle morphology.

Electrochemical Characterization was done through Cyclic Voltammetry (CV) and Galvanostatic Charge Discharge Studies (GCD). The experiments were performed in a three-electrode set-up using Ag/AgCl as the reference electrodes and Platinum as a counter electrode. All half-cell experiments were performed in 1M KOH. The scans were performed at 20 mV/s . A comparison of the CV of bare Cu foil and prepared samples was done. It revealed that the contribution of the bare Cu foil and $\text{Cu}(\text{OH})_2\text{-Cu}$ sample is much less compared to that of sample CuO-Cu . The stability of CuO-Cu was observed to be much better than the $\text{Cu}(\text{OH})_2\text{-Cu}$ sample pointing towards a better stability of oxide materials. The CV of $\text{MnO}_2/\text{Mn}_2\text{O}_3\text{-Cu}$ showed a quasi-rectangular curve in the potential range of 0-0.6V indicating fast charge/discharge behaviour and high rate ability. GCD showed a triangular waveform. Specific capacitance from the CV curve was calculated. The CuO-Cu sample exhibited a specific capacitance of 218 F g^{-1} , while $\text{MnO}_2/\text{Mn}_2\text{O}_3\text{-Cu}$ achieved a higher value of 454 F g^{-1} at a scan rate of 20 mV s^{-1} in 1 M KOH electrolyte [5].

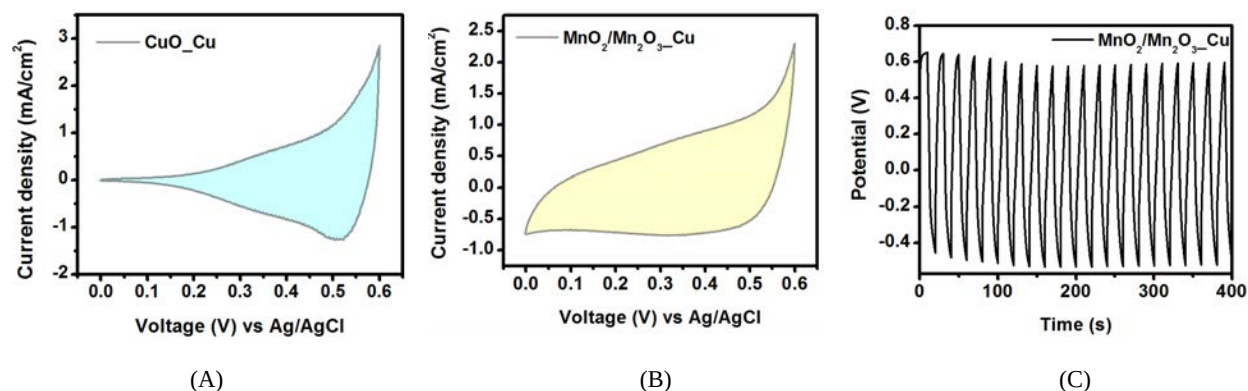


FIGURE 3. Cyclic Voltammetry plots of (A) CuO/Cu, (B) MnO₂/Mn₂O₃-Cu at 20mV/s and (C) GCD plots of MnO₂/Mn₂O₃-Cu at 1A/g

CONCLUSION

The mixed stoichiometry of MnO₂ and Mn₂O₃ provides multiple oxidation states, enabling redox transitions between Mn²⁺ and Mn³⁺ during cycling. This contributes to enhanced redox kinetics, thereby improving both specific capacitance and cycling stability. Additionally, the Cu foil serves as a flexible and conductive substrate, allowing facile nanoscale electrochemical structuring. The resulting increase in surface area further promotes efficient charge storage.

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Synergistic MoSe₂-CuO Heterointerfaces for Enzyme-Free Glucose Monitoring

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Abstract. The design of efficient non-enzymatic glucose sensors is crucial to address the drawbacks of enzymatic systems, which often suffer from instability and limited operational conditions. Herein, the MoSe₂-CuO nanocomposites have been prepared to serve as a highly efficient electrocatalyst for glucose sensing. The integration of two-dimensional MoSe₂ with CuO nanoparticles facilitates strong interfacial coupling, rapid electron transfer, and abundant electroactive sites, leading to superior electrocatalytic activity toward glucose oxidation. The developed sensor exhibits a rapid response time of 3 s, a low detection limit of 0.5 μ M with a sensitivity of 123 μ A mM⁻¹ cm⁻², and a wide linear detection range. Furthermore, its applicability is successfully demonstrated in real sample analysis using fruit juice.

INTRODUCTION

Glucose sensing plays a significant role in healthcare, particularly in diabetes management, where continuous monitoring is essential to prevent life-threatening complications. A varieties of detection techniques, including spectrophotometry, infrared spectroscopy, optical, acoustic, fluorescence, and electrochemistry have been explored; among them, electrochemical sensors have emerged as the most promising due to their excellent sensitivity, great selectivity, rapid response, and cost-effectiveness.^{1,2} However, enzymatic sensors face certain limitations related to environmental instability, prompting a shift toward non-enzymatic alternatives. Till now, researchers have introduced lots of non-enzymatic glucose sensors. However, metal oxides stand out for their excellent electrochemical properties and low cost. Moreover, the copper oxide (CuO) shows relatively high conductivity, affordability, and increased sensitivity, making it a popular choice to use in glucose detection. Also, amongst others, MoSe₂, a 2D transition metal dichalcogenide (TMDC), offers high electrocatalytic activity and biocompatibility. Hence, to enhance performance, researchers have explored hybrid systems like MoSe₂-NiO, CuO-MoS₂, etc., though challenges such as limited detection range and stability persist, motivating further interface-engineered nanocomposite design.

To challenge these difficulties, in this work, CuO-incorporated MoSe₂ is prepared for the non-enzymatic glucose sensing application. The combination of excellent conductivity of MoSe₂ and great catalytic activity of CuO creates a synergistic effect leading to improved glucose oxidation kinetics, high selectivity and sensitivity, prompt response time, better stability and recyclability, and lower detection limit due to enhanced signal-to-noise ratio.

EXPERIMENTAL METHOD

A two-step process has been employed to synthesize MoSe₂-CuO nanocomposite. At first, an easy hydrothermal method has been introduced to produce MoSe₂ nanosheets (NSs). The whole process is given in our previous papers.^{3,4} Here the hydrothermal treatment time is taken as 48 h, and the autoclave is kept at 200 °C. Further, 0.12 g Cu (NO₃)₂·3H₂O; 0.09 g CH₄N₂O, and 0.09 g CTAB are dispersed in 40 ml of water in one beaker. In another beaker, 0.04 g of synthesized MoSe₂ is dispersed in 10 mL of water and sonicated for 30 min. After that, the latter one is mixed with the previous solution and agitated for 1 h. Further, the final solution is transferred to the autoclave maintained at 120 °C for 5 h. The suspension is then repeatedly filtered and rinsed with distilled water and absolute ethanol. Finally, the as-synthesized powder is dried in air at 60 °C for 4 h, and thus, the MoSe₂-CuO nanocomposite is obtained.

RESULTS AND DISCUSSION

The TEM and FESEM characterizations are carried out to analyse the morphologies of the prepared samples. Both the images [Figs. 1(a, b)] have confirmed that MoSe₂ nanosheet (NS) and flake-like CuO are synthesized, and it is also the incorporation of CuO on MoSe₂ NSs have been well established. Also, it is confirmed that the incorporation of CuO prevents the aggregation of MoSe₂ NSs. The MoSe₂ NSs have been found to be of lateral size of 1.4 μm , while the flake size of CuO is ~ 364 nm.

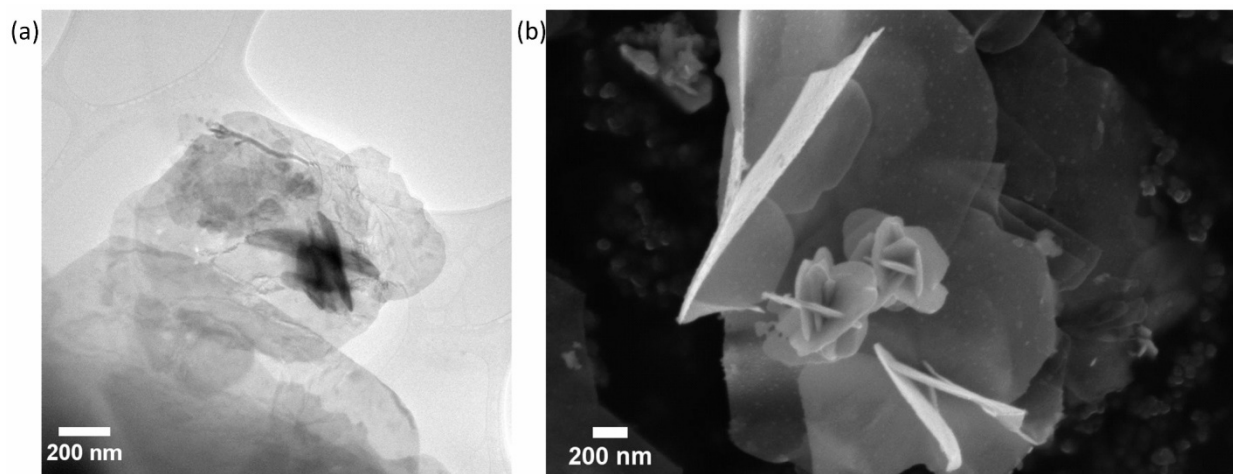


Figure 1. (a) TEM, and (b) FESEM image of MoSe₂-CuO nanocomposite.

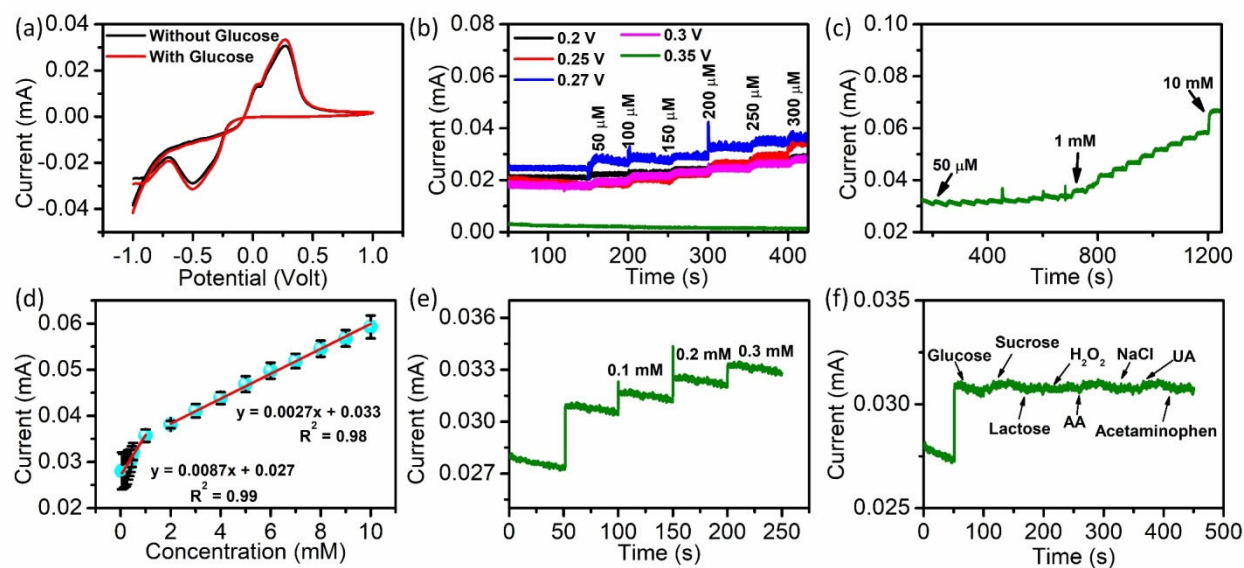


Figure 2. (a) CV profiles of MoSe₂-CuO at 50 mV s⁻¹ scan rate. (b) Amperometric performances of MoSe₂-CuO/GCE at different applied potentials with additions of glucose from 50 to 300 μM in succession. (c) Amperometric performance (at 0.27 V) of MoSe₂-CuO/GCE with sequential glucose addition ranging from 50 μM to 10 mM (the solution is stirred at a rate of 800 rpm). (d) The linear calibration plot of oxidation currents vs. glucose concentrations with error bars ($n = 3$). (e) Amperometric response of MoSe₂-CuO/GCE towards real sample (fruit juice) and spike-and-recovery assays. (f) Amperometric response of MoSe₂-CuO/GCE in the presence of interferents.

The performance of MoSe₂-CuO/GCE towards glucose oxidation is examined at the scan rate of 50 mV s⁻¹ by analysing the CV profiles. The current response is enhanced after adding 50 µM of glucose in 0.1 M PBS, which signifies the capability to sense the glucose.

The amperometric analysis has been conducted to identify the optimal potential for glucose detection. Initially, a series of amperograms [Fig. 2(b)] are recorded at different applied potentials of 0.20, 0.25, 0.27, 0.30, and 0.35 V with the addition of glucose from 50 µM to 300 µM. It is found that the high current response has been shown by MoSe₂-CuO /GCE at the potential of 0.27 V, which is chosen for further investigations. The amperometric analysis is performed by progressively adding glucose from 50 µM to 10 mM in 0.1 M PBS at an applied potential of 0.27 V vs. Ag/AgCl, as depicted in Fig. 2(c). A sharp increment of current is observed upon sequential addition of glucose at 50s intervals.

Figure 2(d) displays the calibration curve, which is plotted by following triplicate measurements, and it shows two dynamic linear ranges of glucose concentration, from 50 µM to 1 mM and 2 mM to 10 mM. The sensitivity and LOD values for the first (second) linear range are determined to be 123 (38) µA mM⁻¹ cm⁻² and 0.5 (1.59) µM, respectively.

Furthermore, the spike-and-recovery experiments are performed, as shown in Fig. 2(e). The glucose concentration of fruit juice (diluted to a 1:100 ratio in 0.1 M KOH) measured from the spectrophotometer is 0.43 mM. The sensor demonstrates a moderate glucose-sensing performance in 0.1 M PBS. The measured glucose concentration is 0.374 ± 0.02 mM, which is a 13.02% underestimation of the actual glucose concentration (0.43 mM), and the RSD value is 5.3%. To assess accuracy and reliability, spike-and-recovery assays are performed with incremental addition of glucose (0.1, 0.2, and 0.3 mM), which yielded recovery values of 78, 75, and 73%, respectively.

CONCLUSION

In essence, MoSe₂-CuO heterostructures are produced by a simple hydrothermal method, and the investigations of electrochemical and electrocatalytic properties of MoSe₂-CuO/GCE are carried out which indicates its effectiveness for highly sensitive and selective glucose detection by amperometry. The MoSe₂-CuO/GCE demonstrates two linear responses for glucose detection over a concentration range of 50 µM to 1 mM and 2 mM to 10 mM, respectively. The developed sensor exhibits the sensitivity of 123 µA mM⁻¹ cm⁻² and LOD of 0.5 µM in the first linear response range, and in the second linear response zone, the sensitivity possessed by the sensor is 38 µA mM⁻¹ cm⁻².

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ZnO/MWCNT Nanocomposite Based Chemiresistive DMC Sensing for Monitoring Thermal Runaway

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Abstract. This study reports the design and characterization of a chemiresistive gas sensor for selective detection of dimethyl carbonate (DMC), a volatile organic compound associated with lithium-ion battery failure. Zinc Oxide (ZnO) nanoparticles were synthesized via co-precipitation method, while multi-walled carbon nanotubes (MWCNT) were acid-functionalized to enhance its interfacial interactions. The sensor fabricated by the ZnO/MWCNT nanocomposite demonstrated a significant response towards low concentrations of DMC (75- 150 ppm), with fast response/recovery time of 95 s/15 s. This enhanced sensitivity is attributed to the synergistic effect arising from the interfacial interaction between ZnO and MWCNT, resulting in improved charge transfer and increased number of active sites, thereby highlighting its potential to be integrated into advanced gas sensing systems for environmental and battery safety applications.

INTRODUCTION

The rapid growth of portable electronics, electric vehicles, and energy storage systems has increased reliance on rechargeable lithium-ion batteries (LIBs), however, battery failures caused by overheating or overcharging can trigger thermal runaway, leading to electrolyte leakage, explosions, and health hazards. A major concern is the release of volatile organic compounds (VOCs), particularly dimethyl carbonate (DMC) with concentrations of 200-250 ppm reported to trigger LIB explosions [1], emphasizing the need for its early detection to ensure battery safety and prevent failure.

Gas sensing technologies provide an effective route for the detection of such VOCs, with metal oxide semiconductors (MOS) emerging as one of the promising sensing materials owing to their sensitivity, robustness and affordability [2]. Zinc oxide (ZnO), a wide bandgap (3.37 eV) n-type MOS, has garnered significant attention due to its high surface area, increased number of adsorption sites and tunable morphology [3]. However, ZnO based sensors require high operating temperatures, which limits their integration into battery safety monitoring. To address this, the incorporation of conductive additives such as multi-walled carbon nanotubes (MWCNT) into ZnO has emerged as a promising strategy wherein MWCNT would not only allow the sensing response at room temperature but also improve the electrical conductivity of the sensor. Furthermore, when functionalized with oxygen-containing groups, MWCNTs provide additional active sites that enhance the gas adsorption and interfacial charge transfer [4]. In the present work, we focus on the fabrication of a ZnO/MWCNT nanocomposite based chemiresistive gas sensor for the selective detection of DMC gas at room temperature. ZnO nanoparticles were synthesized through a simple co-precipitation method, while MWCNT were functionalized through acid treatment to enhance their reactivity. The samples were characterized using X-ray diffraction (XRD) and Raman spectroscopy, and gas sensing performance of the resulting nanocomposite was evaluated over a wide range of DMC concentrations of 75 ppm-150 ppm.

EXPERIMENTAL PROCEDURE

To obtain ZnO nanoparticles, 6 g of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was added to 100 ml of DI water under continuous stirring and 30 ml of aqueous ammonium hydroxide solution was added to it dropwise under continuous stirring for 2 hrs at 70°C. The obtained white precipitates were then washed and dried to obtain the desired ZnO nanoparticles. Subsequently, 0.2 g of commercial MWCNT were treated in 50 ml of 6 M HNO_3 by heating at 60°C for 2 hrs, followed by washing and drying at 80°C for 12 hrs to obtain powdered functionalized MWCNT.

The ZnO/MWCNT nanocomposite was prepared by mixing them into DI water in a ratio of 3:1 through ultrasonication, then the prepared solution was drop-cast onto a glass substrate with pre-deposited silver electrodes,

followed by drying. After that, the DMC sensing performance of the as-prepared nanocomposite based sensor was observed using a static **volumetric** method employing a two terminal source meter (Agilent B2902A) with the sensor placed inside a 1 litre stainless steel chamber. The response % of the chemiresistive gas sensor [S (%)] was calculated by the formula given as follows:

$$S (\%) = \frac{|Ra - Rg|}{Ra} \times 100 \% \quad (1)$$

where Ra and Rg are the resistances of the sensor in the presence of air and the target gas vapors respectively [5]. Furthermore, structural analysis to determine the crystallographic planes of the prepared samples was carried out using X-Ray Diffraction (XRD) (Bruker D8 Focus) with Cu-K α 1 radiation of wavelength 1.5406 Å as the source and the vibrational energy modes of the prepared samples were examined using a Raman spectrometer (micro-Raman microscope inVia reflex confocal, Renishaw).

RESULTS AND DISCUSSION

Figure 1 (a) shows the XRD patterns of the as synthesized ZnO nanoparticles, functionalized MWCNT and the ZnO/MWCNT nanocomposite, where the characteristic peaks observed at 31.7°, 34.4°, 36.2°, 47.5°, 56.6°, 62.8°, and 67.9° correspond to the (100), (002), (101), (102), (110), (103), and (112) planes of the hexagonal wurtzite structure of ZnO, confirming the formation of crystalline ZnO nanoparticles [6]. A broad diffraction peak around 25.8° corresponds to the (002) plane of the functionalized MWCNT, indicating their graphitic nature and the presence of this peak in the composite confirms successful integration of MWCNT into the ZnO matrix [7].

The Raman spectra, Fig. 1 (b), of the ZnO nanoparticles, functionalized MWCNT and the ZnO/MWCNT nanocomposite shows the characteristic peaks at 1315 cm⁻¹ (D-band) corresponding to the disordered and graphitic structures of MWCNT along with a peak obtained around 325 cm⁻¹, which corresponds to the defect-related vibrational modes introduced during functionalization of MWCNT. The sharp peak observed for ZnO at 435 cm⁻¹ corresponds to the E_{2H} (high) mode of ZnO, indicating its wurtzite phase in consonance with the XRD results [7]. Further, the co-existence of both ZnO and MWCNT characteristic peaks in the Raman spectrum confirms the successful formation of the ZnO/MWCNT nanocomposite.

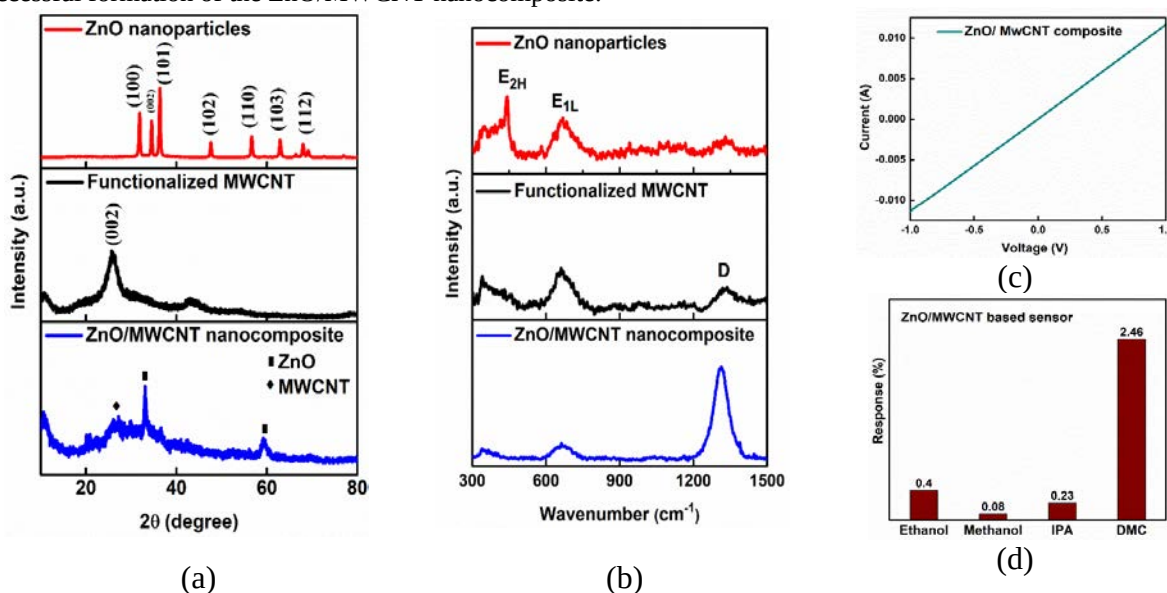


FIGURE 1. (a) XRD pattern and (b) Raman Spectra of ZnO nanoparticles, functionalized MWCNT and ZnO/MWCNT nanocomposite. (c) I - V characteristics and (d) selectivity to different VOCs of the ZnO/MWCNT nanocomposite.

The I-V characteristics, as illustrated in Fig. 1 (c), exhibited a linear ohmic behaviour for the as-prepared nanocomposite, confirming its conductive nature. Additionally, the sensor was exposed to different VOCs and selectivity to DMC was observed, as shown in Fig. 1 (d). Further, to measure the sensitivity of the ZnO/MWCNT based chemiresistive sensor at room temperature, the sensor was exposed to the analyte by injecting a measured concentration of 75 ppm, 100 ppm, 125 ppm and 150 ppm of DMC gas into the chamber and the sensor response was obtained respectively, as shown in Fig. 2 (a-d), with the corresponding sensor parameters depicted in the Table 1.

Upon DMC exposure, an increase in the resistance was observed attributed to the synergistic effect arising due to the presence of electroactive sites in ZnO nanoparticles and effective charge transport pathways introduced by MWCNT. It was observed that the sensor response increased with the rising DMC concentration, achieving a maximum value of 2.46 % at 150 ppm; whereas the response/recovery time was found to decrease with increasing DMC concentration, attaining the lowest value of 95 s/15 s at 150 ppm, indicating faster sensing kinetics, enabling the detection of DMC electrolyte leakage before reaching the hazardous limit.

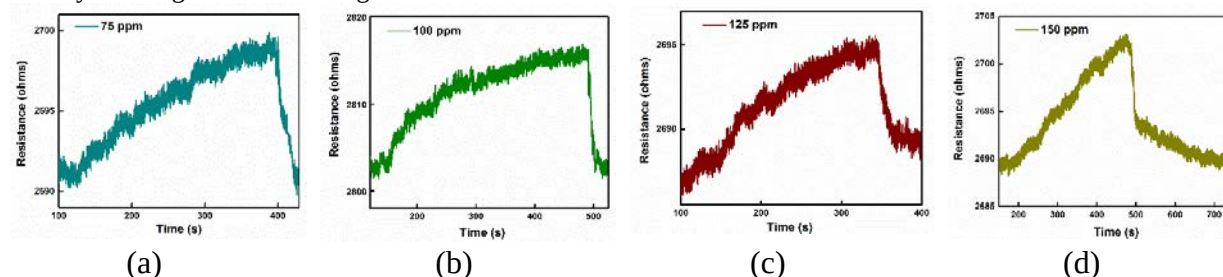


FIGURE 2. Response curves for DMC concentrations of (a) 75 ppm (b) 100 ppm (c) 125 ppm (d) 150 ppm

TABLE 1. Response (%), response time and recovery time for different DMC concentrations.

DMC concentration (ppm)	Response (%)	Response time (s)	Recovery time (s)
75	0.45	160	22
100	0.87	120	20
125	1.43	105	19
150	2.46	95	15

CONCLUSION

Herein, ZnO nanoparticles were synthesized via co-precipitation method which was further integrated with acid functionalized MWCNT to form a ZnO/MWCNT nanocomposite based chemiresistive gas sensor for the detection of DMC. The formation of as prepared ZnO nanoparticles, MWCNT and ZnO/MWCNT nanocomposite was further confirmed through XRD and Raman spectroscopy. The gas sensing studies revealed that the ZnO/MWCNT nanocomposite was highly selective to DMC showcasing a faster response/recovery time of 95s/15s corresponding to 150 ppm concentration of DMC. Overall, the ZnO/MWCNT nanocomposite emerges as a promising candidate for the development of efficient, cost effective, and sensitive gas sensors for battery management systems.

ACKNOWLEDGMENTS

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Electrooxidation of Ethylene Glycol by Au-Ag/C Nano catalyst for Fuel Cell Applications

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Abstract. In this work, we have synthesized Au/C and Au₆₀Ag₄₀/C (20 wt% metal loading on carbon support) bimetallic electrocatalyst with the help of wet chemical synthesis technique. To know about the crystalline structure, surface morphology, we have been employed X-ray diffraction spectroscopy (XRD), Field emission scanning electron microscopy (FESEM) respectively. To investigate about electrochemical performances of the as prepared electrocatalysts, we have implemented Cyclic Voltammetry (CV), Electrochemical impedance spectroscopy (EIS) and Chronoamperometry (CA) measurements. The as-synthesized nano catalyst shows excellent electrocatalytic activities as anode catalyst for ethylene glycol (C₂H₆O₂) electro oxidation in alkaline medium. Our catalyst has also been shown better performances than commercial traditional Au/C catalyst and can be successfully utilized for alkaline ethylene glycol-based fuel cell applications.

INTRODUCTION

A Fuel cell functions as an energy conversion system that steadily transform chemical energy into electrical power as long as both the fuel and oxidizing agents are continuously supplied [3]. A Fuel cell generally consist of three basic components, namely, the anode, electrolyte and cathode and the catalyst is used to accelerate the desired electrochemical reaction. We have chosen Gold-Silver bimetallic Nano catalyst because it shows synergistic effects by modifying the electronic structure of the two metals which improve the overall activity to the electrocatalytic performance. It has also exhibit better durability than gold which is crucial for long term operation of the fuel cell. From last few decades Ethylene Glycol have attracted potential attention as fuel due to its higher boiling point (198°C) and better capacity than methanol [1,2].

EXPERIMENTAL PROCEDURE

SYNTHESIS OF AU/C AND AU-AG/C

Wet chemical synthesis technique was implemented to prepare the Au/C and Ag₄₀Au₆₀/C bimetallic electrocatalyst [3]. At first, we dissolved 115 mg volcan XC-72R black carbon in 30 ml deionized water and ultrasonicated for 1 hr. Thereafter 10 ml aqueous solution of 18.23 mg AgNO₃ was added under continuous magnetic stirring. Then after 15 minutes 10 mg Trisodium citrate (Na₃C₆H₅O₇) with 10 mg DI water was added for keeping the particle size homogeneous by halting the coagulation. A mixture of 10 ml aqueous solution of 150 mg NaBH₄ and 10 ml aqueous solution of 80 mg NaOH was injected dropwise to the previously prepared mixture.

After that, 10 ml aqueous solution of 17.38 mg HAuCl₄ was added dropwise to the above-mentioned mixture at ambient temperature under constant stirring. As sodium borohydride (NaBH₄) is a strong reducing agent, it will reduce Chloroauric acid (HAuCl₄) to the metallic gold while itself being oxidized. After the completion of reduction reactions under about 3 hr. stirring, we have filtered and washed the as prepared mixture with deionized water until the pH becomes 7. After removing the water, the black precipitation was heated at 70°C for about 17 hr. Finally, the Ag₄₀Au₆₀/C and Au/C (without AgNO₃) nano electrocatalysts have been successfully synthesized in powder form.

ELECTROCATALYTIC ACTIVITY MEASUREMENTS

The electrocatalytic activity measurements (cyclic voltammetry, electrochemical impedance spectroscopy, chronoamperometry) were done by a potentiostat/galvanostat (PGSTAT302N, Autolab, Metrohm). In a typical three electrode system, a 5 mm dia glassy carbon electrode (GCE) was used as working electrode, a platinum wire as a counter electrode and an Ag/AgCl filled with 3.5 M saturated KCl was employed as reference electrode. The electrocatalyst ink was prepared by first dissolving 10 mg of polyvinylidene fluoride (PVDF, Alfa Aesar, MW

~534,000) in 10 mL of N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, ≥99.5%) under stirring at room temperature for 12 hr. to obtain a 1 mg/mL PVDF binder solution. Separately, 10 mg of the synthesized catalyst nanomaterial was dispersed in 1 mL of the prepared PVDF binder solution via ultrasonication for 30 minutes, forming a homogeneous suspension. Subsequently, the 20 μ L of final working ink was drop casted on the properly cleaned GCE surface and dried it for 2 hr. under a 200 W electric bulb. The resulting mass loading on the GCE working electrode was 1.02 mg/cm².

RESULTS AND DISCUSSION

We have conducted XRD technique of our synthesized nanomaterials and calculated the average crystallite size by using the Scherrer's equation, which was coming 8.3 nm and 7.5 nm for Au/C and Au-Ag/C catalysts respectively.

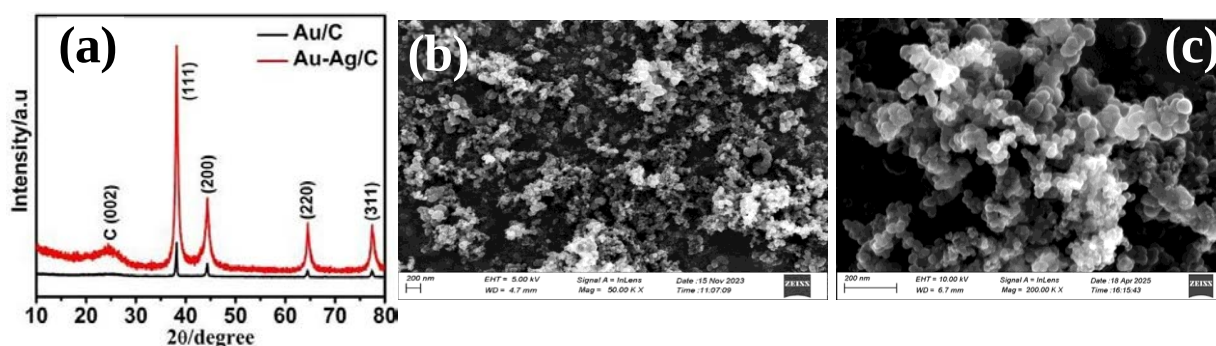


FIGURE 1. (a) XRD patterns of as synthesized catalysts, FESEM images of (b) Au/C and (c) Au-Ag/C.

The above XRD pattern have shown typical face centered cubic crystalline structure of Au and Ag, giving major peaks corresponding to (111), (200), (220) and (311) (hkl) planes (JCPDS: 4-0783 & 0784) [1]. The C (002) is coming due to carbon. The morphology of the nano-catalyst is a crucial parameter and the above two high resolution SEM micrograph reveals the morphological shape of the synthesized nanomaterials and almost globular shape of the particles was observed.

Ethylene glycol (EG, HO-CH₂-CH₂-OH) is a small organic diol molecule widely studied for electrooxidation in alkaline media due to its relevance in direct alcohol fuel cells (DAFCs) [2]. The Au-Ag/C bimetallic nano-catalyst deposited on a glassy carbon electrode (GCE) enhances the catalytic activity due to synergistic electronic effects, bifunctional mechanism, and increased electrochemically active surface area (ECSA) as shown in Fig. 2. At first, we examine the Au/C and Au-Ag/C catalyst modified electrode with 1 M NaOH electrolyte (Fig. 2a) to know how the kinetics of reactions depends in alkaline medium. Then we have investigated the oxidation process of EG through CV by using 1M NaOH+1.8 M EG (Fig. 2b). From the Fig. 2c and 2d, it is clearly seen that peak current density is increasing linearly with square root of scan rate. According to Randles-Ševčík equation, this may indicate diffusion limited processes or adsorption behaviour [1,3].

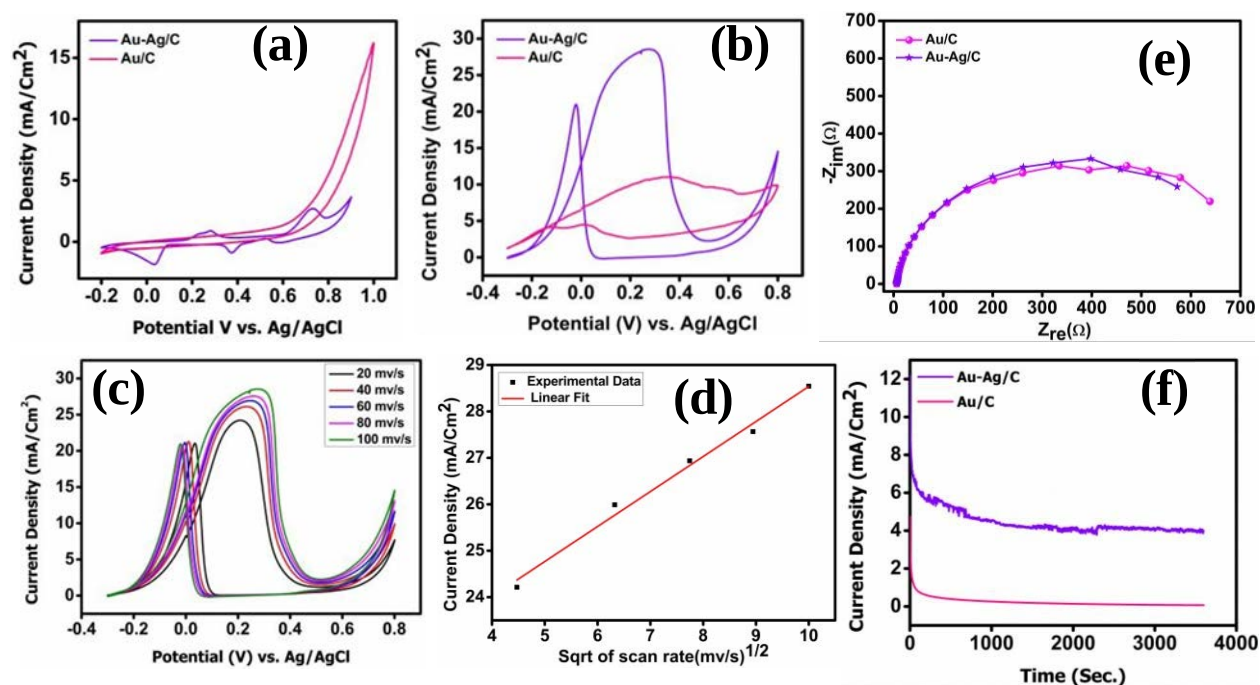


FIGURE 2. CV curves in (a) 1M NaOH (b) 1M NaOH+1.8M EG (c) Corresponding Scan rate variations (d) peak current vs square root of scan rate (e) Nyquist plot (f) Chronoamperometry measurements.

The above graph (Fig. 2e) represents the typical electrochemical impedance spectroscopy (EIS) data of our employed electrocatalysts at 0.28 Volt vs. Ag/AgCl within the frequency range from 1 Hz to 105 Hz. The Au-Ag/C have shown relatively smaller semicircular arc than Au/C which is a sign of better electrocatalytic activity [2,3]. To confirm the stability of our nano catalysts, we have gone through the Chronoamperometry (CA) measurement at 0.28 Volt vs. Ag/AgCl for one hour. We have chosen to apply 0.28 Volt vs Ag/AgCl because around in this voltage the EG oxidized into its intermediates [1,2] and showing the major electrooxidation peak. The Fig. 2f shows the stability of Au-Ag/C and Au/C electrocatalysts for one hour.

CONCLUSION

In summary, we have synthesized Au/C and Au-Ag/c bifunctional electrocatalyst and investigate their electrochemical performance towards direct ethylene glycol fuel in alkaline medium. The crystallinity and morphology were studied by XRD and FESEM respectively. Through CV, EIS and CA; it can be concluded that Au-Ag/C have shown better electrochemical performance than Au/C towards direct alcohol fuel cell applications.

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Upconversion Study of Er^{3+} , $\text{Er}^{3+}/\text{Dy}^{3+}$, $\text{Er}^{3+}/\text{Yb}^{3+}$ in Tellurite Tungstate Glasses for Enhanced a-Si Solar Cells Photocurrent.

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Abstract. The present study reports the influence of Er^{3+} , $\text{Er}^{3+}\text{-Dy}^{3+}$, and $\text{Er}^{3+}\text{-Yb}^{3+}$ doping on the upconversion emission intensity of $\text{TeO}_2\text{-WO}_3\text{-ZrO}_2$ glasses synthesized by melt-quenching technique. The amorphous nature of the glasses has been confirmed from the XRD analysis. Optical absorbance and upconversion luminescence were studied, with pump power-dependent analysis used to determine the upconversion mechanism. The color purity and color-tunability have been analyzed by the CIE chromaticity diagram. When coupled to an a-Si solar cell, Er^{3+} and $\text{Er}^{3+}\text{-Yb}^{3+}$ doped glasses successfully increased photocurrent under 980 nm excitation, demonstrating their potential as spectral converters for photovoltaic applications.

INTRODUCTION

The surge in global population and widespread adoption of electricity dependent technologies have increased the energy requirement. The use of solar energy to meet this demand is increasing. Recent advancements in silicon-based tandem solar cells have increased conversion efficiency up to 36.1% [1], though significant improvement is still possible. Silicon PV cells primarily suffer from thermalization losses from high-energy UV photons and transmission losses from sub-bandgap NIR and IR photons, both reducing overall efficiency. To address this, spectral modification techniques such as Upconversion (UC), Down-Shifting (DS), and Quantum cutting (QC) have been developed. Upconversion allows two or more sub-bandgap photons to combine into one high energy photon, improving silicon's absorption range and bypassing the Shockley-Queisser limit without complex tandem architectures. Lanthanide (Ln^{3+})-doped glasses are promising due to their tunable luminescent properties and suitability for UC applications. Among these, Er^{3+} is commonly used for converting long-wavelength photons to shorter ones via various mechanisms. The first demonstration of upconversion in photovoltaics was by Gilbert et al., who coupled a substrate-free GaAs solar cell with $\text{Er}^{3+}\text{-Yb}^{3+}$ doped vitroceraic, achieving 2.5% efficiency under strong excitation [2]. Later studies using Er^{3+} and $\text{Er}^{3+}\text{-Yb}^{3+}$ doped fluoroindate glasses under 1480-1550 nm excitation showed enhanced silicon cell response, with up to 0.4% external quantum efficiency, strong 980 nm emission, and UC efficiencies reaching 12.7% [3-5]. Tellurite glasses offer benefits like low phonon energy, rare-earth solubility, and broad IR transparency, making them ideal UC hosts. In the present study we explore Er^{3+} -doped tellurite glasses, co-doped with Dy^{3+} and Yb^{3+} and studied upconversion behavior and photocurrent enhancement when coupled with a-Si solar cells.

MATERIALS AND CHARACTERISATION

Tellurite-tungstate-zirconia glasses having general composition $75\text{TeO}_2\text{-(18-x-y)WO}_3\text{-7ZrO}_2\text{-xEr}_2\text{O}_3\text{-y(Dy}_2\text{O}_3/\text{Yb}_2\text{O}_3)$ have been synthesized by conventional melt-quenching method. X-ray diffraction analysis was carried out using Rigaku SmartLab diffractometer with Cu-K_α radiation ($\lambda = 1.5481 \text{ \AA}$), confirming the amorphous nature of the glasses. The density of glass beads (g/cm^3) were obtained using Archimedes' principle at room temperature. Structural and cationic parameters like molar volume, oxygen molar volume, oxygen packing density, ionic concentration, inter-ionic distance, polaron radius were calculated using measured density values and are shown in Table 1. Optical absorption spectra were recorded in the 300-1800 nm range using a Jasco V-770 UV-Vis-NIR spectrophotometer. Upconversion emission spectra were measured under 980 nm diode laser excitation using a Fluoromax-4 spectrofluorometer, and power-dependent studies were also conducted. Emission data were converted to chromaticity coordinates using the CIE 1931 color space to assess spectral characteristics and color purity. Short-circuit

photocurrent was measured using an Agilent 34401A digital multimeter, with an a-Si solar cell placed beneath the doped glass under 980 nm laser excitation.

TABLE 1. Physical and structural parameters of glass samples

Sample Name	Density (g/cm ³)	Molar Volume (cm ³ /mol)	Oxygen Molar Volume (cm ³ /mol)	Oxygen Packing Density(atoms · cm ⁻³ /mol)	Ionic Conc. of Er ³⁺ (×10 ²³ ions/cm ³)	Interionic Distance of Er ³⁺ (×10 ⁻⁸ cm)	Polaron Radius of Er ³⁺ (×10 ⁻⁹ cm)
TWZE3	5.541	31.503	14.451	0.692	1.721	1.797	7.245
TWZE3D1	5.621	31.306	14.361	0.696	1.731	1.794	7.230
TWZE4D1	5.782	30.693	14.079	0.710	2.354	1.619	6.526
TWZE3Y1	5.642	31.229	14.325	0.698	1.735	1.792	7.224

RESULTS AND DISCUSSION

Absorption Studies

In Er³⁺-doped glasses, characteristic absorption bands were observed, with a strong peak near 975-980 nm corresponding to the transition ⁴I_{15/2} to ⁴I_{11/2} of Er³⁺. This transition is crucial for upconversion, as it enables the absorption of 980 nm photons, leading to sequential excitation and visible emission. Co-doped glasses containing Dy³⁺ and Er³⁺ showed additional absorption bands from Dy³⁺ ions, though their overall spectral shape remained similar, indicating limited influence in absorption from varying dopant concentrations. In Yb³⁺/Er³⁺ co-doped glasses, distinct absorption features from both ions were present, with the 980 nm band remaining prominent. The strong and consistent absorption at 980 nm in all Er³⁺ containing glasses confirms the suitability of this wavelength for upconversion excitation.

Upconversion Spectra and Photocurrent measurement

The upconversion emission spectra of Er³⁺-doped and co-doped tellurite glasses exhibit peaks at 487 nm, 520 nm, 545 nm, and 660 nm, attributed to transitions within Er³⁺ energy levels. Co-doping with Dy³⁺ reduces emission intensity, particularly eliminating the 660 nm peak, suggesting interference in energy transfer. In contrast, Yb³⁺ co-doping significantly enhances visible emission, up to five times that of the 3 mol% Er³⁺-doped glass by sensitizing Er³⁺ through efficient energy transfer.

Emission intensity increases with excitation power, confirming a multiphoton upconversion mechanism. The relationship between emission intensity and pump power follows the equation

$$I = AP^n \quad (1)$$

where 'n' indicates the number of photons involved in the process. For TWZE3, $n \approx 2$ suggests a two-photon absorption mechanism, while for TWZE3Y1, $n \approx 1$, indicating saturation effects and a quasi-linear response due to high power of excitation laser. The brighter emission observed in TWZE3Y1 supports stronger Yb³⁺ to Er³⁺ energy transfer. These results confirm that excited-state absorption and energy transfer upconversion are the dominant mechanisms, with Yb³⁺ incorporation effectively boosting upconversion efficiency in the glass matrix.

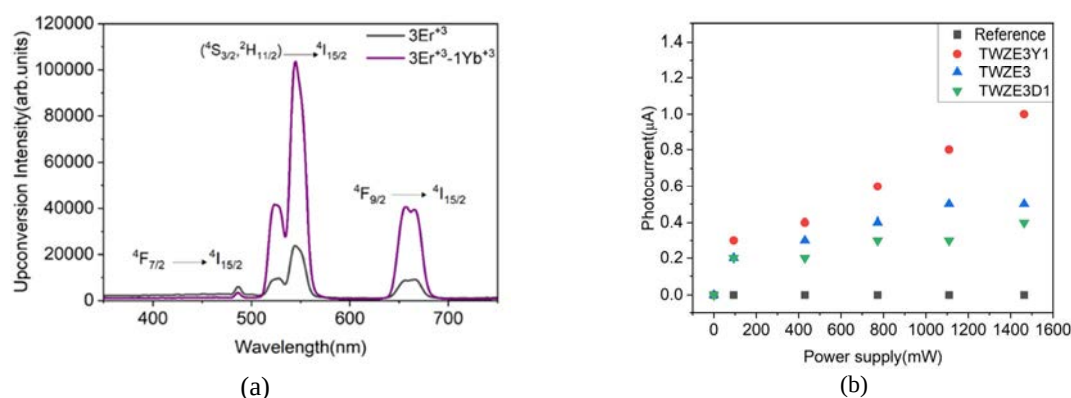


FIGURE 1. (a) Upconversion Spectra of Tellurite glasses doped with Er^{3+} and $\text{Er}^{3+}/\text{Yb}^{3+}$ (b) Photocurrent enhancement of a-Si solar cell under 980 nm excitation with different upconversion glass samples.

The synthesized glass samples showed CIE coordinates ranging from (0.206, 0.278) to (0.283, 0.672) with color purity between 41.3% and 88.8%. Er^{3+} and Dy^{3+} co-doped samples exhibited broadband emission (41-47% purity), beneficial for broader absorption in a-Si solar cells. Yb^{3+} co-doping yielded the highest color purity (88.8%) with strong narrowband green emission, ideal for enhancing photocurrent. Under 980 nm excitation, TWZE3 and TWZE3Y1 glass samples enhance photocurrent in a-Si solar cells via upconverted emissions at 520, 545, and 660 nm. No measurable photocurrent is observed without the upconversion layer, confirming that silicon alone cannot absorb sub-bandgap photons. The variation in photocurrent with laser power is shown in Fig. 1. (b).

CONCLUSION

The tellurite glasses exhibited strong visible upconversion emissions, primarily from Er^{3+} transitions. Dy^{3+} co-doping adversely affects the upconversion intensity. Yb^{3+} co-doping significantly enhances emission intensity via efficient energy transfer, while Dy^{3+} co-doping leads to quenching. Power-dependent studies confirm multiphoton absorption processes. The CIE chromaticity analysis confirmed that the UC emissions fall within the spectral response range of a-Si solar cells, ensuring effective photon utilization. Photocurrent measurements reveal a significant enhancement when upconversion glasses are coupled, due to the optimal alignment of their emission photons with the spectral response.

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rGO Enhanced SnO₂ Photocatalysts for Efficient Photocatalytic Degradation of Antibiotics

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Abstract. The growing presence of pharmaceutical residues in our aquatic environments and their potential risk to human health is not a simple problem to solve. Antibiotics are among the most persistent of all pharmaceuticals. Nitrofurantoin is a widely used pharmaceutical that is often detected in aquatic environments, it is also able to resist a wide variety of methods commonly used to treat water so that its removal is more challenging. A visible-light-active photocatalyst was designed that was based upon SnO₂ fused combined with reduced graphene oxide (rGO). The catalyst improves light utilization, strengthens charge recombination, and improves photocatalytic activity. Under natural sunlight, the optimized SnO₂/rGO catalyst achieved over 92% degradation of nitrofurantoin from aqueous solution. The improved performance is due to enhanced charge transfer mechanism that increases the generation of reactive oxygen species. This has provided an effective and sustainable route for removing persistent antibiotics from contaminated water.

INTRODUCTION

Bacterial infections are a worldwide public health threat and antibiotics such as furans, macrolides, and tetracyclines, play an important role in their treatment^{1,2}. However, inappropriate disposal practices contribute to environmental accumulation³ and therefore contribute to antimicrobial resistance². Nitrofurantoin is used for infections of the urinary tract and possesses nitro, furan, and hydantoin groups⁴. These pollutants can degrade into toxic (and in some cases, carcinogenic) byproducts, for example, nitrofurantoin breaks down to semi carbazide⁴, and has been flagged by EFSA. Photocatalyst provides a sustainable means for degradation of pollutants and has been identified as an important area of research. SnO₂, is a widely used photocatalyst due to its reasonable stability, easy of abundance, and low cost, unfortunately, it has many limitations including low surface area to volume ratio, low visible light response, and fast charge recombination⁵.

MATERIALS AND METHODOLOGY

Analytical grade reagents (Graphite, SnCl₄·5H₂O, H₂SO₄, KMnO₄, H₂O₂, HCl, and CuCl₂·2H₂O) were obtained from Sigma Aldrich and used without further purification. Pristine SnO₂ and rGO were synthesized from co-precipitation and a modified hydrothermal reduction process, respectively [24,25]. SnO₂/rGO nano composites with different proportions (SG-I (80:20), SG-II (60:40) and SG-III (50:50)) were hydrothermally prepared.

RESULTS AND DISCUSSIONS

Structural and morphological analysis

X-ray diffraction (XRD) measurements ([Fig. 1a](#)) determined the crystalline phases for pure SnO₂, reduced graphene oxide (rGO), and the SnO₂/rGO composites containing varying rGO content. The peaks appearing at 26.79°, 34.16°, 38.21°, and 52.01° correlate well with the tetragonal rutile phase of SnO₂ (JCPDS No. 41-1445)¹⁰. The wide peak at ~23.93° in the rGO relates to the (002) plane (JCPDS No. 75-1621). The composites showed new peaks at 24.78°, 32.02°, and 49.92°, including the decreasing intensity of the SnO₂ peaks as the amount of rGO increased, this may indicate diminished crystallinity due to lattice distortion in the SnO₂. Therefore, the peak shifts indicate electron

transfer between SnO_2 and rGO and this is evidence that the composites are formed¹¹. In the surface characterizations of the optimized SnO_2/rGO composite (SG-I), SEM (Fig.1b) illustrated that layered rGO sheets are surrounded by rGO flakes containing SnO_2 nanoparticles. The rGO network displayed a wrinkled type of morphology that increased surface roughness and created a larger surface area for photocatalytic reaction sites. The close contact illustrated between SnO_2 and rGO particles shows that they are integrated and could help keep charge carriers together, allowing for more efficient electron transport, harnessing visible light, and leading to the improved degradation of nitrofurantoin^{12,13}.

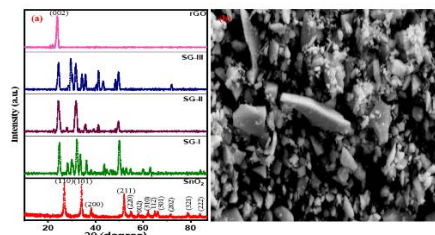


Figure 1. a) XRD patterns of SnO_2 , rGO, and SnO_2/rGO composites; b) SEM image of SG-I nanocomposite

Optical properties analysis

The optical properties of SnO_2 , rGO, and their composites were evaluated using UV-Vis diffuse reflectance spectroscopy (Fig. 2a). SnO_2 showed significant UV absorption while rGO displayed broad absorption in the visible range. The bandgap values were determined from Tauc plots as 3.49 eV for SnO_2 , 2.80 eV for rGO, 3.41 eV for the SnO_2/rGO composite that contained 80% SnO_2 , and 2.96 eV for 50% SnO_2/rGO . Photoluminescence (PL) measurements were performed to analyze the presence of oxygen vacancies, the recombination of electrons and holes and the mobility of charge carriers in SnO_2 , rGO and their composites (Fig. 2b). PL intensity closely relates to the recombination rates; thus, stronger emission indicates higher carrier recombination. The pure SnO_2 sample had a robust emission peak at 428 nm, where emissions in the wavelength range in the UV-blue typically occur preferentially from oxygen defects in the crystal lattice. Pristine SnO_2 sample exhibited the largest PL intensity among all samples, indicating rapid recombination. However, when rGO was integrated into the hybrid at weight ratios of 20%, 40%, and 50%, there was a large decrease in the PL emissions, indicating improved charge separation efficiencies due to rGO gaining electrons as an acceptor.

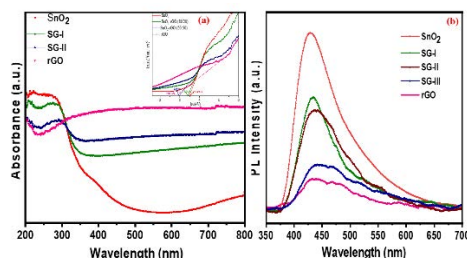


Figure 2. a) UV-Vis absorption spectra and corresponding band gap values b) Photoluminescence spectra of SnO_2 , rGO, and SnO_2/rGO composites

Estimation of the radical tests hydroxyl

The capacity of SnO_2 , rGO, and SnO_2/rGO composites (SG-I, SG-II, SG-III) to produce hydroxyl radicals under sunlight exposure was evaluated using terephthalic acid (TA) as a reactive probe (Fig. 3a). TA produces fluorescent 2-hydroxyterephthalic acid upon reaction with hydroxyl radicals, showing fluorescence at 427 nm. The EIS plots (Fig. 1e) provided insight into the charge transfer kinetics of the materials. SG-I had the smallest arc in the Nyquist plot, suggesting the lower the interfacial resistance and higher charge conductivity relative to the other materials. At 20% rGO loading, the material had the best electron mobility and minimized charge recombination, allowing for higher yields of reactive species and enhanced photocatalytic performances. Under sunlight, the SG-I photocatalyst showed strong ability to degrade antibiotics like Nitrofurantoin, with its absorption peak at 360 nm steadily decreasing and almost disappearing after 60 minutes. No major changes were seen in control tests (without light or catalyst), confirming that degradation was due to photocatalysis, not adsorption or photolysis. SG-I achieved up to 92% degradation (Fig. 3b) proving its high efficiency in removing antibiotics through light-driven radical generation^{17,18}.

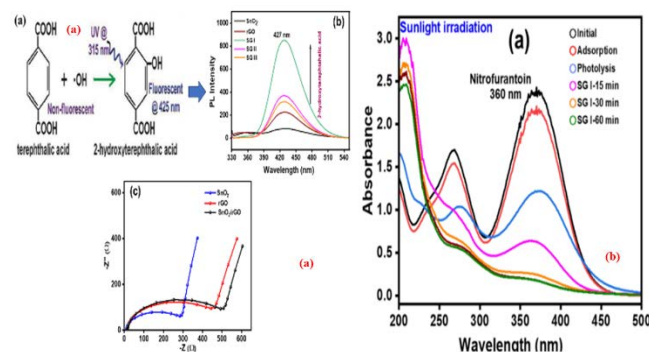


Figure 3. a) $\text{OH}^\bullet$ generation via TA-to-HTA conversion and EIS Nyquist plots showing charge transfer behaviour b) Absorbance spectra of Nitrofurantoin

CONCLUSIONS

This work focused on the problem of antibiotic contamination in water, achieving the development of a sunlight-active SnO_2/rGO nanocomposite. The SG-I formulation (80% SnO_2 /20% rGO) showed outstanding photocatalytic activity yielding 92% degradation of nitrofurantoin under natural light. This impressive activity was due to good charge carrier separation and minimal recombination. While the lab scale results show promise, this study has some limitations. It lacks from long-term validation, and a lack of detailed degradation intermediate analysis

ACKNOWLEDGMENTS

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Comparative Study for Shape Stability of Paraffin/SEBS and Paraffin/polyaniline Composites

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Abstract. Leakage during phase transitions of phase change materials (PCMs) is a critical issue that hinders their utility in practical applications. Therefore, shape stabilization of PCMs becomes essential to address this challenge. In the present work, an attempt has been made to investigate the shape stability of paraffin wax (melting point: 58–60 °C) by incorporating two different supporting materials: polyaniline and SEBS (styrene-ethylene-butylene-styrene). The composite PCMs are synthesized using the direct melt mixing method, with various weight ratios of paraffin and the supporting materials. X-ray diffraction (XRD) has confirmed the successful synthesis of both polyaniline- and SEBS-based composite PCMs. A leakage test is carried out at 70 °C for more than 500 thermal cycles with 30 min cycle each, to investigate the shape stability of the composite PCMs. The leakage test has demonstrated that SPCM2 (20 wt% SEBS) and PPCM2 (20 wt% polyaniline) have exhibited excellent shape stability and maximum leakage in SPCM2 and PPCM2 was found to be 0.3% and 0.08%, respectively. In conclusion, PPCM2 demonstrated superior shape stability and can be an effective material for thermal energy storage applications.

1. INTRODUCTION

Thermal energy storage (TES) is one of the emerging areas of research for resolving the issue of energy crisis due to its dependency over solar energy. A phase-change material (PCM) is a TES material that can absorb and release a substantial quantity of latent heat during the phase transition process^[i]. Among all types of PCMs, the organic PCM Paraffin is considered due to its excellent storage density and easy availability over a wide range of melting temperatures, non-toxicity, low supercooling, non-corrosiveness and high thermal stability^[ii, iii]. However, it suffers from the issue of leakage during phase transition, which may lead to serious pollution damage and equipment failure^[iv]. In order to reduce the leakage in the molten state of PCM, various approaches such as microencapsulation, core shell composite and polymer mixing process are being employed. Among all shape stabilizations, polymer mixing is an efficient technique as this is cost-effective and an easy-to-synthesize approach.

Because of their lightweight and porous structures, SEBS and polyaniline are used as supporting materials to avoid paraffin leakage in the current study. A leakage test is carried out to evaluate the form stability of the composite materials. X-ray diffraction (XRD) is used for structural study. Finally, a comparison of the leakage resistance of composite PCMs based on polyaniline and SEBS is provided.

2. EXPERIMENTAL METHODS

2.1. Materials Used

Paraffin wax with a melting temperature of 58°C-60°C is purchased from Hi-Media, India and Polystyrene-b-poly(ethylene-ran-butylene)-b-polystyrene (SEBS) tri-block copolymer (average molecular weight~118,000 gmol⁻¹), Aniline monomer (C₆H₅N, 97%), hydrochloric acid (HCl, 99%), ammonium persulphate (APS) [(NH₄)₂S₂O₈, 99%] purchased from Sigma Aldrich.

2.2. Composite Preparation

The paraffin/polyaniline shape-stable PCMs have been prepared by melting Paraffin wax at 55°C and adding different weight % of polyaniline using a microbalance. The mixture was stirred at 65°C for 1 hour and then probe-sonicated for 30 minutes. The resulting paraffin/polyaniline composites, PPCM1, PPCM1.5, and PPCM2, have polyaniline wt% are 10%, 15%, and 20%, respectively.

To prepare the paraffin/SEBS shape-stable PCMs, pre-weighed SEBS was added after paraffin was dissolved in hot cyclohexane (~70°C). For uniform blending, the mixture is stirred for 2 hours at 200–300 rpm. After filtering, the final solid is dried for around 48 hours at 60 to 65 °C in a hot air oven. finally, cylindrical samples with a diameter of 13 mm and a thickness of 3 mm are formed from the dried composites. Composites with weight percentages of 10%, 15%, and 20% SEBS are designated as SPCM1, SPCM1.5, and SPCM2, respectively.

2.3. Characterizations

X-ray diffraction (XRD) is performed at a scanning rate of 5° (2θ)/min to examine the crystalline structure of pure paraffin, paraffin/SEBS, and paraffin/polyaniline composites. Leakage performance has been assessed by placing the composite PCMs in a hot air oven at 70 °C. Weight loss is recorded in every 30 minutes.

Total leakage (%) is calculated as follows

$$\text{Total leakage (\%)} = \frac{M_o - M_n}{M_o} \times 100$$

Where, M_o is the initial mass of the sample while M_n is the mass after ‘ n ’ thermal cycles.

3. RESULTS AND DISCUSSION

3.1. Leakage Test Analysis of Composite PCMs

Leakage test results for paraffin/polyaniline (PPCM1, PPCM1.5 and PPCM2) and paraffin/SEBS (SPCM1, SPCM1.5 and SPCM2) composites are shown in **FIGURE 1(a)** and **(b)**.

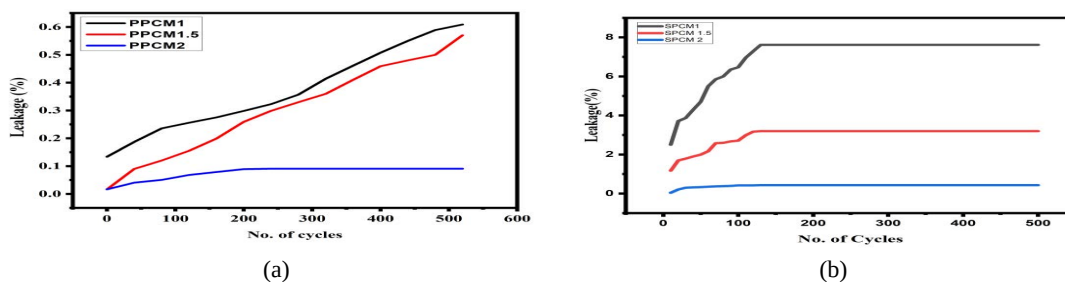


FIGURE 1. Leakage curves of (a) PPCM and (b) SPCM composite PCMs

In SPCM2, the leakage rate stabilized at ~0.3% after 100 thermal cycles, attributed to the gel-like network formed by SEBS. In contrast, PPCM2 exhibited a significantly lower leakage rate of ~0.08% even after 500 cycles, due to the 3D nanofiber structure and porous morphology of polyaniline that effectively restricts paraffin migration.

3.2. XRD Analysis

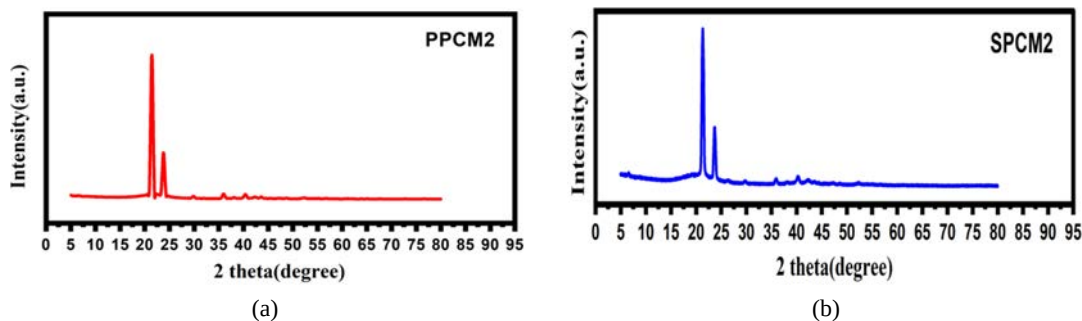


FIGURE 2. XRD patterns of (a) PPCM2 and (b) SPCM2 composite PCM

The XRD patterns of PPCM2 and SPCM2 are presented in **FIGURE 2(a)** and **(b)**. PPCM2 exhibits paraffin peaks at $2\theta \approx 21.37^\circ$ and 23.72° , along with broad peaks around $20\text{--}25^\circ$, indicating the amorphous nature of polyaniline. The presence of both sets of peaks confirms successful composite formation. SPCM2 exhibits sharp paraffin peaks at $2\theta \approx 21.37^\circ$ and 23.72° , while a broad peak at $\sim 20^\circ$ corresponds to amorphous SEBS. The retention of paraffin peaks without new ones suggests no chemical interaction occurred between paraffin and SEBS.

4. CONCLUSION

In the present work, leakage-proof Paraffin/SEBS (SPCM) and Paraffin/polyaniline (PPCM) composites have been synthesized for TES application. The XRD results have confirmed the successful formation of the composite PCM without any chemical interaction. Furthermore, the leakage test indicates that the shape of SPCM2 and PPCM2 has no virtual change after thermal treatment of more than 500 thermal cycles. A comparative analysis of leakage behaviour reveals that both SEBS and polyaniline improve the shape stability of paraffin by reducing leakage. However, the leakage rate of paraffin/polyaniline composites (PPCM2) exhibits superior leakage resistance, maintaining a leakage rate as low as $\sim 0.08\%$ even after 500 thermal cycles, compared to $\sim 0.3\%$ for Paraffin/SEBS composites (SPCM2) after 500 cycles. Therefore, polyaniline demonstrates better long-term leakage resistance and is more suitable as a supporting matrix for paraffin in thermal energy storage (TES) applications.

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Enhanced Supercapacitor Performance Through Lithium Substitution In Nickel Ferrite

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Abstract. Sustainable energy systems require efficient storage to manage renewable intermittency; supercapacitors offer fast charging and high-power delivery. This study highlights the impact of lithium substitution on the electrochemical properties of nickel ferrite. X-ray diffraction analysis confirmed the cubic spinel crystalline structure. Electrochemical measurements were carried out with a three-electrode setup in a 6 M KOH electrolyte solution. The GCD measurements show a notable increase in specific capacitance, rising from 156 F/g to 534 F/g upon the lithium substitution. These findings imply that doping nickel ferrite with lithium improves the material's electrochemical characteristics, positioning it as a promising candidate for supercapacitor electrodes.

INTRODUCTION

The growing demand for efficient energy storage has highlighted supercapacitors' high power density, fast charge/discharge, and long cycle life. Their performance depends on electrode materials, electrolytes, and device architecture. Optimizing the electrode material is especially important for maximizing storage performance.[1],[2] Numerous materials, such as conducting polymers, carbon-based structures, and transition metal complexes, have been thoroughly investigated. Recently, transition metal oxides have received special attention due to their abundance of redox-active sites and high theoretical capacitance, and cycle life make them exceptional for efficient energy storage. Problems like structural stability, slow charge-transfer kinetics, and conductivity limit their practical use.

Techniques such as surface modification and dopant engineering have been employed to overcome these limitations.[3] Among them, doping-induced engineering has proven effective in modifying the electrochemical performance of materials. This substitution induces structural modifications in the material, facilitating ion diffusion, reducing charge-transfer resistance, and improving conductivity. Herein, lithium substitution in nickel ferrite is explored for its electrochemical performance for high-performance supercapacitor applications.

EXPERIMENTAL DETAILS

Lithium-substituted nickel ferrite ($\text{Li}_{0.25}\text{Ni}_{0.5}\text{Fe}_{2.25}\text{O}_4$) was synthesized via a simple co-precipitation route. Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), lithium nitrate (LiNO_3), and ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were used as starting precursors without further purification. Initially, Nickel ferrite was synthesized by dissolving two mmol of $\text{Fe}(\text{NO}_3)_3$ and 1 mmol $\text{Ni}(\text{NO}_3)_2$ in 100 mL of deionized water, followed by continuous stirring for 1 hour. The pH was adjusted to ~ 11 using 2 M NaOH added dropwise under constant stirring. The mixture was heated at 80 °C for 3 hours to induce precipitation. After cooling naturally, the precipitate was filtered with DI water and ethanol, then dried at 60 °C overnight. For lithium substitution, the appropriate amount of LiNO_3 was added with the metal nitrates before precipitation. The dried powders were calcined at 600 °C for 3 hours and used for further characterization. In this study, nickel ferrite is referred to as NF, while its lithium-substituted counterpart is denoted as LNF.

RESULTS AND DISCUSSION

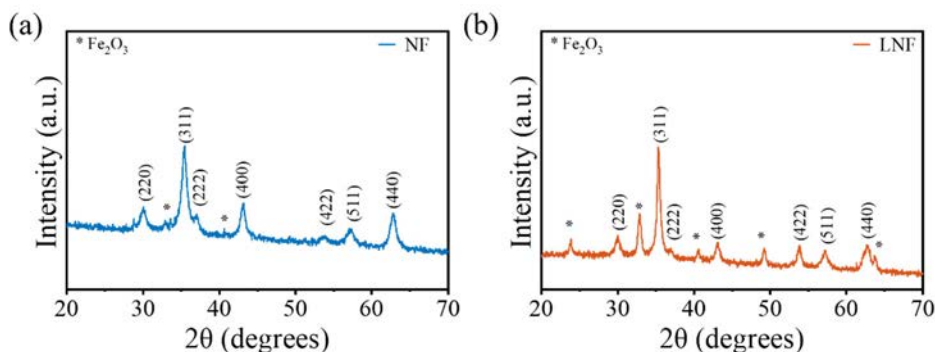


FIGURE 16. Powder X-ray diffraction pattern for (a) NF (b) LNF sample.

X-ray diffraction patterns of both nickel ferrite (NF) and lithium doped nickel ferrite (LNF) are presented in Fig. 1. The diffraction peaks corresponding to (220), (311), (222), (400), (422), (511), and (440) planes exhibit strong concordance with the standard JCPDS card no.00-010-0325, confirming the formation of a cubic spinel phase in both samples.[4] The peaks marked with an asterisk (*) indicate residual Fe_2O_3 as a secondary phase.

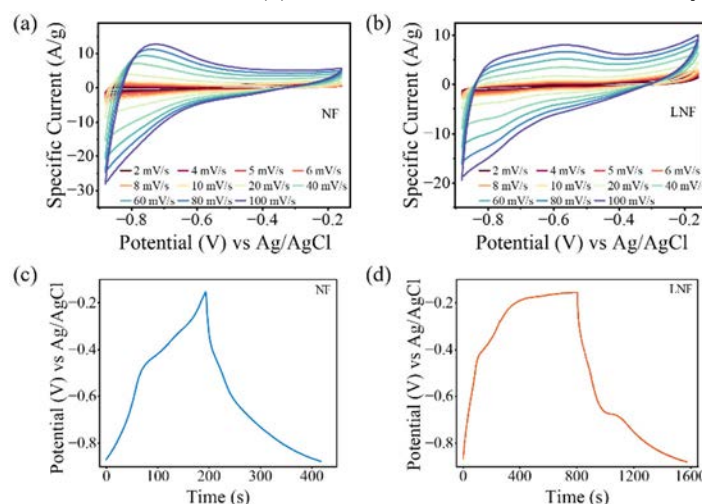


FIGURE 17. CV curves of (a) NF and (b) LNF electrode; GCD curves of (c) NF and (d) LNF at 0.5A/g current density.

Electrochemical performance was investigated using a three-electrode configuration, employing platinum (Pt) as the counter electrode and Ag/AgCl as the reference electrode in 6 M KOH aqueous electrolyte. The working electrodes were prepared by coating the active material onto a 1 cm × 1 cm area of a graphite sheet. Figure 2a, b presents the cyclic voltammetry (CV) curves of NF and LNF electrodes, recorded at scan rates ranging from 2 to 100 mV/s within a potential window of −0.85 to −0.155 V. The CV curves suggest the presence of both faradaic and non-faradaic charge storage processes. Galvanostatic charge–discharge (GCD) measurements were also conducted to investigate the capacitive characteristics further. The GCD profiles for both NF and LNF electrodes at a current density of 0.5 A/g are shown in Figure 2c, d, which show nonlinear reinforcement of the pseudocapacitive nature of the electrodes. Notably, the LNF electrode exhibits a longer discharge time than NF, reflecting enhanced charge storage. The specific capacitance (C_s) was calculated using the GCD data using the following equation: $C_s = \frac{It}{mV}$ where symbols have their usual meaning. The LNF electrode delivered a specific capacitance of 534 F/g, significantly higher than the 156 F/g

obtained for the pristine NF electrode. This enhancement is attributed to improved diffusion-controlled charge transport facilitated by lithium substitution.

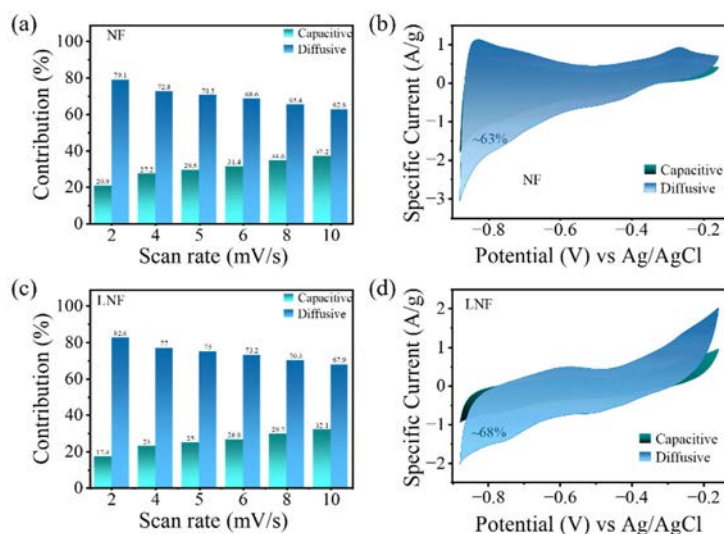


FIGURE 18. Percentage contributions of capacitive and diffusive kinetics at scan rates (2–10 mV/s) for (a) NF and (c) LNF electrode; Deconvoluted CV showing capacitive and diffusive regions for (b) NF and (d) LNF electrodes at 10 mV/s scan rate.

To quantitatively distinguish the capacitive and diffusion-controlled contributions, Dunn's method was employed, based on the power-law relationship: $i(V) = k_1v + k_2v^{0.5}$ where k_1v represents the capacitive current, and $k_2v^{0.5}$ accounts for the diffusion-limited current. The values of k_1 and k_2 were extracted from the linear fitting of $i/v^{0.5}$ vs $v^{0.5}$. Figure 3a,c illustrates the relative contributions of capacitive and diffusion-controlled processes in NF and LNF, across scan rates from 2 to 10 mV/s. While both materials show increasing capacitive contributions with scan rate, the LNF sample consistently exhibits dominant diffusion-controlled behavior across the entire scan rate range. The deconvoluted current responses at 10 mV/s and a representative potential of -0.25 V are shown in Fig. 3b, d for NF and LNF, respectively. A diffusion-controlled charge storage contribution of 68% was observed for LNF, compared to 63% for NF, indicating that lithium substitution enhances ion diffusion kinetics and charge transfer efficiency in the electrode material.[5] This significant enhancement in specific capacitance highlights the material's potential as a promising electrode candidate for supercapacitor applications.

CONCLUSION

Nickel ferrite and lithium-substituted nickel ferrite were successfully synthesized via a co-precipitation method. Among the two samples, LNF demonstrated markedly superior super capacitive performance, delivering a specific capacitance of 534 F g^{-1} when tested in 6 M KOH electrolyte solution at 0.5 A g^{-1} current density. The improved electrochemical behavior is attributed to enhanced ion diffusion kinetics induced by lithium incorporation.

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Facile Synthesis of Ammonium Jarosite for Cost-Effective and Stable Oxygen Evolution Catalysis

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Abstract. In this study, ammonium jarosite thin films were fabricated on flexible stainless steel (SS) substrates using a simple, low-cost chemical bath deposition (CBD) method. XRD and Raman spectroscopy confirmed the formation of crystalline ammonium jarosite. The films electrocatalytic activity for the oxygen evolution reaction (OER) in alkaline conditions was evaluated against bare SS. The ammonium jarosite films showed significantly improved catalytic performance, with enhanced reaction kinetics and a higher density of active sites. At 10 mA/cm², they required a lower overpotential of 421 mV, compared to 670 mV for SS, and exhibited a Tafel slope of 113 mV/dec, indicating better charge transfer than SS (250 mV/dec). These results highlight ammonium jarosite as an efficient, low-cost OER electrocatalyst with strong potential for scalable, sustainable water-splitting applications.

1. INTRODUCTION

The development of efficient, stable, and low-cost electrocatalysts for the OER remains a critical challenge in the pursuit of sustainable energy technologies¹. The OER is a kinetically sluggish, multi-step reaction that demands a substantial overpotential to proceed efficiently, thereby limiting the overall performance of water electrolysis systems². Although noble metal-based catalysts such as ruthenium dioxide (RuO₂) and iridium dioxide (IrO₂) are widely regarded as benchmark materials for OER due to their exceptional catalytic activity, their scarcity and high cost hinder widespread commercial implementation³. To overcome these limitations, extensive research has focused on earth-abundant alternatives, including transition metal-based oxides, hydroxides, sulfides, and phosphides⁴⁻⁶. While these materials offer promising catalytic activity, many still suffer from issues related to structural instability, limited electrical conductivity, and poor long-term durability under operational conditions. Ammonium jarosite (NH₄Fe₃(SO₄)₂(OH)₆), a naturally occurring iron-based sulfate mineral, has recently garnered attention as a potential non-noble metal OER electrocatalyst⁷. Composed entirely of earth-abundant and environmentally benign elements, ammonium jarosite presents several intrinsic advantages over conventional transition metal-based catalysts. Its layered crystal structure provides an ideal framework for ion transport and surface redox reactions, while its inherent chemical robustness ensures structural integrity during prolonged electrochemical operation. Moreover, ammonium jarosite exhibits favorable electronic properties, which support efficient charge transport during catalysis. Its structural versatility allows for compositional tuning and surface modifications that can further enhance catalytic performance. These combined characteristics—electrical conductivity, chemical stability, and structural adaptability—position ammonium jarosite as a compelling candidate for next-generation OER electrocatalysts aimed at scalable and cost-effective hydrogen production. Hence, the present study focuses on the simple and cost-effective synthesis of ammonium jarosite on a flexible SS substrate, demonstrating its potential as a stable electrocatalyst for oxygen evolution applications.

2. EXPERIMENTAL

2.1 Synthesis of Ammonium Jarosite

Ammonium jarosite thin films were synthesized using a simple chemical bath deposition (CBD) method. A 0.2 M $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution and a 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution were prepared separately in 100 mL of DI water. The FeSO_4 solution was heated to 70 °C in an oil bath, and the ammonium persulfate solution was slowly added under continuous stirring. A pre-cleaned SS substrate was vertically immersed in the reaction mixture (Figure 1), and deposition proceeded for 8 hours. Afterward, the films were rinsed with DI water and dried at room temperature. To assess the effect of temperature on structural and OER performance, synthesis was conducted at both 70 °C (A&J-A) and 60 °C (A&J-B).

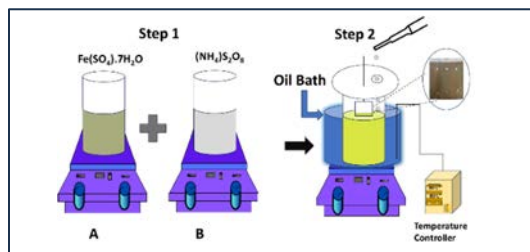


FIGURE 1. Represent the chemical bath deposition method of Ammonium Jarosite

2.2 Structural and Morphological Analysis

Structural characterization of the synthesized ammonium jarosite thin films was carried out using X-ray diffraction (XRD) analysis (Bruker AXS D8 Advance, Germany), as shown in Figure 2(a). The diffraction patterns confirm the crystalline nature of the films, exhibiting a rhombohedral crystal structure⁷ consistent with JCPDS card No. 00-026-1014. Peaks observed at 2θ values of 43°, 44°, 50°, and 75° are attributed to the underlying SS substrate⁸. Films synthesized at both 60 °C and 70 °C exhibited no significant variation in phase or crystallinity, indicating thermal stability across this temperature range. Further insight into the chemical bonding of the films was obtained through Raman spectroscopy (Renishaw In Via 0120-02 model, UK), as presented in Figure 2(b). The Raman spectra showed characteristic peaks at 452 cm^{-1} , 622 cm^{-1} , 1008 cm^{-1} , 1095 cm^{-1} , and 1163 cm^{-1} , corresponding to the vibrational modes of sulfate (SO_4^{2-}) groups within the jarosite structure. Additional peaks at 217 cm^{-1} and 429 cm^{-1} are attributed to Fe–O bond vibrations⁹, confirming the presence of iron-oxygen coordination. These results collectively validate the successful synthesis and chemical integrity of the ammonium jarosite thin films.

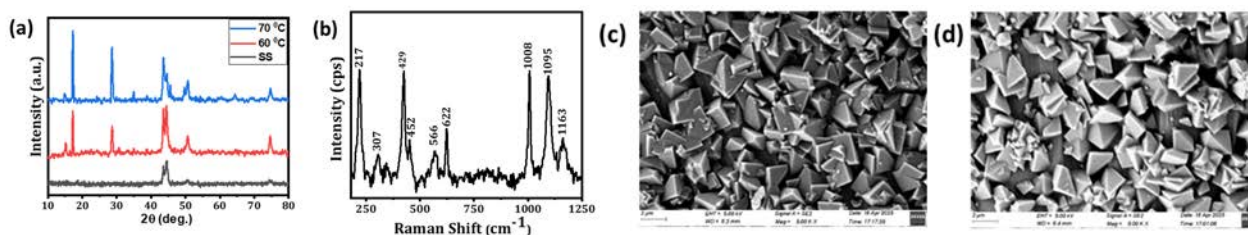


FIGURE 2. (a) XRD study of SS and ammonium jarosite all thin films, (b) The RAMAN study of ammonium jarosite, (c) (d) SEM image of ammonium jarosite at 70 C° and 60 C° respectively.

Surface morphology of the ammonium jarosite thin films was examined using Scanning Electron Microscopy (SEM). The films exhibited a convex quadrilateral-type morphology. As the synthesis temperature increased from 60 °C to 70 °C, surface uniformity also improved, as shown in Figure 2(c) and 2(d). Notably, the sample synthesized at 70 °C (A&J-A) displayed a more uniform and well-coated surface, which is expected to enhance OER activity by providing increased active surface-area.

2.3 Electrochemical and Oxygen Evolution Study

Electrochemical measurements were carried out in 1 M KOH using three electrode setup. The working electrodes were $1 \times 1 \text{ cm}^2$ ammonium jarosite films, with a platinum wire as the counter and an Ag/AgCl electrode as the reference electrode. The potential versus the reversible hydrogen electrode (RHE) was calculated using the equation $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 V \times \text{pH} + 0.1976 V$. Linear sweep voltammetry was carried out at a scan rate of 5 mV/s to investigate the OER in the positive potential range, and the overpotential (η) was calculated using $\eta = E_{\text{RHE}} - 1.23 V$, where 1.23 V is the theoretical standard potential for water splitting⁶. At a current density of 10 mA/cm², the calculated overpotentials were 421 mV for A&J-A, 467 mV for A&J-B, and 670 mV for the SS plate as noted from Figure 3(a), indicating that the ammonium jarosite sample synthesized at 70 °C (A&J-A) required

less energy for OER compared to the others. Tafel slope analysis that reflects the reaction kinetics, showed values of 113 mV/dec for A&J-A,

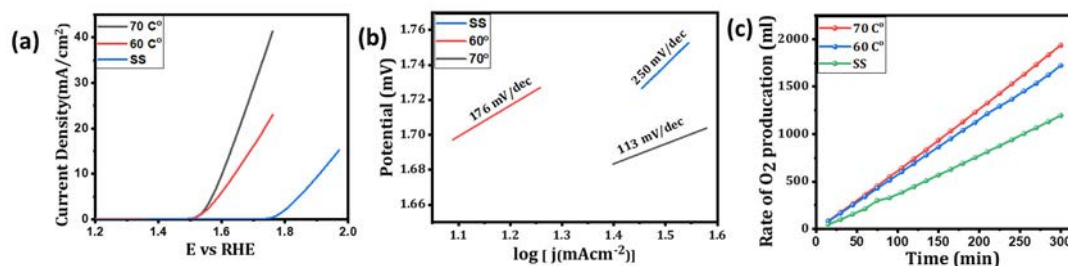


FIGURE 3. (a) represent the LSV plot, (b) comparative Tafel slope of all electrocatalyst thin films, (c) oxygen evolution on the prototype setup of all films.

176 mV/dec for A&J-B, and 250 mV/dec for the SS plate in Figure 3(b), confirming that A&J-A exhibited the fastest kinetic behaviour. Oxygen evolution was further evaluated using a prototype setup, with the ammonium jarosite films as the anode electrode and a SS plate as the cathode electrode in 1 M KOH electrolyte under an applied voltage of 2.2 V. As shown in Figure 3(c), the oxygen evolution rates were 387 mL/h for A&J-A, 344 mL/h for A&J-B, and 293 mL/h for the SS configuration. These results clearly indicate that the film synthesized at 70 °C (A&J-A) exhibits superior electrochemical performance and enhanced OER efficiency compared to the other electrodes tested.

3. CONCLUSION

Ammonium jarosite ($\text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$) thin films were synthesized on flexible SS substrates via a simple, low-cost chemical bath deposition method. XRD confirmed their crystalline rhombohedral structure. The ammonium jarosite synthesis at 70 °C resulted in uniform convex quadrilateral morphology. The electrode showed excellent electrochemical performance, with a low overpotential of 421 mV and a Tafel slope of 113 mV/dec, indicating higher active for water splitting. Although the overpotential is relatively low, the initial results indicate that ammonium jarosite is a promising and cost-effective material for electrocatalytic applications, with potential for enhanced performance through further doping or nanostructuring.

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Structural and Electrochemical Investigation of Dendritic-Fibrous CeO₂/a-rGO Edifices for Smart Supercapacitors

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Abstract. With the escalating demand for high-performance energy storage systems, the development of advanced electrode materials with enhanced conductivity and redox activity has become essential. In response to the growing need for efficient and durable energy storage materials, this study presents the synthesis and detailed characterization of dendritic fibrous CeO₂/amorphous-reduced graphene oxide (CeO₂/a-rGO) composites. The material was derived through pyrolysis of cerium-based metal-organic frameworks (Ce-MOFs) integrated with graphene oxide, using an organic ligand-assisted solvothermal approach followed by thermal treatment at 500 °C. Structural analysis via Rietveld-refined X-ray diffraction confirmed the formation of nanocrystalline fluorite-phase CeO₂ with an average crystallite size of 8.28 nm. The amorphous nature of the rGO matrix was validated through high-resolution XPS of the C 1s region, revealing characteristic oxygen functionalities and the absence of π - π^* satellite peaks. HR-TEM images showed uniform dispersion of dendritic fibrous CeO₂ nanocrystallites within the a-rGO framework. Electrochemical measurements conducted in a three-electrode system demonstrated excellent performance, with the CeO₂/a-rGO composite achieving a specific capacitance of 1190.58 F g⁻¹ at 1 A g⁻¹ and an energy density of 382.60 Wh kg⁻¹ at a power density of 4.00 kW kg⁻¹. These results underscore the potential of CeO₂/a-rGO as a high-performance electrode material for next-generation smart supercapacitors, offering superior charge storage, structural robustness, and long-term cycling stability.

INTRODUCTION

The growing dependence on renewable energy and electric vehicles has heightened the need for efficient and stable energy storage systems [1]. Supercapacitors are increasingly favoured for their high power density and rapid charge-discharge capabilities [2,3], but their performance largely hinges on the development of advanced electrode materials [4,5,6]. Cerium oxide (CeO₂), known for its excellent redox properties and structural stability, holds great promise in this area. However, issues such as limited conductivity and nanoparticle aggregation restrict its full potential in practical devices.

This study presents a CeO₂/a-rGO nanocomposite synthesized via pyrolysis of a Ce-MOF precursor using 2,6-naphthalene dicarboxylic acid as the ligand. The a-rGO matrix, rich in defects and oxygen functionalities, promotes efficient ion transport and uniform dispersion of dendritic CeO₂ nanoparticles. Structural analyses confirmed the fluorite CeO₂ phase and amorphous carbon support, while electrochemical studies revealed high specific capacitance, excellent energy density, and long-term stability, underscoring the potential of ligand-assisted MOF-derived materials for sustainable development and advanced energy storage [7].

SYNTHESIS PROTOCOL

The CeO₂/a-rGO composite was synthesized via a solvothermal method using a Ce-MOF/GO precursor prepared from 2,6-naphthalene dicarboxylic acid [1], 5 wt% graphene oxide (from streamlined Hummers' method [8]), and a 3:1 water-ethanol mixture. After stirring, ultrasonication, and addition of cerium nitrate, the solution was heated at 160 °C for 24 hours in a Teflon-lined autoclave. The resulting product was washed, dried, and vacuum-annealed at 500 °C for 3 hours to yield CeO₂/a-rGO. For electrode fabrication, 1 mg of the composite was dispersed in ethanol, ultrasonicated to form a uniform ink, and drop-cast onto a glassy carbon electrode to create the working electrode.

RESULTS AND DISCUSSION

Structural and Morphological Characterizations

The structural and morphological features of the CeO₂/a-rGO composite were extensively characterized using XRD, Rietveld refinement, HR-XPS, and HR-TEM techniques. XRD analysis (Fig. 1 (a)) confirmed the formation of nanocrystalline cerium oxide with a fluorite cubic structure (JCPDS #03-065-5923), while the absence of sharp peaks from reduced graphene oxide supported its amorphous nature. Rietveld refinement further validated the phase purity, revealing a well-fitted cubic fluorite structure with refined lattice parameters ($a = b = c = 5.41 \text{ \AA}$) and a low χ^2 value of 1.73, with an estimated crystallite size of $\sim 8.28 \text{ nm}$. HR-XPS of the C 1s region (Fig. 1 (b)) showed the presence of sp² carbon along with various oxygenated functional groups (C–O, C=O, O–C=O), confirming partial reduction and disordered structure in the rGO matrix. The absence of the characteristic π – π^* satellite peak reinforced its amorphous and defect-rich nature. HR-TEM imaging revealed dendritic fibrous CeO₂ nanoparticles uniformly dispersed over spherical a-rGO sheets, forming a porous three-dimensional architecture that facilitates ion/electron transport (Fig. 1 (c1,c2)). Well-defined lattice fringes observed in the CeO₂ nanoparticles (Fig. 1 (d1,d2,d3)) further supported their crystalline quality and aligned with the XRD findings, highlighting the composite's suitability for advanced energy storage applications.

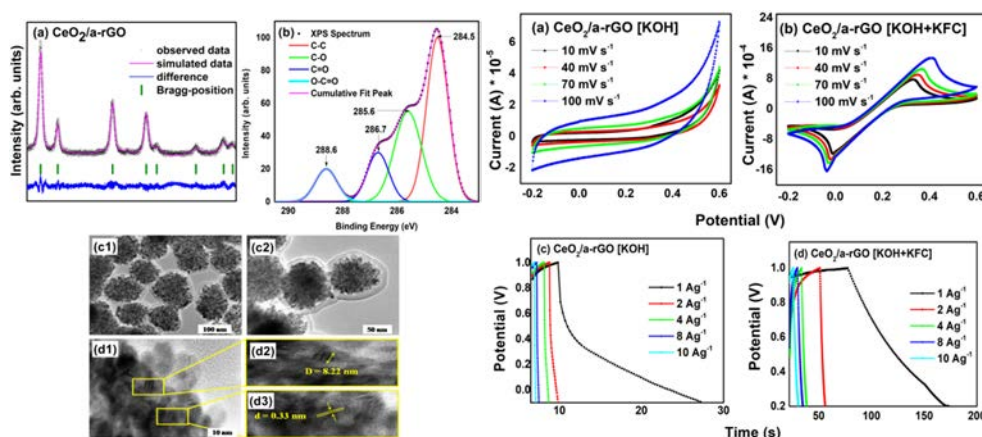


FIGURE 1. (a) Rietveld refined XRD pattern, (b) deconvoluted HR-XPS pattern, (c1,c2) HR-TEM micrographs, and (d1,d2,d3) lattice fringes in enlarged micrographs, for CeO₂/a-rGO.

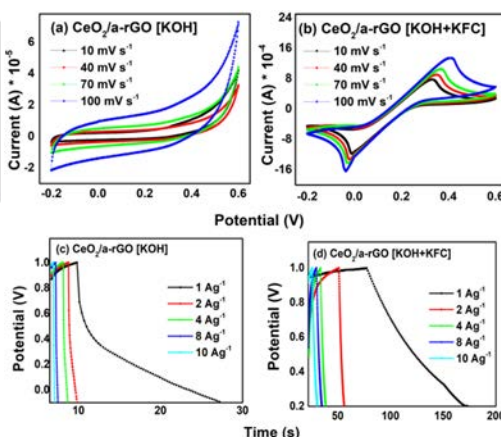


FIGURE 2. (a) CV curves in KOH, (b) CV curves in KOH+KFC, (c) GCD curves in KOH, and (d) GCD curves in KOH+KFC, for CeO₂/a-rGO.

Electrochemical Characterizations

The electrochemical behavior of the CeO₂/a-rGO composite was evaluated through cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) in both 3 M KOH and a redox-active [KOH + K₄Fe(CN)₆] electrolyte. In CV analysis, the electrode showed quasi-rectangular curves in 3 M KOH (Fig. 2 (a)) with a peak specific capacitance of 225.83 F g⁻¹ at 10 mV s⁻¹, which significantly increased to 1190.58 F g⁻¹ in the redox-additive electrolyte (Fig. 2 (b)) due to enhanced faradaic activity. GCD profiles demonstrated symmetric charge/discharge curves, with CeO₂/a-rGO achieving 222.50 F g⁻¹ (71.20 Wh kg⁻¹ at 4.00 kW kg⁻¹) in 3 M KOH (Fig. 2 (c)), and a much higher 1195.63 F g⁻¹ (382.60 Wh kg⁻¹ at 4.00 kW kg⁻¹) in the redox electrolyte (Fig. 2 (d)), confirming that the composite benefits greatly from the synergistic interaction between the material and electrolyte, leading to superior charge storage and energy performance.

CONCLUSION

In conclusion, this study highlights the impact of ligand-directed synthesis on the structure and electrochemical behavior of CeO₂/a-rGO composites. Using a planar ligand, 2,6-naphthalene dicarboxylic acid (NDC), the resulting

CeO₂/a-rGO composite featured a spherical a-rGO matrix with well-dispersed dendritic CeO₂ nanoparticles. Structural characterization confirmed the fluorite CeO₂ phase and amorphous nature of rGO, while electrochemical testing demonstrated high specific capacitance, redox activity, and long-term cycling stability. These results underscore the significance of ligand geometry in tuning the microstructure and optimizing the performance of MOF-derived nanomaterials for advanced energy storage applications.

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Exploring the Effect of Exfoliated Graphite Incorporation in CrCo_2O_4 Electrodes for Advanced Supercapacitors

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Abstract. The pursuit of high-performance supercapacitor electrodes has driven research into advanced composite materials that integrate the advantages of metal oxides with conductive carbonaceous components. In this study, we explore the impact of exfoliated graphite incorporation into chromium cobalt oxide (CrCo_2O_4) electrodes synthesized via a simple co-precipitation method for application in advanced aqueous supercapacitors. Pristine CrCo_2O_4 demonstrated a specific capacitance of 90 F g^{-1} at 0.5 Ag^{-1} , which significantly increased to 204 F g^{-1} upon compositing with 1 wt% exfoliated graphite. The enhancement is attributed to the synergistic effects arising from the conductive network of exfoliated graphite and the pseudocapacitive nature of CrCo_2O_4 , leading to improved charge transport and greater electrochemical surface area. Moreover, the composite electrode exhibited excellent cycling stability, maintaining 90% coulombic efficiency and 79% capacitance retention after 5,000 charge-discharge cycles. These results underscore the effectiveness of exfoliated graphite as an additive to boost the electrochemical performance and operational longevity of metal oxide-based supercapacitor electrodes.

1. INTRODUCTION

The growing demand for energy storage has led to the development of supercapacitors, which bridge the gap between capacitors and batteries. Their performance can be significantly improved by optimizing electrode materials, particularly transition metal oxides, which offer excellent electrochemical properties. Because the two metal ions work in concert, binary transition metal oxides (BTMOs), especially spinel cobaltite (MCo_2O_4 , where M is a transition metal), have better electrical conductivity and increased redox activity. This gives them several advantages over single-metal oxides. In the meantime, materials based on carbon provide a great conductive framework with a lot of surface area, which facilitates effective passage of electrolytes and electrons. By combining these materials, the inherent drawbacks of BTMOs, such as low conductivity and restricted cycle performance, are successfully addressed, leading to enhanced specific capacitance, rate capability, and long-term stability[1]. The present study involved the synthesis of CrCo_2O_4 using a straightforward co-precipitation method and its integration with exfoliated graphite (EG) sheets at different weight percentages (0%, 1%, and 1.5%). The resulting composites were designated as CCOEG0, CCOEG1, and CCOEG1.5. Notably, the 1% EG-loaded composite (CCOEG1) exhibited the highest specific capacitance, while a further increase to 1.5% led to a decline in performance. This indicates that CrCo_2O_4 /exfoliated graphite composites, particularly at optimal EG content, are promising electrode materials for advanced supercapacitor applications.

2. SYNTHESIS AND STRUCTURAL CHARACTERISATIONS

CrCo_2O_4 powder was synthesized via co-precipitation using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (5 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (10 mmol), which were dissolved in 100 mL of distilled water and stirred at room temperature for 4 hours. The 5 mL liquid NH_3 was added dropwise until the pH reached 9, resulting in the precipitation of metal hydroxides. The precipitate was filtered, washed with distilled water, dried at 80°C for 6 hours, and calcined at 600°C for 2 hours to

obtain crystalline CrCo_2O_4 . For composite preparation, exfoliated graphite (EG) was added at 1% and 1.5% by weight, producing CCOEG1 and CCOEG1.5 for electrochemical testing. The crystal structures of the synthesized materials were analyzed by XRD, as shown in Fig. 1(a). Pure CrCo_2O_4 (CCO) exhibited distinct peaks at 18.62° , 31.0° , 36.55° , 38.23° , 44.81° , 54.95° , 58.7° , and 64.55° , corresponding to the characteristic planes of the spinel phase and matching JCPDS card no. 024-0326, confirming its successful formation.[2] The significant peak at 26.13° in the exfoliated graphite (EG) is attributed to the (002) plane, confirming its presence in CCOEG1 and CCOEG2. Notably, EG incorporation did not alter the main diffraction peaks of CrCo_2O_4 , indicating that the spinel structure remains intact in the composites.

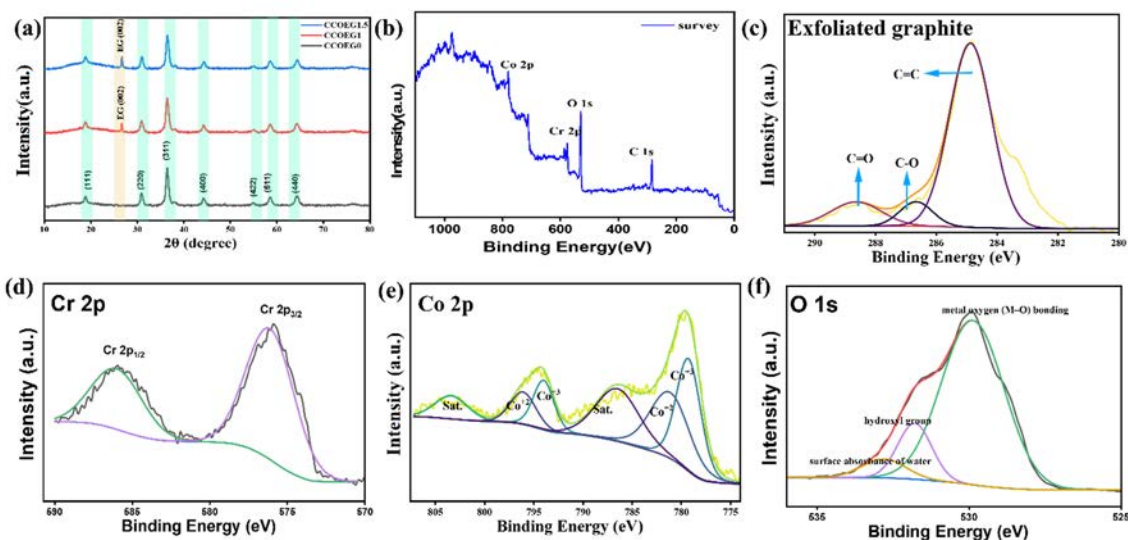


FIGURE 1. (a) XRD pattern of CCOEG0, CCOEG1, and CCOEG2, (b) XPS survey spectra of CCOEG1, (c-e) XPS of Exfoliated graphite, Cr, Co, and O, respectively.

Wide-scan XPS confirmed the presence of Cr, Co, O, and C in CrCo_2O_4 /exfoliated graphite composite, with carbon attributed to graphite. High-resolution spectrum (Fig. 1b) revealed oxidation states of all elements. The Cr 2p spectrum (Fig. 1d) exhibited two characteristic peaks at 576.2 and 586.8 eV, corresponding to Cr $2p_{3/2}$ and Cr $2p_{1/2}$ spin-orbit components of Cr^{3+} . Co 2p spectrum (Fig. 1e) displayed peaks at 780.6 and 795.9 eV assigned to Co^{3+} , while peaks at 781.5 and 797.1 eV indicated the presence of Co^{2+} , accompanied by satellite peaks at 788.8 and 804.9 eV.[3] O 1s spectrum (Fig. 1f) exhibited three components at 530.1, 531.8, and 533.4 eV, corresponding to lattice oxygen, surface hydroxyl groups, and adsorbed water molecules, respectively. The C 1s spectrum of exfoliated graphite showed peaks attributed to C-C, C-O, and O-C=O bonds, indicating retention of functional groups after composite formation. Overall, XPS results confirm the successful incorporation of exfoliated graphite into CrCo_2O_4 matrix without altering the chemical states of the elements, thereby preserving the structural and chemical integrity of the composite.[2],[5].

3. ELECTROCHEMICAL ANALYSIS.

A three-electrode system with 6 M KOH electrolyte was employed to evaluate the electrochemical performance of the nanocomposites. Cyclic voltammetry (CV) of all samples at 5 mV s^{-1} (-0.2 to 0.5 V) in Fig. 2(a) revealed quasi-rectangular curves with redox peaks, indicating combined faradaic and non-faradaic charge storage and confirming pseudocapacitive behavior due to reversible interactions between CrCo_2O_4 and OH^- ions. Among all samples, CCOEG1 exhibited the largest CV area, suggesting superior electrochemical activity. Galvanostatic charge-discharge (GCD) in Fig. 2(b) is compared for all samples, measured at 0.5 A g^{-1} show nearly symmetric profiles, indicating good reversibility, with distinct voltage plateaus further supporting pseudocapacitance. CCOEG1 delivered the longest discharge time and highest specific capacitance (204 F g^{-1}), outperforming CCOEG1.5 (132 F g^{-1}) and CCOEG0 (90 F g^{-1}), calculated using formula $C_s = I \cdot \Delta t / m \cdot \Delta V$. The incorporation of exfoliated graphite (EG) enhanced ion/electron transport and increased the electrode-electrolyte interface, thereby improving faradaic activity. However,

further increasing EG content to 1.5 wt% led to reduced performance due to its inherently low capacitance and agglomeration, which blocked active sites and decreased the capacitance of CCOEG1.5.[3]

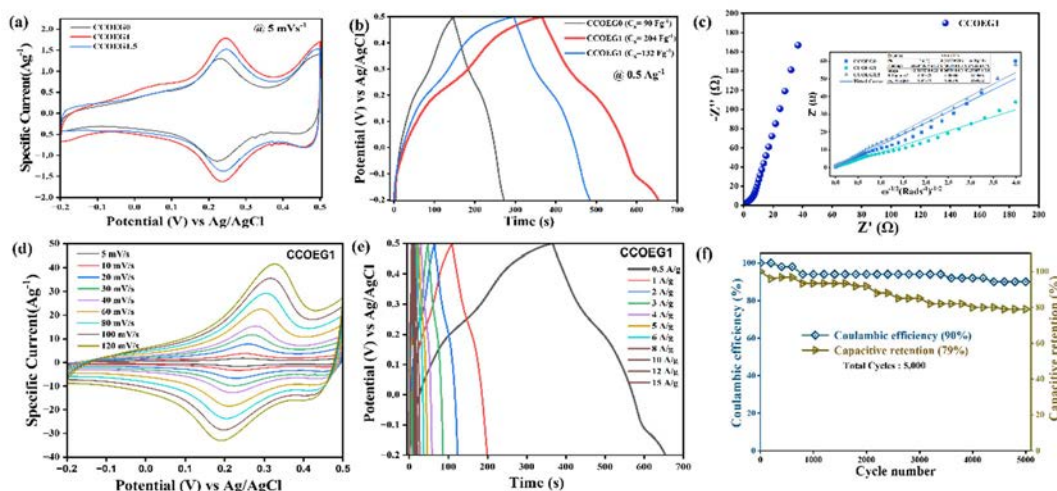


FIGURE 2. (a-b) CV, GCD of all three materials, (c) EIS of CCOEG1, and the inset is the Randles plot of all materials. (d-e) CV at different scan rates and GCD at different current densities of CCOEG1. (f) Stability data of CCOEG1

Figures 2(c–e) give in-depth insight into the electrochemical behavior of CCOEG1 using EIS, CV, and GCD analyses. The EIS plot shows low resistance and a nearly vertical low-frequency line, indicating efficient ion diffusion. CV curves retain symmetric redox peaks even at high scan rates, reflecting excellent reversibility and fast kinetics. GCD profiles exhibit symmetric shapes with voltage plateaus, confirming pseudocapacitive behavior and high stability. Warburg analysis (Fig. 2e inset) revealed ion diffusion coefficients of 5.82×10^{-12} , 8.04×10^{-11} , and $6.84 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for CCOEG0, CCOEG1, and CCOEG1.5, respectively, confirming the superior ion transport in CCOEG1. Additionally, CCOEG1 exhibited 79% capacitance retention after 5,000 cycles at 12 A g^{-1} (Fig. 2f), along with a stable coulombic efficiency of 90%, demonstrating excellent durability and reversibility.

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Synergistic co-doping Fe and W Driven Hierarchical Nanoflakes Morphology for Enhanced Electrochromic Performance in V_2O_5

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Abstract. This study focuses on the synergistic impact of co-doping of Fe and W dopants-induced structural, morphological, and electrochromic performance. The XRD spectra reveal that the co-doping of Fe and W in V_2O_5 caused a decrease in crystallite size with a peak broadening. Co-doping tunes the morphology of V_2O_5 nanostructure. Cyclic voltammetry suggest improved charge storage capabilities and faster ion transport kinetics due to the higher charge state of V. Thus, the analytical results reveal that the co-doped V_2O_5 is a potential candidate with improved electrochromic performance in comparison with V_2O_5 .

INTRODUCTION

Supercapacitors have been the subject of recent research due to the growing need for energy storage devices with better performance [1] [2]. V_2O_5 has become a promising transition metal oxide, due to its exceptional redox characteristics, various oxidation states, and distinctive layered structure[3]. It has been employed for various applications such as photocatalysts, thermoelectric, energy storage devices, optoelectronics applications, supercapacitors, photodetectors, and optical sensors [4], [5], [6]. It is essential for comprehending the redox behaviour, charge storage mechanism, and reversibility of electrode reactions in V_2O_5 -based systems [7]. In this study, we examine the synergistic effect and optimize the doping percentage of Fe and W for the enhancement of electrochromic performance.

EXPERIMENTAL SECTION

V_2O_5 and its co-doped nanoparticles were synthesized by a sol-gel method. These samples are named as pristine, and co-doped samples [Fe (1%) +W (0.5%)] and [Fe (2%) + W (0.5%)], referred as pristine, VF₁W and VF₂W respectively. The room temperature XRD pattern was recorded with a wavelength of 1.54 Å in the 2θ range of 10° to 65°. To investigate the morphology of the surface, Field Emission-Scanning Electron Microscopy (FESEM) - FEI made NOVA NANOSEM 450 was used at IUC, Indore. The drop casting method was used to prepare the electrode on the ITO substrate. V_2O_5 pristine and co-doped V_2O_5 were used as the working electrode for electrochemical tests in three-electrode cell arrangements using a Metrohm Autolab (Germany). Platinum wire and Ag/AgCl as counter and reference electrodes.

RESULT AND DISCUSSION

Structural Investigations

The X-ray diffraction (XRD) patterns of pristine and Fe-W co-doped V_2O_5 samples are shown in Figure 1, which reveal structural changes caused by co-doping. The pristine V_2O_5 sample exhibits strong peaks that correspond to the orthorhombic phase of V_2O_5 (JCPDS No. 41-1426) [3]. Table 1 illustrated the structural parameters calculated from XRD pattern. In the co-doped sample VF₁W, the peaks remain recognisable, but show minor broadening and lower intensity, indicating a decrease in crystallite size to 42.75 nm and the reduction in micro-strain due to co-doping. The

VF₂W shows more broadening and intensity reduction, indicating a reduction of crystallite size to 35.71 nm with high structural disorder due to increment in micro-strain. The lattice parameter also decreases with the increment of dopant % of Fe in V₂O₅ as mentioned in Table 1.

Table 4 Structural parameters calculated from XRD pattern.

Samples	Lattice Parameter, a (Å)	Lattice Parameter, b (Å)	Lattice Parameter, c (Å)	Average Crystallite size, D (nm)	Dislocation density, (nm ⁻²)	Micro-strain (10 ⁻³)
Pristine	11.51	3.482	4.373	47.81	0.434	5.17
VF ₁ W	11.50	3.48	4.377	42.75	0.547	4.15
VF ₂ W	11.48	3.478	4.372	35.71	0.783	5.00

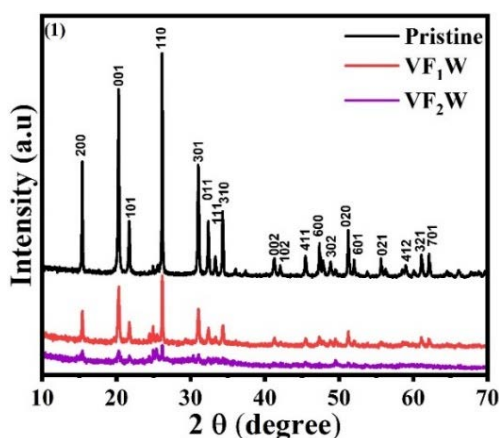


FIGURE 1. XRD patterns of Pristine and co-doped V₂O₅ nanoparticles.

Field Emission-Scanning Electron Microscopy (FESEM)

The Figure 2 depicts a noticeable morphological change in V₂O₅ caused by co-doping with Fe and W, which has a high impact on the material's electrochemical performance. The morphology V₂O₅ shows platy with rod like morphology. During electrochemical processes, the pristine V₂O₅ (Figure 2a) may inhibit ion diffusion. The decrease in the number of available active sites is due to its dense and compact nanorod-like shape with restricted porosity and surface area [8]. However, the structure drastically changes into a highly porous, loosely packed, petal-shaped nanoflakes upon co-doping with 1% Fe and 0.5% W (Figure 2b) [9]. The morphology becomes more stacked and non-uniform, with the nanosheets looking thicker and more densely layered, when the Fe concentration is increased further to 2% with a constant W concentration (Figure 2c).

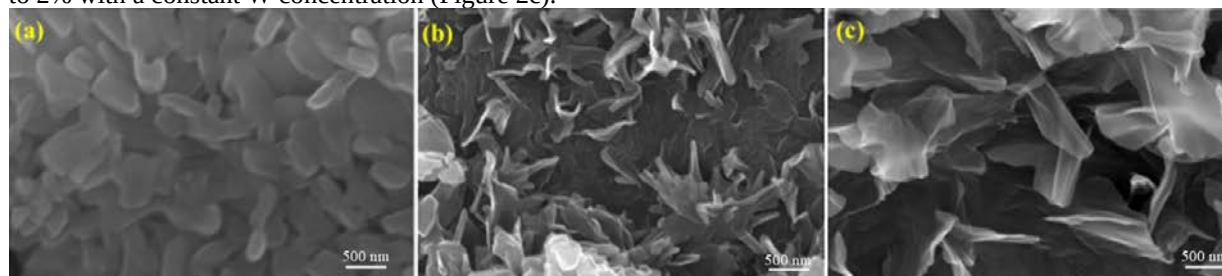


FIGURE 2. The morphological images (a) Pristine, (b) VF₁W, (c) VF₂W.

Electrochemical Analysis

Cyclic voltammetry (CV) was used to study the electrochemical properties of pure and Fe-W co-doped V₂O₅ samples at different scan rates (10-100 mV/s). Figure 3 (a) shows that the pure V₂O₅ has modest current responses and roughly rectangular CV curves, indicating typical pseudocapacitive behaviour. In contrast, the co-doped V₂O₅ sample (VF₁W, Figure 3 b) displays significantly higher current density across all scan rates, with more pronounced redox characteristics. This suggests improved charge storage capabilities and faster ion transport kinetics due to the higher charge state of V in comparison with the other samples [1]. This shows that as the doping concentration of Fe increases,

that suppresses the electrochemical activity as shown in Figure 3 (c). Figure 3 (d and e) demonstrated the scan rate of 10 mVs^{-1} and 100 mVs^{-1} respectively.

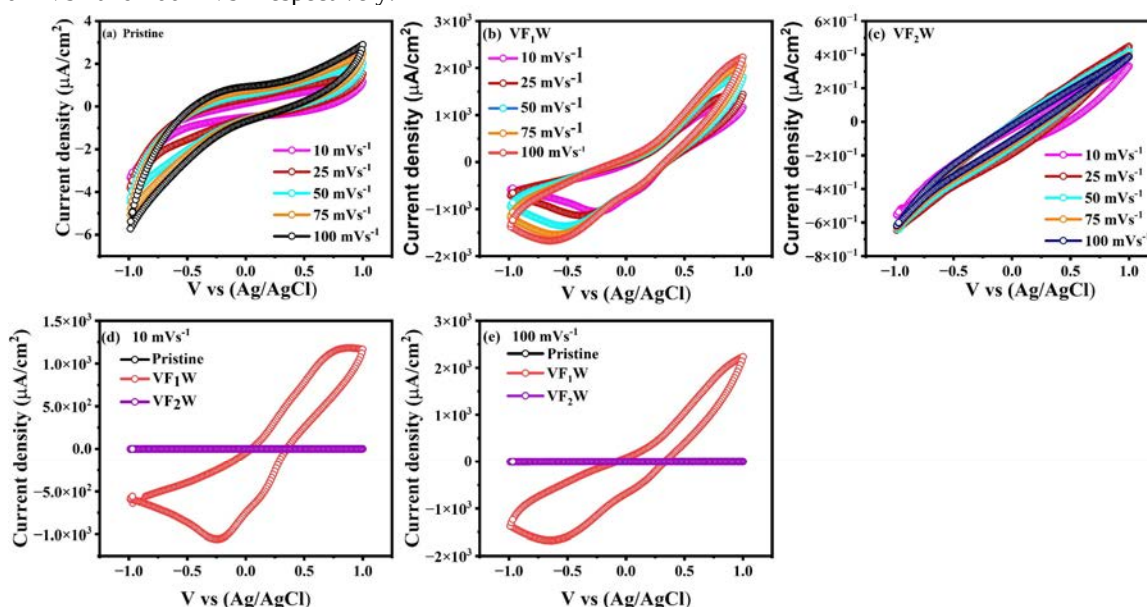


FIGURE 3. The CV curves of (a) pristine (b) VF₁W, (c) VF₂W, the scan rate of (d) 10 mVs^{-1} and (e) 100 mVs^{-1} .

CONCLUSION

Pristine and co-doped V_2O_5 samples are prepared by sol-gel method and drop-cast on an ITO substrate. The XRD patterns revealed that as the doping concentration increases, the crystallite size is reduced with the orthorhombic phases of V_2O_5 . The morphology of V_2O_5 and co-doped V_2O_5 was platy with rods and nano-flakes morphology, respectively. The CV curve of VF₁W was enhanced in comparison with the other samples. Thus, the optimized crystallite size and modified morphology correlated with the improved electrochemical performance in VF₁W than in the other samples.

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Crystal Structure and Stability of Aluminum-Ion Battery Materials: A Density Functional Theory Study

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Abstract. Aluminum-ion batteries (AIBs) have emerged as promising alternatives to conventional lithium-ion batteries due to their high theoretical capacity, low cost, and environmental sustainability. The performance of these systems is strongly influenced by the structural stability of electrode materials during aluminum ion intercalation. In this study, Density Functional Theory (DFT) calculations were performed using the ORCA software package to investigate the crystal structures, stability, and ion diffusion behavior of selected electrode materials, including graphite, graphyne, Al_2O_3 , V_2O_5 , and AlN . Structural parameters, formation energies, and electronic properties were evaluated to understand the interaction of aluminum species (Al^{3+} , AlCl_4^- , and AlF_4^-) with host lattices. The results indicate that 2D materials such as graphyne and AlN provide enhanced stability and ion mobility, making them promising candidates for next-generation aluminum-ion batteries.

INTRODUCTION

The rapid growth in energy demand has intensified the search for alternative energy storage technologies beyond lithium-ion batteries. Aluminium-ion batteries (AIBs) are considered attractive due to the abundance, low cost, and high charge storage capability of aluminium. Unlike lithium ions, aluminium ions can transfer three electrons per ion, resulting in significantly higher energy density.

Despite these advantages, the development of AIBs is limited by the difficulty of accommodating multivalent aluminium ions within host materials. Strong electrostatic interactions often lead to structural instability and slow diffusion kinetics. Therefore, understanding the role of crystal structure, lattice spacing, and material flexibility is essential for designing efficient electrode materials.

Density Functional Theory (DFT) provides a powerful computational framework to investigate these properties at the atomic level. This study focuses on evaluating the structural and electronic behaviour of various candidate materials using DFT.

COMPUTATIONAL METHODS

2.1 DFT Framework

All calculations were performed using the **ORCA software package**. The exchange–correlation interactions were described using the Perdew–Burke–Ernzerhof (PBE) functional within the Generalized Gradient Approximation (GGA). Appropriate basis sets and effective core potentials were employed.

Dispersion interactions were included using the DFT-D3 correction method. Tight convergence criteria were applied for energy and geometry optimization to ensure accurate results.

2.2 Structure Optimization

Initial crystal structures of graphite, graphyne, Al_2O_3 , V_2O_5 , and AlN were obtained from reliable databases and optimized using DFT.

Aluminium ions and complexes (Al^{3+} , AlCl_4^- , and AlF_4^-) were introduced into the host structures to simulate intercalation. Geometry optimization was carried out to determine stable configurations. Formation energies and lattice changes were calculated to assess structural stability.

2.3 Diffusion and Stability Analysis

Ion diffusion pathways were evaluated using the **CI-NEB method**, allowing calculation of energy barriers for aluminium migration. Phonon dispersion analysis was performed to verify dynamic stability. Bader charge analysis was used to investigate charge transfer between aluminium species and host materials.

RESULTS AND DISCUSSION

3.1 Crystal Structure of Host Materials

- **Graphite:** Maintained its hexagonal $P6_3/mmc$ symmetry with minimal expansion upon $AlCl_4^-$ intercalation. Interlayer spacing increased from 3.35 Å to ~6.8 Å.
- **Graphyne:** Showed a larger pore size than graphite, allowing easier diffusion and lower deformation energy under Al^{3+} insertion.
- **AlN Monolayer:** Exhibited hexagonal symmetry with lattice constants ~3.11 Å. Stable under AlF_4^- insertion with low volume expansion (<5%).
- **Al_2O_3 (Corundum Phase):** Orthorhombic symmetry with high structural rigidity. Insertion of Al^{3+} resulted in significant distortion, indicating limited reversibility.
- **V_2O_5 :** Layered orthorhombic structure (space group C_{2h}^2), showed moderate accommodation of Al^{3+} ions, with calculated diffusion barriers around 0.65 eV.

The optimized crystal structure of the electrode material was obtained using DFT calculations.

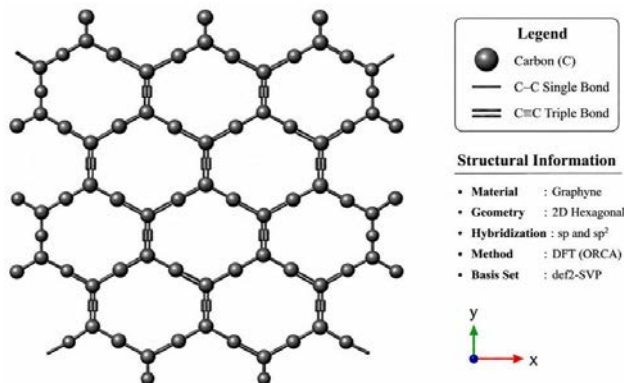


FIGURE 1. Optimized crystal structure of graphyne obtained using DFT calculations in ORCA.

The structural optimization confirms the stability of the material and its suitability for aluminum-ion battery applications.

3.2 Structural Stability and Formation Energies

- **Formation energy (ΔE_f)** was calculated for all intercalated structures.
 - Graphyne- $AlCl_4^-$ complex: $\Delta E_f = -1.92$ eV
 - AlN- AlF_4^- complex: $\Delta E_f = -1.47$ eV
 - Al_2O_3 intercalated with Al^{3+} : $\Delta E_f = +0.65$ eV (unstable)
- Phonon dispersion curves showed no imaginary frequencies for graphite and AlN structures, confirming their dynamic stability. In contrast, Al_2O_3 showed lattice instability after intercalation.

The formation energies of different electrode materials were calculated to evaluate their thermodynamic stability.

3.3 Aluminum Ion Intercalation and Diffusion

- $AlCl_4^-$ and AlF_4^- complexes were more stable in host lattices than bare Al^{3+} due to reduced coulombic repulsion.
- Diffusion barriers (calculated via CI-NEB):
 - Graphite: ~0.45 eV
 - Graphyne: ~0.38 eV
 - V_2O_5 : ~0.65 eV
- Bader charge analysis revealed partial charge transfer (~1.8 e) from $AlCl_4^-$ to graphyne, enhancing electronic conductivity.

3.4. Electronic Structure Analysis

- **Density of States (DOS)** analysis showed:
 - o Metallic behavior of graphite remains intact post intercalation.
 - o AlN shows a slight band gap narrowing after AlF_4^- insertion (~ 2.1 eV to 1.8 eV).
 - o In V_2O_5 , insertion of Al^{3+} introduced mid-gap states, possibly reducing its ionic mobility and reversibility.
- **Partial DOS** confirmed orbital hybridization between Al and O/N atoms in Al_2O_3 and AlN, respectively.

SUMMARY TABLE

TABLE 1. Comparison of formation energies

Crystal Materials for Aluminium			Ion Batteries (AIBs) Studied via DFT			
Material	Crystal Structure	Intercalant Ion	Formation Energy (eV)	Diffusion Barrier (eV)	Stability After Intercalation	Remarks
Graphite	Hexagonal (P6 ₃ /mmc)	AlCl_4^-	-1.20	~ 0.45	Stable	Minimal volume expansion; known cathode
Graphyne	Hexagonal (2D)	AlCl_4^-	-1.92	~ 0.38	Stable	Larger pores; better ion mobility
AlN Monolayer	Hexagonal (2D)	AlF_4^-	-1.47	~ 0.40	Stable	High capacity; low expansion
V_2O_5	Orthorhombic (Pmmn)	Al^{3+}	-0.85	~ 0.65	Moderately stable	Layered oxide; slow Al^{3+} diffusion
Al_2O_3	Rhombohedral (corundum)	Al^{3+}	+0.65	> 0.80	Unstable after intercalation	High rigidity; not favourable
PTCDA/ TDK	Molecular crystal	AlCl_2^+	-2.10	~ 0.55	Partially stable	High capacity; solubility issues
AlCl_4^- cluster	N/A (complex ion)	—	—	—	—	Used as mobile ion in ionic liquid systems

CONCLUSION

This study provides a detailed DFT-based analysis of aluminium-ion battery materials. Graphyne and AlN were identified as the most promising candidates due to their favorable stability and low diffusion barriers. Graphite remains a reliable material with stable intercalation behavior, while V_2O_5 shows moderate performance. Al_2O_3 is unsuitable due to structural instability. The results emphasize the importance of structural flexibility and compatibility with complex aluminum ions for efficient battery performance.

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Structural and Optical studies of Sn doped In_2Te_3 Crystals

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Abstract. This research investigates the impact of Tin (Sn) doping on the structural and optical properties of Indium Telluride (In_2Te_3) crystals. In_2Te_3 crystals with varying Sn concentrations were successfully grown using the Bridgman-Stockbarger melt growth method. The powder XRD of ($\text{In}_{2-x}\text{Sn}_x\text{Te}_3$, $x=0.00, 0.05$), crystals were obtained & analyzed. The FTIR in the range between 400cm^{-1} to 5500cm^{-1} wave numbers were obtained and analyzed.

INTRODUCTION

Indium Telluride (In_2Te_3) is important in its crystalline form due to its unique defect-rich structure, which gives rise to its valuable semiconductor properties for applications in electronics and energy conversion. The crystal lattice of In_2Te_3 naturally contains a high concentration of vacancies, or empty atomic sites [1]. Indium Telluride (In_2Te_3) is a well-known semiconductor famous for its use in thin film devices, where its properties can change with thickness due to the quantum size effect [2-4]. However, the real excitement now lies with In_2Te_3 nanostructures. While less studied, these structures offer significantly better chemical and physical properties because of their high surface area [5]. This makes them excellent candidates for advanced thermoelectric and optoelectronic applications. Since it's also environmentally friendly, its potential for creating new, efficient, and safe technologies makes it a highly interesting subject for research.

EXPERIMENTAL DETAILS

For the crystal growth the Quartz ampoule was washed and cleaned with nitric acid, acetone and distilled water. This cleaned Quartz ampoule was heated it in a furnace at 70°C for 1hr. The stoichiometric amount of all the materials (5N purity) were weighed accurately using microbalance. The materials were filled into the cleaned quartz ampoule then vacuum sealed at pressure about 10^{-5} Pa using Vacuum sealing unit (Hind High Vacuum Model: VS-75).

The sealed quartz ampoule was placed in the Heating zone of furnace. The temperature in the furnace was gradually increased and then after the desired 717°C temperature was achieved. By using gear mechanism ampoule was rotated for 2hr at 1 rpm. Then the temperature was gradually reduced up to room temperature and ampoule was taken out.

The quartz ampoule was suspended at the Heating zone of Bridgeman furnace. The temperature in the furnace was gradually increased up to desired temperature (717°C). The ampoule was kept steady for 24hr in the heating zone of furnace and was solidified at steady lowering rate in the rate of 3 mm/hr. Then the temperature was gradually reduced up to room temperature and ampoule was taken out from the vertical Bridgeman furnace.

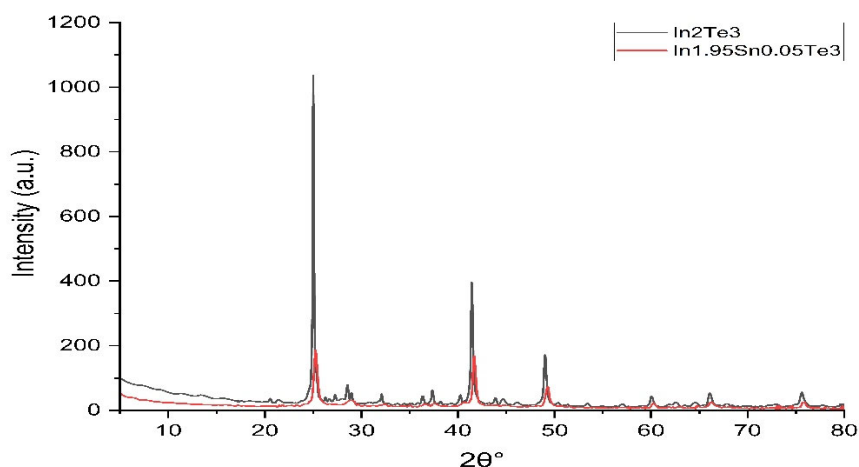
RESULTS AND DISCUSSION

Figure 1 shows that top free surface features of Sn doped In_2Te_3 crystals grown by Bridgman method and having 2.4 cm in length and 1 cm diameter. The powder XRD of grown crystal were carried out using XRD (Rigaku Japan, Model: SmartLab SE, 3KW). The obtained X-ray diffraction (XRD) data reveals the successful incorporation of tin (Sn) into the indium telluride (In_2Te_3) crystal lattice.

FIGURE 1: As grown crystal of Sn doped In_2Te_3

Analysis of XRD Patterns

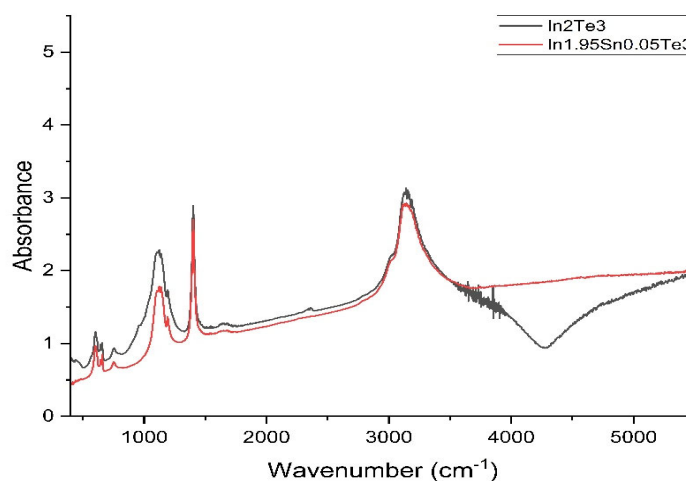
Figure 2 shows the diffraction patterns for pure In_2Te_3 and Sn-doped In_2Te_3 crystals. Both crystals show high crystallinity as per the XRD graph and no change observed in crystal structure with increasing Sn concentration [6]. The primary peaks show consistency for the undoped In_2Te_3 having known its cubic structure. There is a progressive shift in the diffraction peaks towards higher 2θ angles as the concentration of Sn increases. This shift is a strong indication of a change in diffraction angles of Sn doped In_2Te_3 crystals [7]. The substitution of larger indium (In) atoms with smaller tin (Sn) atoms leading to a minor contraction of the crystal lattice, resulting in the observed peak shift which is in good agreement with Vegard's law [8].

FIGURE 2: XRD of In_2Te_3 crystal with Sn doping.

When the main diffraction peaks of the In_2Te_3 structure are retained in the Sn doped samples, there are minor changes occurred in the relative intensities of the peaks. This suggests that the Sn atoms are not just occupying random sites but are systematically substituting the In atoms within the crystal structure.

The crystallographic data for pure In_2Te_3 crystals, the calculated lattice parameters are $a = b = c = 18.4961$ Å, and the angles are $\alpha = \beta = \gamma = 90^\circ$, with a direct cell volume of 6327.6582 Å³ [9]. The prominent peaks observed in the Rietveld refinement of In_2Te_3 correspond to the (333), (660), and (933) crystallographic planes. Chi2 value is 0.987 and 10 cycle. The experimental data shows good agreement with the JCPDS#16-445.

The results obtained from the Fourier-transform infrared spectroscopy (FTIR) analysis of pure and tin-doped Indium Telluride (In_2Te_3) displays several characteristic features in the scanned range. A notable peak system is present at approximately 1200 cm^{-1} . A sharper absorption peak is visible around 1500 cm^{-1} . Figure shows broader peak which is centered near 3200 cm^{-1} .

FIGURE 3: FTIR of In_2Te_3 with Sn doping

The intensity of the absorption peaks, particularly the broad feature around 3200, appears to decrease as the concentration of Sn dopant increases. The overall signal intensity across the spectrum is generally lower for the doped samples compared to the pure In_2Te_3 crystals [10].

CONCLUSIONS

The authors have grown successfully crystals using Bridgman method and from XRD analysis no structural change found in the present crystals. The pure and Sn doped In_2Te_3 crystals displays several characteristic features in the observed wave number range.

ACKNOWLEDGMENTS

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Material Synthesis and Characterization of NbFeSb and NbFeSb_{0.85}Sn_{0.15} Thermoelectric Material

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Abstract. Half Heusler are promising thermoelectric material for the mid-temperature range application due to their good mechanical stability, and moderate zT . In present paper we have investigated the thermoelectric response of NbFeSb and NbFeSb_{0.85}Sn_{0.15} under inclusion of ball-milling step after arc-melting. Interestingly, inclusion of milling resulted in the formation of a metastable amorphous microstructure along with the crystalline peaks corresponding to NbFeSb and FeSb₃ phases. Intermediate milling has shown significant improvement in the power factor value of the material, showing a maximum power factor value of 150 $\mu\text{W}/\text{m}\cdot\text{K}^2$ and 308 $\mu\text{W}/\text{m}\cdot\text{K}^2$ for NbFeSb and NbFeSb_{0.85}Sn_{0.15}, respectively. The results are explained in term of Sb loss and formation of antisite defects.

INTRODUCTION

Half Heusler semiconductors with a valence electron count of 18, crystallises in a non-centro symmetric FCC space group $F\bar{4}m$, and shows promising thermoelectric material in mid-temperature range (≥ 500 C). These compounds crystallise in a cubic structure with chemical formula XYZ (where X, Y are transition metal and Y corresponds to Sb). [1,2] This structure comprises four interpenetrating FCC which offers abundant possibility to select dopants and formation of intrinsic defects like vacancies, interstitial etc. For designing thermoelectric devices both n-type and p-type materials are required comprising compatible thermoelectric properties in the desired temperature range. In this work we have investigated the NbFeSb based HH material which exhibits a band gap of ~ 0.54 eV with p-type conductivity and maximum reported $zT \sim 1.6$ at 1200 K. [3]

EXPERIMENTAL DETAILS

High-purity elements Nb, Fe, Sb, and Sn were weighed out in the stoichiometric ratios for NbFeSb (S1) and NbFeSb_{0.85}Sn_{0.15} (S2). Synthesis is carried out under approaches (i) Single step which includes arc-melting (AM) followed by RF sintering and (ii) Two step synthesis which includes arc-melting, followed by SPEX milling (BM) at 300 RPM for 24 hours. In arc melting high negative voltage is applied to a Tungsten tip, held at the end of movable copper rod (water cooled), which causes the breakdown of the Ar gas and the plasma is accelerated towards target material which is in contact with the positively charged copper base plate. Once the elements are melted individually, their chunks are retrieved, weighed and remelted in Ar multiple times to form the alloy. To avoid oxidation of material inside the chamber, a prior melting a Ti chunk is carried out, which react with any leftover O₂ inside. The retrieved powdered samples were compacted in RF furnace at 1000 C for 15 minutes in vacuum of 10^{-3} mbar, under fast heating and cooling rate of 125°C/min. The pellets were then cut and measured in Proto make XRD for phase identification, and in Linseis make LSR-1000 set-up for temperature dependent characterization in temperature range 30-600°C. The work function measurement of the samples is carried out using Kelvin probe measurement at room temperature, using Au reference tip.

RESULTS AND DISCUSSIONS

Figure 1(a) shows the XRD pattern of the powder samples, after arc-melting, followed by 24-hour milling. Identified Bragg positions clearly shows the formation of NbFeSb phase (space group F-43m) with lattice parameter $a=b=c$ 5.944 Å, in addition to secondary FeSb₃ phase (space group: Im-3) with lattice parameter $a=b=c$ 9.154 Å. Interestingly, along with crystalline peaks a broad hump between 30°- 40° has also been observed, showing the presence of amorphous phase. The coexistence of amorphous and crystalline regions in the milled powder can be thermodynamically explained by the Gibbs free energy relationship ($G = H - TS$). During milling, the enthalpy (H) increases due to defect accumulation, while the configurational entropy (S) rises with atomic disorder. As a result, the free energy difference between amorphous and crystalline phases diminishes, allowing the system to stabilize in a metastable amorphous state in regions where kinetic barriers partially suppress long-range atomic ordering. These changes in structure directly influence carrier transport and phonon scattering, thereby impacting the overall thermoelectric behavior of the material.

Figure 1(b-c) shows 2D plot of the work function (ϕ) measurement carried out on NbFeSb and NbFeSb_{0.85}Sn_{0.15} sintered samples. The overall homogenous value of ϕ in the measured region suggests the homogeneity on the surface of the material. NbFeSb shows the value of $\phi \sim 4.78$ eV, which on doping ~15 % Sn at Sb site increases to ~4.85 eV. This shows an increase in the band gap of material, which may be attributed to the band structure modification due to lattice distortion. The increased ϕ value suggests a downwards shift of the Fermi level towards the valence band, implying the dominance of holes as majority charge carrier.

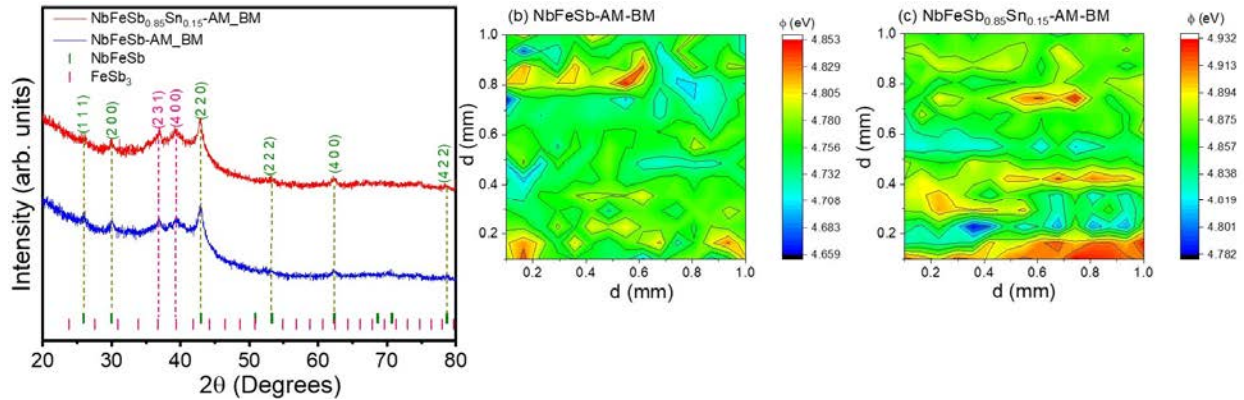


FIGURE 1. (a) XRD pattern of powder NbFeSb and NbFeSb_{0.85}Sn_{0.15}, (b), 2D plot for work function measurement

Figure 2(a-c) shows the temperature dependent transport properties of the samples. The undoped NbFeSb sample exhibits negative Seebeck coefficient (α) which increases with rise in temperature. NbFeSb follows 18-valence electron rule, and is theoretically predicted (DFT) to be semiconductor with an indirect band gap of 0.52 eV. DFT calculation of NbFeSb shows that the valence band in this system is primarily made up of Fe-3d and Sb-5p hybridization, possessing high density of states near the Fermi level, favoring hole conduction. However, the observed negative polarity in NbFeSb system shows the electron as majority charge carriers which occurs as a result of the non-equilibrium condition developed during arc-melting due to bigger sample size, leading to non-uniform temperature distribution across the sample. This non-equilibrium at high processing temperature leads to Sb losses generating donor like antisite defects along with the precipitation of new secondary metallic phases (Nb₃Sb, Nb₅Sb₄), shifting the Fermi level towards conduction band. Furthermore, Nb, being less electronegative, can act as a donor under certain conditions, especially in a Sb deficient environment, thereby favoring *n*-type conduction. The sample S1-AM-1000 exhibits very low α value varying between -5 μ V/K to -8 μ V/K showing the metallic behaviour of the sample. It is observed that doping 15 at % Sn at Sb site leads to *p*-type conduction in the material with slight improvement in the α value of $\sim 18 \mu$ V/K. The Sn has lesser electron than Sb, excess of Sn at Sb site can generate electron deficiency, leading to holes as dominating charge carrier. The samples synthesized under two-step shows improvement in the

Seebeck value in both the samples after sintering, which may be attributed to the minor enhancement in the carrier density in the material. The maximum Seebeck coefficient value of $\sim -38 \mu\text{V/K}$ at 600°C and $+42 \mu\text{V/K}$ at 175°C has been achieved in NbFeSb-AM-BM-1000 and $\text{NbFeSb}_{0.85}\text{Sn}_{0.15}\text{-AM-BM-1000}$, respectively. The samples exhibit metallic behavior in resistivity, fig. 2(b), which decreases further upon Sn doping due to increased hole concentration. However, samples synthesized via the two-step route (AM-BM) show increased resistivity, attributed to enhanced

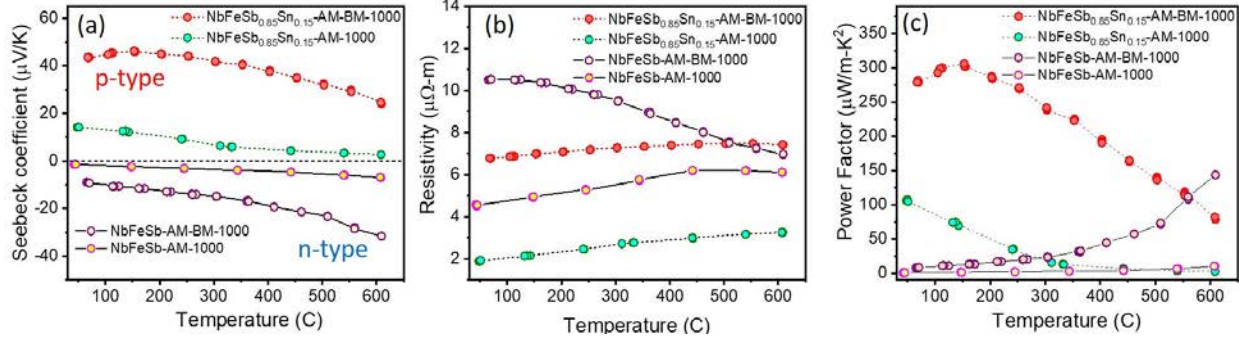


FIGURE 2. Temperature dependent (a) Seebeck coefficient, (b) resistivity, and (c) power factor of samples.

grain boundary scattering and defects hindering charge mobility. The power factor value of the samples has been calculated using relation: $PF = \alpha^2/\rho$, shown in figure. Both the NbFeSb samples shows low PF $\sim 5.35 \mu\text{W/K}^2$ near room temperature. A drastic increase in PF with temperature in $\text{nNbFeSb-AM-BM-1000}$ is observed, attaining the maximum value of $150 \mu\text{W/K}^2$ at 600°C . This increase in PF value is attributed to the improvement in the Seebeck coefficient value. In sample $\text{NbFeSb}_{0.85}\text{Sn}_{0.15}\text{-AM-1000}$ however the maximum PF value $100 \mu\text{W/K}^2$ near room temperature is observed, which reduces to $4.1 \mu\text{W/K}^2$ at 600°C . Among all the four samples the maximum PF value of $308.9 \mu\text{W/K}^2$ (at 175°C) is achieved in $\text{NbFeSb}_{0.85}\text{Sn}_{0.15}\text{-AM-BM-1000}$ sample, which is attributed to the higher electrical conductivity value along with the reasonably good Seebeck coefficient.

CONCLUSIONS

We could synthesize both n-type and p-type composition of NbFeSb based half Heusler material. Intermediate milling after arc-melting shows significant improvement in thermoelectric properties of the material. Doping 15 % Sn at Sb shows transmission in the charge polarity from n-type to p-type, which has been explained in terms of structural disorder and antisite defects formation. Using Sn doping we could achieve maximum power factor of $308 \mu\text{W/K}^2$, which is ~ 2 times higher than host NbFeSb material.

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Exploring the Electrochemical Performance of SrMoO₄

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Abstract. The scheelite structured SrMoO₄ is synthesized via co-precipitation method. Through the XRD analysis the crystal structure and lattice parameters have been analyzed. The electrochemical studies reveal that the sample, calcinated at 800 °C, coated on nickel foam shows high specific capacity of 344 C g⁻¹ at the specific current of 1 A g⁻¹. It holds the Coulombic efficiency of 99.5 % at the specific current of 10 A g⁻¹ after 10000 charge-discharge cycles, which exhibits the good stability of the electrode material.

INTRODUCTION

The energy crisis increases day by day as technology develops. In the present days, people adopted modern life, which requires energy to run their needs. The primary energy sources like fossil fuels, even though they provide better performance, they offer the environment in a bitter way like the emission of greenhouse gases, pollution, and global warming. Here the alternative comes in the form of renewable energy sources such as wind, solar, tidal, biomass, geothermal, and hydropower, which exhibit their yields through the unharmed way. But it has some limitations such as intermittency. There is a need to store energy to recover from the energy crisis. This requirement leads to the discoveries and inventions of energy storage devices[1-3]. Although common storage devices like batteries produce high energy density, it requires long charging time and low-specific power[4-5]. This inconvenience recruits the supercapacitors, which arise as a bridge between the batteries and capacitors with their high specific power and long cycle life. The supercapacitors are classified into three major types, based on their charge storage mechanism. They are (i) Electric Double Layer Capacitor (EDLC), which follows electrostatic interactions (non-faradaic), (ii) Pseudocapacitor which stores charges through faradaic redox reactions, and (iii) Hybrid supercapacitor which is the combination of both faradaic and non-faradaic redox reactions[6-10]. In this work, SrMoO₄, the scheelite structure (ABX₄) material has been synthesized and characterized for the supercapacitor application.

EXPERIMENTAL SECTION

Synthesis of SrMoO₄

The SrMoO₄ material was synthesized via two methods such as co-precipitation without calcination and co-precipitation followed by calcination. At first, Sr(NO₃)₂ and Na₂MoO₄·2H₂O each of 0.1 M dispersed in 10 mL of deionized water (DI), separately. These solutions were mixed after 10 min of stirring and the solution was named S1. The mixed S1 stirred continuously for 24 h. The precipitate was collected and washed with ethanol and DI followed by drying in vacuum for 12 h, named SM0. In the second method, followed by drying, S1 was calcinated at 800 °C for 12 h and the resultant was named as SM1. In both methods, the final product was collected and ground using agate mortar. The structural analysis was done using BRUKER USA D8 Advance, Davinci X-ray diffractometer with copper K α (λ =1.5406 Å) radiation and the electrochemical studies were analyzed using BioLogic SP-200 electrochemical workstation.

Electrochemical measurements

Through the electrochemical workstation, cyclic voltammetry (CV), and galvanostatic charge-discharge (GCD) studies were analyzed. These studies were done using three electrode configurations. At first the active material (AM), binder (PVDF – Polyvinylidene fluoride), and carbon black were well mixed with NMP (N-Methyl-2-pyrrolidone) in

the ratio of 8:1:1 to make the slurry. 1 mg of slurry was coated on precleaned nickel foam (NF) in 1 cm² area and it was dried at 60 °C in vacuum for 12 h. This AM@NF, platinum electrode, Ag/AgCl electrode, act as the working, counter, and reference electrode, respectively. 2 M KOH solution acts as the electrolyte. This combination makes the three-electrode configuration. From GCD analysis, the specific capacity is calculated using equation 1.

$$C_s = \frac{I\Delta t}{m} \quad (1)$$

here I , Δt , and m represent the constant current in Amperes, discharge time in second, and active material's mass in gram.

RESULTS AND DISCUSSION

Structural analysis

XRD patterns exhibit pure crystalline form with their clear observed peaks as shown in **Figure 19(a)**. The diffraction patterns of all three samples are well matched and confirmed with COD card number 96-400-1304. The peaks are observed at 2θ values of 27.9, 29.9, 33.4, 45.4, 47.9, 51.7, 56.2, 57.4, and 72.9, which correspond to their miller indices planes (112), (004), (200), (204), (220), (116), (312), (224), and (316), respectively. The XRD analysis exhibits that both samples have the tetragonal phase with lattice parameters of $a = b = 5.3954 \text{ \AA}$ and $c = 12.0264 \text{ \AA}$.

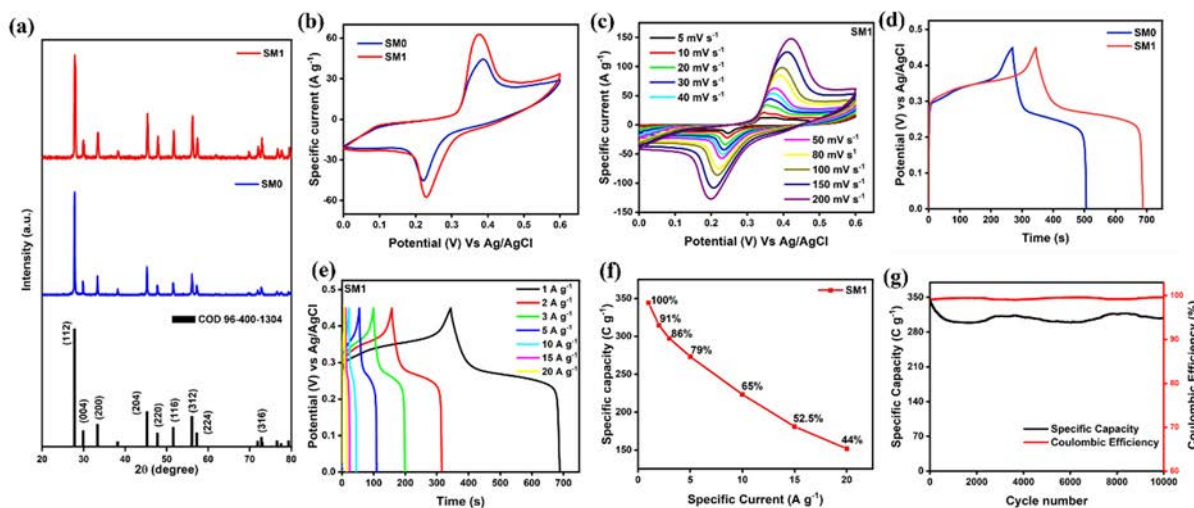


Figure 19:(a) XRD patterns of SrMoO₄ samples, (b) CV curves of SrMoO₄ at a scan rate of 50 mV s⁻¹, (c) CV curves of SM1 at different scan rates, (d) GCD curves of SrMoO₄ at specific current of 1 A g⁻¹, (e) GCD curves of SM1 at various specific currents, (f) specific capacity at different specific currents, (g) Specific capacity and Coulombic efficiency at specific current of 10 A g⁻¹ of a three electrode system.

Electrochemical analysis

CV measurement was conducted in the potential range of 0.0-0.6 V at the scan rate of 50 mV s⁻¹ for both samples, which is represented in **Figure 19(b)**. By observing the CV curves, it clearly states that the area of the SM1 sample at the scan rate of 50 mV s⁻¹ is higher, which leads to higher charge storage than the SM0 sample. In the CV curves, the presence of oxidation and reduction peaks exhibits the pseudocapacitive behavior of the sample. The CV studies were done for SM1 sample at various scan rates of 5-200 mV s⁻¹ and plotted as shown in **Figure 19(c)**. The area of the enclosed curve increases as scan rate increases, which illustrates the shift in the oxidation and reduction peaks toward higher and lower potential, respectively. The shift in the peak position is mainly due to the constraint in

intercalation of electrolytic ions through the porous sites of the electrode material. The process of redox reaction in the interface between the electrolyte and the surface of electrode is mainly activated by the Mo atoms by leaving an electron during the oxidation process and gaining an electron during the reduction process, which is shown in equation 2.



Similarly, GCD studies were done at the specific current of 1 A g⁻¹ within the range of 0.0-0.45 V, demonstrated in **Figure 19(d)**. Through the GCD curves, the specific capacity is determined as 250 and 344 C g⁻¹ for SM0 and SM1 sample, respectively. The electrode contains SM1 sample further scanned at various specific current of 1, 2, 3, 5, 10, 15, and 20 A g⁻¹, that exhibits the specific capacity values of 344, 315, 291, 273, 223, 181, and 152 C g⁻¹, respectively, which is illustrated in **Figure 19(e)**. At low specific currents, the time interval required for electrolytic ions to intercalate or deintercalate is higher. In Fig.1(e), specific capacity decreased to 46 % of its initial value when the specific current increased from 1 A g⁻¹ to 20 A g⁻¹, which is clearly portrayed in **Figure 19(f)**. The Coulombic efficiency has been determined by charging (t_c) and discharging time (t_D), which is represented in equation 3

$$\eta = \frac{t_D}{t_c} \times 100 \% \quad (3)$$

Figure 19(g) represents the Coulombic efficiency and stability of the electrode material, which is explored at 10 A g⁻¹ specific current. The SM1 material exhibits capacity retention of 44 % of its initial value. Also, it shows Coulombic efficiency of 99.5 % even after 10000 charge-discharge cycles.

CONCLUSION

The SrMoO₄ is synthesized using co-precipitation method with 800 °C calcination and without calcination for supercapacitor application. Through the XRD analysis the crystal structure and lattice parameters are confirmed. The electrochemical studies reveal that SM1 sample exhibits a higher specific capacity value of 344 C g⁻¹ at the specific current of 1 A g⁻¹. It shows capacity retention of 44 % and gives the Coulombic efficiency of 99.5 % at the specific current of 10 A g⁻¹ after 10000 charge-discharge cycles. From these analyses, it is clearly shown that the SrMoO₄ material, prepared at 800 °C, is a good choice for supercapacitor application.

ACKNOWLEDGMENTS

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Theoretical Insight Into The Excitonic Effects In The PtSSe Janus Layer

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Abstract. Two-dimensional transition metal dichalcogenide Janus layers exhibit strong light-matter interactions and pronounced dielectric responses. Here, we present the structural, electronic, and optical properties of the PtSSe Janus layer using first-principles calculations based on Density Functional Theory (DFT). Many-body effects are incorporated through the GW approximation, and excitonic effects are analysed by solving the Bethe-Salpeter Equation (BSE). A systematic analysis is carried out to optimize the exciton binding energy by tuning the parameters used GW-BSE calculations. The obtained dielectric spectra reveal the presence of bound excitons in PtSSe Janus layer, and the bright and dark excitons are distinguished based on their oscillator strengths. Fat band analysis provides insight into the spatial distribution of excitons which is found to be along the reciprocal lattice direction Γ -K-M.

INTRODUCTION

Optically active two-dimensional transition metal dichalcogenide monolayers have recently attracted significant interest in the research areas such as design of photodetectors, sensors, light emitting diodes, optical modulators and catalytic applications. The most explored structures in this family are 1T and 2H structures with structural formula MX_2 , where M is post transition metal atom and X is the chalcogenide. Some of the as mentioned structures are MoS₂, WS₂, PtS₂, and PtSe₂. The strong intra layer covalent bonds and weak inter layer van der Waals interactions enable them to peel as monolayers from the bulk structure. As a layer with ultra-low thickness, they possess attractive characteristics such as enhanced Coulomb interaction, quantum confinement effect, strong light-matter interaction.

Wide range of optical experimental studies are already performed in the few layer TMDs. The experimental study conducted by Lin et al. show that the TMD layers with MX_2 structure shows optical properties in the range 1-3.5 eV. The electron-hole interaction experimentally first reports in MoS₂ monolayer. This finding leads to further excitonic studies in the other TMD structures also. Further, the arrival of modified TMDs which are called TMD Janus layers got much research due to its broken symmetry in the out of plane direction. Apart from the symmetric structures, they could exhibit new features in the absorption spectra due to the asymmetric charge distribution in the interlayer spacing. In 2023, P. Jamdagni et al. reported the presence of bound excitonic effects in the PtSSe monolayer. The excitonic binding energy (E_{xc}) of these layers are reported to be less than that of its parent structures PtS₂ and PtSe₂. However, the excitonic studies are found to be incomplete. Herein, we explore the excitonic properties in the PtSSe Janus layer using GW-BSE mechanism in detail.

COMPUTATIONAL METHODOLOGY

The electronic structure calculations are performed using the Vienna ab initio simulation package (VASP). The self-iteration scheme is carried out with the blocked Davidson algorithm. The exchange-correlation functional used for the

calculation was Perdew-Burke-Ernzerhof (PBE) within generalised gradient approximation (GGA). For the relaxation of monolayers and heterostructure, kinetic energy cut off for plane-wave basis set selected as 650 eV. The energy and force convergence criteria for the ionic relaxation are chosen to be 1×10^{-6} eV and $0.001 \text{ eV/\AA}$ respectively. The k points $16 \times 16 \times 1$ are selected using the monkhorst- pack scheme for accurate calculation. The vdw interaction between the monolayers was represented using DFT-D2 method of Gremme. The GW- BSE calculations are performed by varying the kpoints from $8 \times 8 \times 1$ to $14 \times 14 \times 14$. Also we varied frequency grid points from 15 to 50. A set of 512 virtual bands are used for GW calculations. In GW-BSE calculation, 8 occupied and 16 unoccupied bands are considered.

RESULT AND DISCUSSION

Structural properties

Initially, we have designed PtSSe Janus layers from the already constructed PtS_2 TMD monolayer. The geometrically relaxed structure of PtSSe including the charge dispersion is presented in Figure 1. The obtained PtSSe structure posses space group P-3m1 point group C3v. Here the Pt atom sandwiched between sulfur atoms and selenium atoms. The lattice parameters of the PtSSe is obtained to be 3.63 Å, which is matching with the previous literature. The bond length and bond angle of the PtSSe are calculated to be 2.43(Pt-S), 2.50(Pt-Se) and 100.3° (S-Pt-Se) respectively[1][2]. To obtain the charge distribution in the designed Janus layer, Bader charge calculation was performed. The Bader charge analysis shows that the charge is depleted from the Pt atom and distributed around the sulfur and selenium atom. The charge accumulated near the sulfur and selenium atom are found to be 0.302e and 0.066e respectively. This difference in charge accumulation, which is noted to be 0.236e cause formation of electric field in the out of plane direction of the Janus layer.

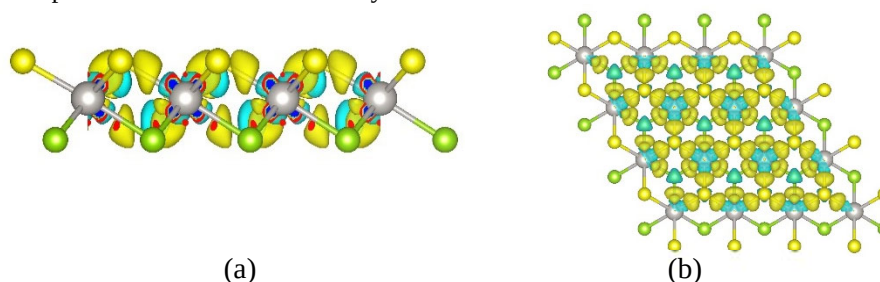


FIGURE 1: The side (a) and top (b) view of the differential charge density plot of PtSSe Janus layer. The yellow and blue coloured region represent charge accumulated and charge depleted.

Optical properties

To study the optical properties accurately we choose to perform many body perturbation theory based GW-BSE calculations. The GW calculations incorporate presence of quasiparticle in the dielectric spectra, whereas GW-BSE calculations incorporate excitonic effects. The Table 1 shows variation of quasiparticle gap, direct bandgap and the E_{xc} with respect to *k*points and *NOMEGA*. It is found that the kpoints are $12 \times 12 \times 1$ and *NOMEGA* 35 is required to optimise the E_{xc} in the PtSSe Janus layer.

TABLE 1 Calculated optical gap, GW direct bandgaps, and excitonic binding energies at various kpoints and *NOMEGA*

kpoints	Optical gap	GW direct bandgap	Excitonic binding energy
8x8x1	1.91	2.72	0.81
10x10x1	1.93	2.76	0.83
12x12x1	1.95	2.66	0.71
14x14x1	1.94	2.66	0.72
NOMEGA	Optical gap	GW direct bandgap	Excitonic binding energy
15	2.24	2.99	0.85

25	1.94	2.78	0.84
35	1.95	2.79	0.84
50	1.93	2.76	0.83

Further the dielectric spectra was calculated using these optimized parameters ($12 \times 12 \times 1$ k-points and *NOMEGA* of 35). The obtained spectra with and without including excitonic effects are presented in the Fig.2 (a). The GW-BSE spectra shows intense excitonic peaks in the visible light region. The E_{xc} in the Janus layer was calculated as the difference between optical gap and the GW-direct bandgap. The extracted exciton binding energy of the Janus layer is 0.71 eV. Further, the spatial distribution of the excitons was analysed from the fat band analysis. The figure shows excitonic coupling strength is large in the K-Gamma region. Later, to study the presence of excitonic effects in the real space, excitonic wave function was calculated for the first bright exciton. We have noticed that the excitons are more spatially distributed in between Pt-S layer compared to Pt-Se layer.

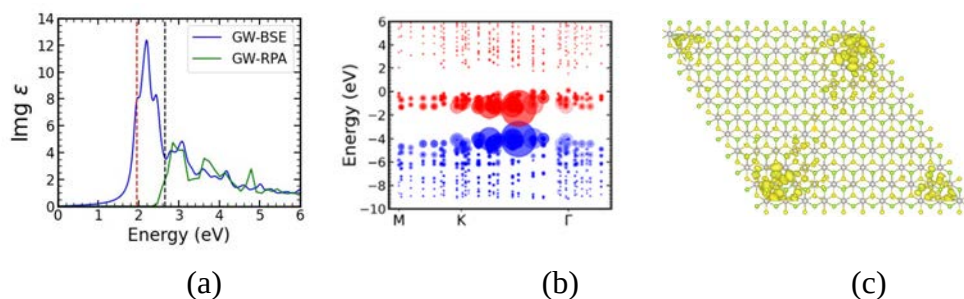


FIGURE 2: The imaginary part of the dielectric function calculated using GW-BSE and GW-RPA functionals (a), fatband analysis (b), and excitonic wavefunction distribution in real-space (c). The red and blue circles in (b) represent electron and hole respectively. The electron-hole coupling is represented by the radius of the circle.

CONCLUSION

In summary, we designed and explored the optoelectronic properties in the PtS₂ Janus layer using density functional theory calculation. The GW method predicts the direct bandgap of the PtS₂ Janus layer to be 2.66 eV. Further, we found that the presence of intense excitonic effects in the PtS₂ Janus layer with E_{xc} 0.71 eV. The fatband analysis shows the excitons are localized in between K to Γ region in the Brillouin zone. We also identified the localization of the excitonic wave function in the real space.

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Enhanced Specific Capacitance in Ni-doped Mn_2O_3 Nanoparticles

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Abstract. In the present study, we report the effects of Ni doping on the structural and electrochemical properties of Mn_2O_3 nanoparticles synthesized by sol-gel method. X-ray diffraction pattern demonstrates the cubic structure with space group of Ia-3. The cyclic voltammetry (CV) results confirm that the $\text{Mn}_{1.90}\text{Ni}_{0.10}\text{O}_3$ electrode shows the maximum specific capacitance 454 F/g, in 2M KOH at 10 mV/s scan rate. This research demonstrates that the incorporation of Ni in Mn_2O_3 improves the conductivity of the nanomaterial and enhances the pseudo-capacitance.

INTRODUCTION

The increasing demand for durable electronic devices, including smartphones, electric vehicles, smart wearable watches, and digital cameras, has grown in recent years, which typically require an extended power backup source with higher power density and energy density. To meet this need, substantial research has focused on developing innovative energy storage systems. Among various available energy storage systems, such as traditional batteries and fuel cells, the supercapacitors have attracted due to their high power density, rapid charge discharge rate, robust operational reliability, and longer cycling stability [1]. Transition metal oxides have emerged as a promising electrode material for pseudocapacitor due to their numerous properties, such as low production cost, variable oxidation state, widespread availability and environmental friendly nature. Until now, various transition metal oxides, like NiO, MnO_2 , Fe_2O_3 , etc. and mixed transition metal oxides such as MnCo_2O_4 , CoFe_2O_4 , NiCo_2O_4 etc, have been extensively studied as pseudocapacitor electrodes [2–7]. Among them, Mn_2O_3 offers several advantageous properties, including flexible structural characteristics, non-toxicity and excellent chemical and physical stability in different electrolytes. Here, we have studied the structural and electrochemical properties of $\text{Mn}_{2-x}\text{Ni}_x\text{O}_3$ ($x = 0$ and 0.10) nanoparticles prepared by sol sol-gel method and calcined at 600 °C. The electrochemical properties are examined by using the cyclic voltammetry (CV) technique.

EXPERIMENTAL DETAILS

Manganese nitrate hexahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, AlfaAesar), and Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%, HIMEDIA) were mixed in 60 ml of doubly-ionized water under constant stirring and heated at 90 °C for 2 hours followed by addition of citric acid as the chelating agent and ethylene glycol to link the metal ions. Further, the mixture was stirred continuously at 90 °C for an additional 6 hours. The resultant xerogel was kept in a vacuum oven at 100 °C for 12 hours and calcined at 600 °C for 10 hours to obtain the final product.

Crystallinity and phase purity of the prepared samples were observed using powder X-ray diffraction (Rigaku Miniflex 600) in the range of 20 to 90° diffraction angle with Cu-K α radiation ($\lambda = 1.54\text{\AA}$). Microstructural analysis of synthesized samples was explored via scanning electron microscopy (FESEM; Nova Nano SEM 450). Further, electrochemical properties were investigated with a three-electrode setup consisting of an electrochemical workstation (Corrtest CS 310). To fabricate the working electrode, the synthesized active material, activated carbon and polyvinylidene fluoride (PVDF) were used in a 70:20:10 mass ratio and mixed with N-methyl pyrrolidone (NMP) solvent. Further, the prepared ink was drop cast onto a $1 \times 1 \text{ cm}^2$ nickel foam (NF) substrate and kept in an oven at 60 °C for 24 h. The active material loading was approximately 2 mg. To evaluate the electrochemical performance, CV experiments were conducted in a 2M KOH electrolyte solution using three electrode setup. In this configuration, an Ag/AgCl acted as the reference electrode, a platinum wire functioned as the counter electrode and nickel foam coated

with the active material was employed as the working electrode. The specific capacitance was evaluated from CV curves by using the Equation,

$$C_s(\text{F/g}) = \frac{\int I(V) dV}{2mk\Delta V} \quad (1)$$

where, C_s stands for specific capacitance, k stands for scan rate, m stands for mass of the active material (g), I and ΔV are the current and voltage, respectively.

RESULTS AND DISCUSSION

Figure 1 (a) depicts the XRD patterns for parent Mn_2O_3 and $\text{Mn}_{1.90}\text{Ni}_{0.10}\text{O}_3$. The observed diffraction peaks are well matched with the cubic phase (JCPDS card no. 044–1442). The absence of any impurity phase confirms the single phase of cubic crystal structure and the substitution of Ni at the Mn site in Mn_2O_3 . The shift in the diffraction peak at approximately 33° to a higher angle, suggesting a lattice contraction compared to that of the parent Mn_2O_3 , which is attributed to the incorporation of the smaller ionic radii of Ni as compared to the Mn ion. Fig. 1 (b) and (c) represent the FE-SEM micrographs of $x = 0.0$ and 0.10 , respectively. The micrographs reveal that the particles are homogeneously distributed with irregular shapes of the polygons with a certain degree of agglomeration, which arises due to the synthesis conditions.

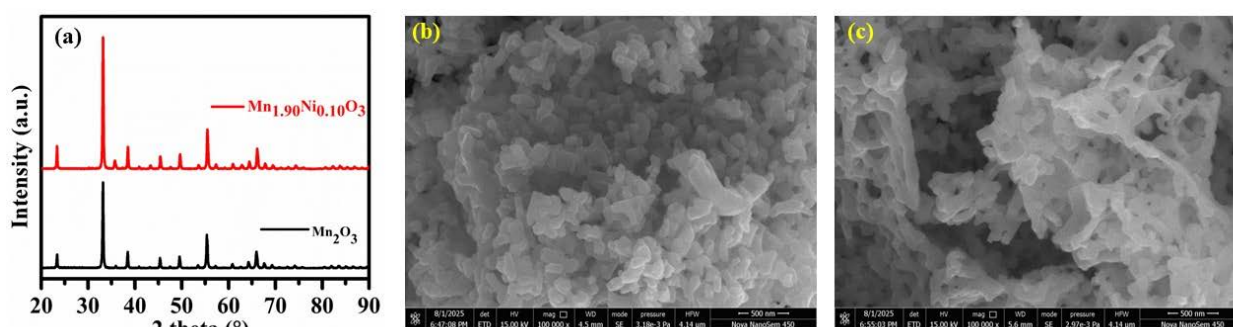


FIGURE 1. Represents (a) the XRD pattern in the 2θ range $20\text{--}90^\circ$ and HRSEM images of (b) Mn_2O_3 , (c) $\text{Mn}_{1.90}\text{Ni}_{0.10}\text{O}_3$.

Further, to explore energy storage properties of $\text{Mn}_{2-x}\text{Ni}_x\text{O}_3$ ($x = 0.0$ and 0.10), CV measurements are performed in the potential range of 0 V to 0.5 V with respect to Ag /AgCl at different scan rates from 10 to 90 mV/s in a three-electrode cell, as shown in Fig. 2 (a,b). The observation of a pair of Faradaic redox peaks in the plot for both samples signified a battery-type electrode behaviour. At the same mass loading, the area under the CV curve is found to be maximum for $x = 0.10$ at 10 mV/s compared to Mn_2O_3 , signifying the higher charge storage capacity of the electrode material. The specific capacitance calculated from CV curves at 10 mV/s using Equation (1) is found to be 287 F/g for $x = 0$ and 454 F/g for $x = 0.10$, as shown in Fig. 2 (c). The improvement in the specific capacitance is ascribed to the incorporation of Ni ions, which induce more redox sites in Mn_2O_3 . This confirms the positive effect of the incorporation of Ni on the pseudocapacitive performance of the Mn_2O_3 electrode.

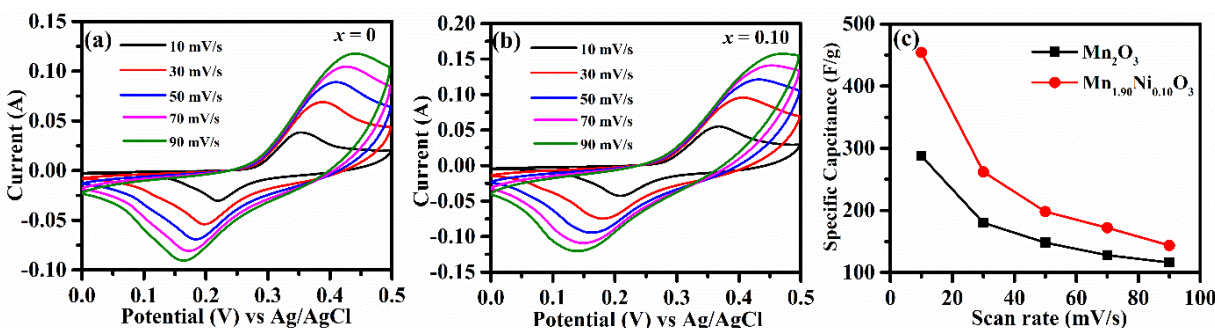


FIGURE 2. Cyclic voltammetry curve of (a) $x = 0$, (b) $x = 0.10$ and (c) Calculated specific capacitance of Mn_2O_3 and $\text{Mn}_{1.90}\text{Ni}_{0.10}\text{O}_3$

CONCLUSIONS

In summary, $\text{Mn}_{2-x}\text{Ni}_x\text{O}_3$ ($x = 0$ and 0.10) were successfully synthesized via sol-gel method. Structural analysis confirmed that the doping of Ni didn't affect the crystal structure but shifted the peak position slightly to higher diffraction angle, suggesting the lattice contraction. Electrochemical measurements confirmed that Ni doping improved the performance of Mn_2O_3 by enhancing the conductivity, the electrochemical activity as well as the electrode electrolyte interface area. The highest specific capacitance of 454 F/g was observed for $\text{Mn}_{1.90}\text{Ni}_{0.10}\text{O}_3$, which was found to be higher compared to Mn_2O_3 .

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Reinforcement of Magnetic Filler in Polyaniline for X-band EMI Shields

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Abstract: Polyaniline nanocomposites have gained so much of attention due to conducting behavior of polyaniline for electromagnetic interference shielding studies. The present work aims at introducing LSMO (Lanthanum Strontium Manganite) in polymer matrix during *in-situ* oxidative polymerization technique. The synthesis of hybrid nanocomposite has been done in the ratio of 1:0.5, and 1:1 of polyaniline and LSMO named as P1L0.5, and P1L1 respectively. The conductivity of polyaniline increases with increasing LSMO content due to its colossal magneto resistive behavior. The highest value of conductivity has been achieved by P1L1 = 0.2 S/cm. The electromagnetic shielding study has been performed using vector network analyzer. The nanocomposite achieving highest value is P1L1 having SE ~28.5 dB. Shielding effectiveness is dominated by absorption with value ~20.5 dB while reflection appears to be ~8 dB. The achieved value of shielding effectiveness makes this material to be used as shield for communication purposes.

INTRODUCTION

Electromagnetic interference is a major issue due to ongoing growth in the field of science and technology. In order to resolve this issue, shielding is necessary. Shielding of any material is calculated in terms of shielding effectiveness. The ratio of incident signal to the transmitted signal is termed as shielding effectiveness[1]. Total shielding effectiveness of any material is calculated by adding the shielding effectiveness due to absorption, reflection and transmission. The material turns out to be a good shield if it has more value of absorption, than reflection and transmission. The researchers suggested that shielding material must have high conductivity and also contributes towards effective dielectric and magnetic losses. Metals were the first choice towards this issue but its corrosive behaviour, high density, etc. comes out as its drawback. In order to replace metals, polymers with fillers were introduced. Polymers provides flexibility and using magnetic and dielectric filler will provide necessary losses contributing towards higher shielding effectiveness. Conducting polymer gained more attention as they provide conductive network to filler and contributes towards conduction losses. Polyaniline is conducting polymer known for its stability. It exists in various states such as leucomeraldine, pernigraniline, and emeraldine base. Along with polyaniline, fillers will enhance the overall shielding properties of materials[2]. $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) is a ferromagnetic insulator having perovskite structure. LSMO has good value of saturation magnetization (58 emu/g). The current study focuses on the shielding effectiveness of LSMO based polyaniline nanocomposites.

SYNTHESIS AND CHARACTERIZATION

The polymer nanocomposites were synthesized via *in-situ* chemical oxidative polymerization technique. The precursors used for synthesis process were aniline monomer, iso-propyl alcohol (IPA) purchased from Loba Chemie, and 4-dodecylbenzenesulfonic acid (DBSA), ammonium persulfate (APS) from Sigma Aldrich and LSMO was synthesized using sol-gel route. In de-ionized water, 1M of DBSA was dissolved followed by addition of aniline. DBSA acts as surfactant and dopant in the reaction process. Upon dissolution, LSMO was incorporated to the solution. The homogenization of solution was performed at 3°C using chiller. After complete mixing, 1M of APS was added to the solution which will act as oxidant to start the actual polymerization[3]. The homogenization continued for 24 hours and precipitates formed. The precipitates were washed using isopropyl alcohol and de-ionized water. The as prepared sample was freeze dried. The samples were prepared in the ratio of 1:0.5 and 1:1 for aniline: LSMO named as P1L0.5 and P1L1, respectively.

To confirm the formation of nanocomposites X-ray diffraction pattern of nanocomposites were studied. The magnetic behaviour of sample was studied using vibrating sample magnetometer. The current voltage characteristics was evaluated using Source measuring unit. Shielding effectiveness was calculated using S-parameters obtained from vector network analyzer.

RESULTS AND DISCUSSION

XRD data of LSMO based polyaniline nanocomposites has been shown in **Figure 1(a)**. The characteristics peaks of LSMO appears at $2\theta = 23^\circ, 32^\circ, 40^\circ, 47^\circ, 52^\circ, 58^\circ, 68^\circ,$ and 78° which corresponds to (012), (110), (202), (024), (122), (214), (208), and (128) diffraction planes, respectively[4]. The data confirms the formation of polyaniline nanocomposites. LSMO possess rhombohedral structure and the figure confirms the inclusion of LSMO in polyaniline matrix

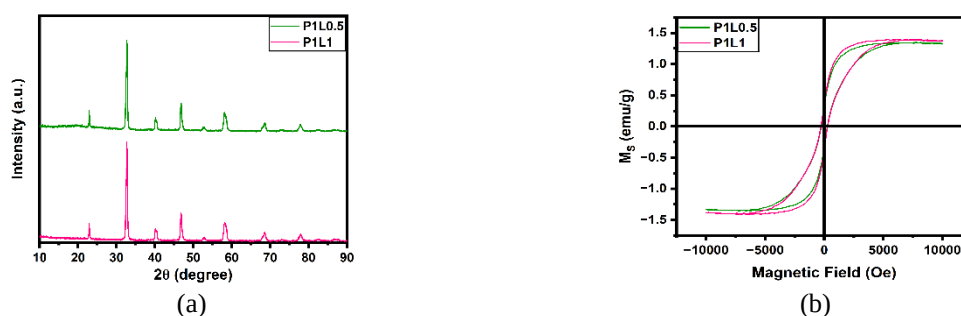


FIGURE 1 (a) XRD spectra, and (b) magnetic behaviour of P1L0.5 and P1L1 nanocomposites.

The magnetic behavior of nanocomposites has been visualized in **Figure 1(b)**. The formation of hysteresis loop indicates towards ferromagnetic behavior of nanocomposites. The higher value of saturation magnetization (M_s) is 1.4 emu/g achieved by P1L1 as the presence of magnetic filler is higher in P1L1. The value of M_s achieved by P1L0.5 is 1.3 emu/g. The value of M_s reduced due to presence of non-magnetic polyaniline. The magnetic properties in LSMO arises due to double ion exchange mechanism between Mn^{3+} and Mn^{4+} ions[5].

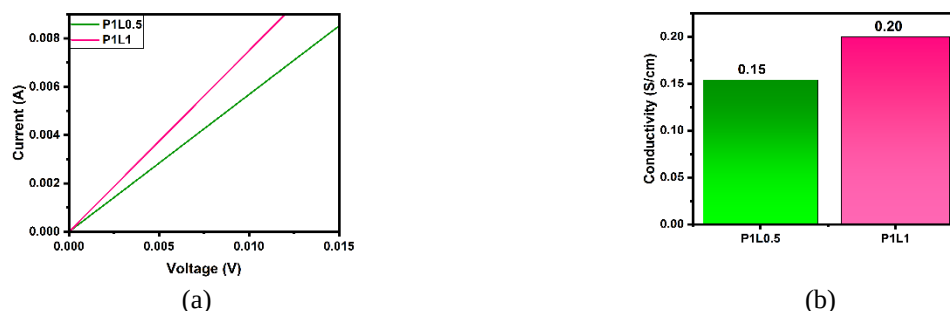


FIGURE 2 (a) I-V characteristics, and (b) conductivity of P1L0.5 and P1L1 nanocomposites.

Current voltage characteristics shown in **Figure 2(a)** appears to be linear showing ohmic behaviour of nanocomposite and then its conductivity has been calculated. The value of conductivity comes out to be higher i.e., 0.2 S/cm for P1L1 nanocomposite as shown in **Figure 2(b)**. The conductivity is higher with increasing LSMO content due to presence of Mn^{3+} and Mn^{4+} ions which are responsible for magnetic properties as well. Due to the inclusion of LSMO in polymer matrix, the overall conductivity improved although LSMO itself is an insulator.

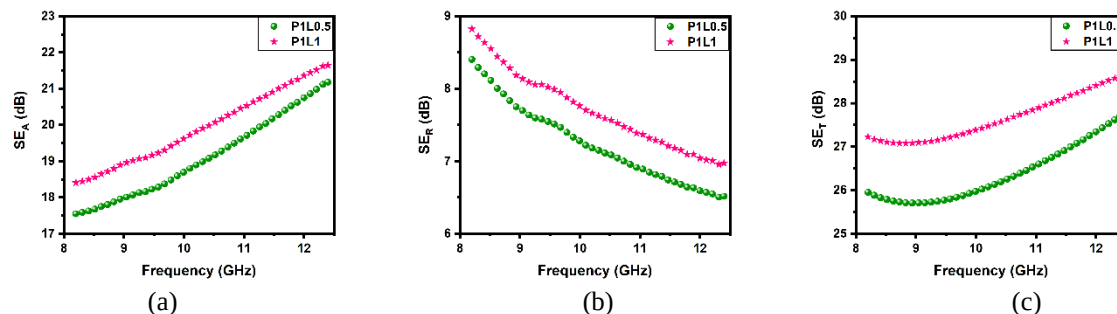


FIGURE 3 Shielding effectiveness due to (a) absorption, (b) reflection, and (c) total shielding effectiveness of P1L0.5 and P1L1 nanocomposites.

The electromagnetic interference shielding effectiveness of nanocomposites has been studied in X-band regime (8-12GHz) to find. The highest achieved value of shielding effectiveness is ~28.5 dB by P1L1 nanocomposite shown in **Figure 3(c)**. The shielding effectiveness due to absorption and reflection is ~20.5 dB and ~8 dB for P1L1 and ~19 dB and ~7dB for P1L0.5 respectively shown in **Figure 3(a)** and **(b)**. The higher loading of LSMO in polyaniline gives higher value of shielding effectiveness.

CONCLUSION

LSMO based polyaniline nanocomposites has been prepared via *in-situ* chemical oxidative polymerization technique. The as synthesized polymer nanocomposite shows ferromagnetic properties where highest value is 1.4 emu/g for P1L1. The conductivity of P1L1 nanocomposite is 0.20 S/cm is highest between both nanocomposites. The shielding effectiveness of nanocomposites has been studied and found that the higher LSMO content in polyaniline matrix gives higher value of shielding effectiveness. P1L1 shows higher shielding effectiveness of ~28.5 dB, which makes it suitable to be used for communication purposes, defense and stealth technology.

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Structural, Electronic and Photocatalytic Properties of WS₂/bg-C₃N₄ Hetero-Structure: A DFT study

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Abstract. This work studies the suitability of the WS₂/bg-C₃N₄ heterostructure as an efficient photocatalyst for hydrogen evolution. Utilizing DFT methods, its structural and electronic properties were studied. The results reveal a notable changes in the electronic structure, including reduced band gap and enhanced charge separation arising from heterojunction formation. These factors ultimately enhance the photocatalytic efficiency by promoting more efficient electron transfer across the interface. Overall, the results highlight WS₂/bg-C₃N₄ heterostructure as a strong candidate for sustainable hydrogen evolution in acidic medium via photocatalytic water splitting.

INTRODUCTION

Photocatalysis has emerged as a promising approach to harness clean solar energy [1]. However, traditional photocatalysts often limited by poor light absorption and rapid charge recombination [2]. Two-dimensional materials such as tungsten disulphide (WS₂) and buckled graphitic carbon nitride (bg-C₃N₄) have attracted considerable attention, but their standalone performance is constrained by fast electron-hole recombination and inadequate redox capability [3,4]. Graphitic carbon nitride (g-C₃N₄) is a photocatalyst driven by visible light. However, its efficiency is limited by low light absorption [5]. This study examines the photocatalytic potential of a heterostructure of WS₂/bg-C₃N₄ composite for hydrogen production. First-principles calculations shows that the formation of a heterostructure between these materials can enhance photocatalytic efficiency by tuning their electronic structures and facilitating improved charge separation.

COMPUTATIONAL DETAILS

Troullier-Martin relativistic pseudopotentials were used for DFT calculations within SIESTA [6] along with GGAPBESol exchange-correlation functional and VDW-LMKLL functional for van der Waals interactions. Double Zeta Polarization (DZP)s basis sets and a 10x10x1 Monkhorst-Pack k-point mesh was used to achieve accurate Brillouin zone integration. To achieve convergence, a mesh cutoff of 300 Ry was taken with the confinement energy of 20 meV. A 20 Å vacuum was introduced to reduce periodic image interactions, with all structures relaxed to a force convergence of 0.01 eV/Å.

RESULT AND DISCUSSION

A WS₂/bg-C₃N₄ heterostructure was created using 2x2 tungsten disulfide monolayer (WS₂ML) and a 1x1 bg-C₃N₄ unit cell, with a 3.07 Å interlayer distance. We began by examining bg-C₃N₄ and WS₂ML individually for the evaluation of their lattice constants and band gaps. The relaxed structures of the studied systems are shown in FIGURE 1, and the optimized structural parameters of the WS₂/bg-C₃N₄ heterostructure are listed in TABLE 1.

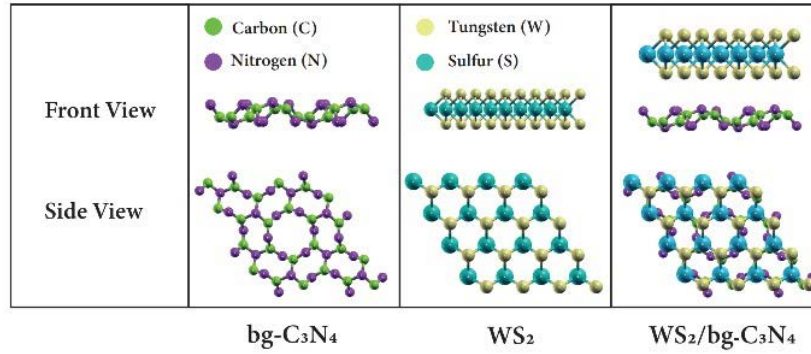


FIGURE 1: Electronic structure of bg-C₃N₄, WS₂ML and WS₂/bg-C₃N₄ heterostructure.

TABLE 1. Lattice Constant (a), Interlayer distance (d), binding energy (Eb) and energy band gap (Eg) for GGA-PBESol and VDW-LMKLL functional of the studied systems.

Materials	a (Å)	d (Å)	E _b (eV)	E _g (eV)	E _g (VDW) (eV)	E _f (eV)
bg-C ₃ N ₄	6.141 (7.080 (LDA)) [8]	-	-5.9	2.37	-	-
WS ₂ ML	3.178	-	-6.15	1.93 (2.1) [9]	-	-
WS ₂ /bg-C ₃ N ₄	6.255	3.078	-6.01	1.37	1.40	-0.15

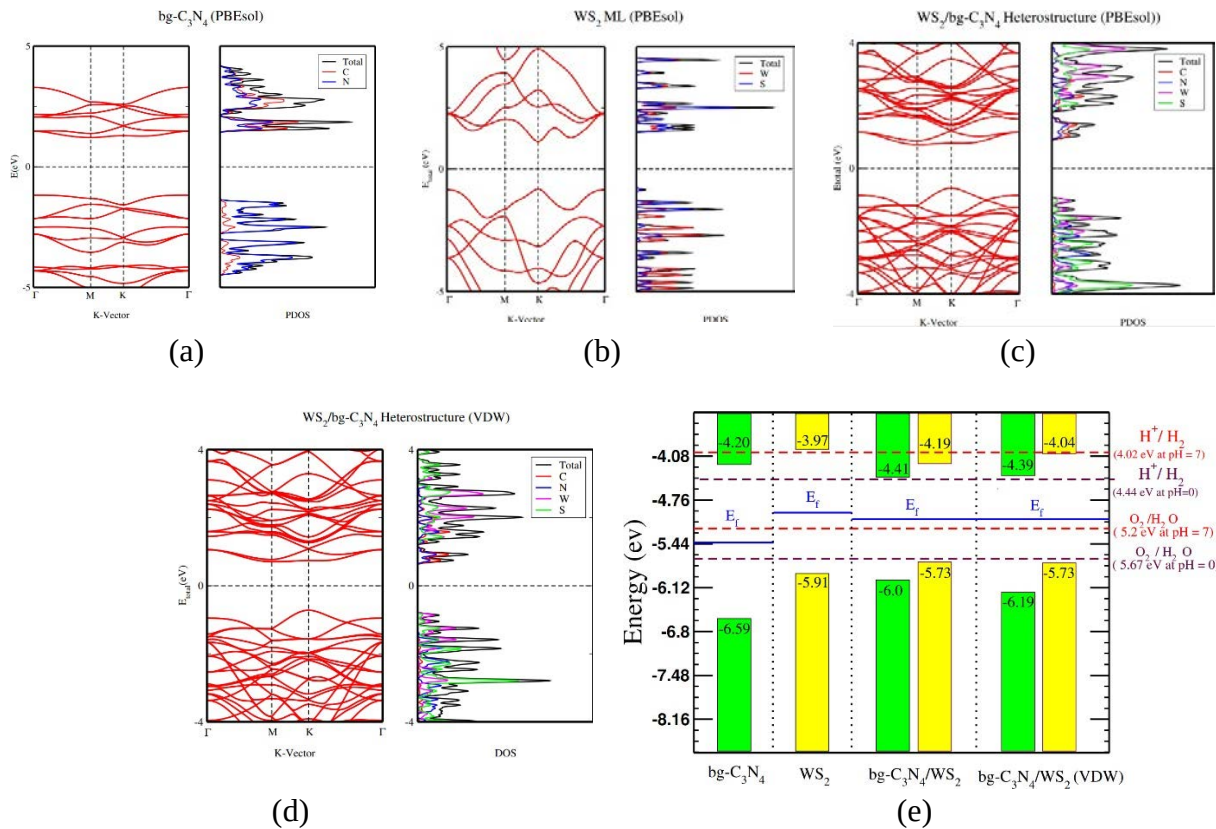


FIGURE 2: Electronic band and PDOS of (a) bg-C₃N₄, (b) WS₂ML, (c) WS₂/bg-C₃N₄ heterostructure (PBESol), (d) WS₂/bg-C₃N₄ heterostructure (VDW), and (e) band alignment of all the studied systems

The calculated lattice constants are 6.141 Å, 3.178 Å and 6.255 for bg-C3N4, WS2ML and WS2/bgC3N4 heterostructure respectively. Binding energy and formation energy of WS2/bg-C3N4 heterostructure was calculated. Binding energies for each system were calculated by using the appropriate formula [7]:

$$E_b = \frac{E_{hetero} - (nE_a + mE_b \dots)}{n + m + \dots} \quad (1)$$

The calculated binding energies are -5.9 eV for bg-C3N4, and -6.15 eV for WS2ML and -6.01 eV for WS2/bgC3N4 heterostructure. Calculated formation energy for WS2/bg-C3N4 heterostructure is -0.15 eV (TABLE 1) which is obtained by using formula [10].

$$E_f = E_{total} - (E_a + E_b) \quad (2)$$

The energy band structure of the studied systems (FIGURE 2 (a-d)) were calculated using two different functionals. The GGA-PBEsol functional yielded band gaps of 2.37 eV for bg-C3N4, 1.93 eV for WS2, and 1.37 eV for the WS2/bg-C3N4 heterostructure. The VDW-LMKLL functional was used to determine the band gap of the WS2/bg-C3N4 heterostructure, which was 1.40 eV. These values are tabulated in TABLE 1.

The total/projected density of states (T/PDOS) of the studied systems are also shown in FIGURE 2 (a-d) and it revealed that the conduction band minima (CBM) and valence band maxima (VBM) of both WS2 and bg-C3N4 in the heterostructure exhibited a significant downward shift. These shifts led to a considerable reduction in the band gap from the individual layer value of 2.364 eV (for bg-C3N4) to 1.372 eV in the heterostructure. However, by using the HSE06 hybrid functional, a more accurate electronic band gap can be predicted, which is expected to be higher than the currently calculated band gap. The heterostructure shows type II (staggered) band alignment which is beneficial in charge separation, improves redox efficiency and absorbs light broadly.

CONCLUSION AND APPLICATIONS

Our results suggest that WS2/bg-C3N4 heterostructure is a promising candidate for photocatalytic applications due to its reduced band gap which results in a type II (staggered) band alignment which enables enhanced charge separation and broader light absorption. These features make it a strong candidate for photocatalytic water splitting in acidic environments. However, with further optimization of its electronic properties, water splitting in neutral environments may also be achievable. This work provides a theoretical base for designing WS₂/bg-C₃N₄ heterostructures as efficient photocatalysts and encourages additional experimental studies to confirm these predictions.

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Study of Optical and Electrochemical Properties of $\text{Mg}_{0.7}\text{Co}_{0.3}\text{Fe}_2\text{O}_4$ Nanoparticles

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Abstract. $\text{Mg}_{0.7}\text{Co}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles were synthesized using the coprecipitation method and were annealed at 900 °C. X-ray Diffraction (XRD) studies confirmed the formation of a single-phase cubic spinel ferrite structure with a crystallite size of 21.7 nm. UV-Vis spectroscopy revealed a direct band gap of 1.86 eV. The electrochemical properties, evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS), demonstrated promising supercapacitor behavior. The nearly rectangular CV curves indicate reversible and stable redox activity, while the GCD measurements yielded a maximum specific capacitance of 23.4 F g⁻¹ at a current density of 0.5 A g⁻¹. The specific capacitance decreased with the increase in current density. The absence of a distinct semicircle in the high-frequency region of the EIS Nyquist plot indicates low charge-transfer resistance and dominant capacitive behavior.

Keyword. Cubic spinel ferrite, Nanoparticles, UV-Vis spectroscopy, Electrochemical analysis, Specific capacitance

INTRODUCTION

The rapid growth of the global population and industrialization has increased the demand for efficient energy storage systems. Conventional batteries offer high energy density but limited power density, while ordinary capacitors provide high power density but low energy density. Supercapacitors (SCs), or electrochemical capacitors, bridge this gap by combining high power density with moderate energy density. Developing advanced electrode material is crucial for improving SC performance¹. Transition metal oxides, especially spinel ferrites, are found to exhibit high specific capacitance, excellent cyclic stability, and long lifespan, making them promising candidates for efficient SC electrodes². The non-toxicity and lower cost attracted ferrite-based SC electrodes³. Spinel ferrite may exhibit different properties when synthesized by various methods, such as co-precipitation, sol-gel auto-combustion, hydrothermal synthesis, spray pyrolysis, and microwave combustion technique^{4,5}.

Although $\text{Mg}_{0.7}\text{Co}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles have been explored for different applications⁶, in the present work, they were investigated as a potential SC electrode. In this study, $\text{Mg}_{0.7}\text{Co}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles were synthesized using the coprecipitation method, and their electrochemical performances were evaluated.

EXPERIMENTS

$\text{Mg}_{0.7}\text{Co}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles were synthesized by the coprecipitation method using stoichiometric amounts of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and FeCl_3 in 50 mL of deionized water. The detailed procedure is reported elsewhere⁷. The salt solution was magnetically stirred at 750 rpm for 15 minutes, followed by the dropwise addition of NaOH solution (reducing agent) until the pH reached 12 at 60 °C. The resulting muddy color precipitate was aged for 2 hours, collected by centrifuging at 2500 rpm for 15 minutes, washed with deionized water, and dried at 150 °C for 14 hours in an oven. The dried powder was ground well and annealed at 900 °C for 4 hours in air. Structural analysis was performed using Rigaku Miniflex 600 benchtop X-ray diffractometer with Cu-K α radiation ($\lambda=1.5406$ Å), and optical properties were studied using Agilent Cary UV-Vis-NIR spectrophotometer over the wavelength range of 200-1200 nm.

For electrochemical studies, the working electrode was prepared by mixing $\text{Mg}_{0.7}\text{Co}_{0.3}\text{Fe}_2\text{O}_4$ nanoparticles (0.8 mg) with carbon black (conducting agent) and polyvinylidene difluoride (PVDF) in an 8:1:1 weight ratio using N-Methyl-2-pyrrolidone (NMP), followed by brush-coating onto a graphite foil ($1 \times 1 \text{ cm}^2$)⁸. Measurements were carried out in a three-electrode system with a saturated calomel electrode (SCE) as the reference electrode, a platinum wire as the counter electrode, and 1 M KOH as the electrolyte solution, using a BioLogic SP-240 electrochemical workstation.

RESULTS AND DISCUSSIONS

Figure 1(a) shows the XRD pattern of the sample. It was analyzed using the ICDD PDF# 01-073-2410 and PDF# 01-074-6402 for MgFe_2O_4 and CoFe_2O_4 , respectively. As seen in Fig. 1(a), the peaks observed at 30.05° , 35.39° , 43.11° , 56.98° , and 62.58° correspond to (220), (311), (400), (511), and (440) planes, respectively, confirming a single-phase cubic spinel (Fd-3m) ferrite structure. The lattice constant was found to be 0.839 nm. The average crystallite size calculated using Scherrer's formula was found to be 21.7 nm.

The inset in Fig. 1(b) presents the reflectance spectrum of the sample exhibiting an absorption edge in the visible region. Figure 1(b) shows Tauc plot, which was plotted using the equation,

$$(F(R)hv)^2 = C(hv - E_g) \quad (1)$$

where $F(R)$, $h\nu$, C , E_g are the absorption coefficient, photon energy, proportionality constant, and optical band gap energy, respectively⁹. A direct band gap of 1.86 eV was estimated for this material, and it shows semiconducting behavior. This narrow band gap can facilitate efficient charge transport and enhance surface redox activity, making the material suitable for SC applications.

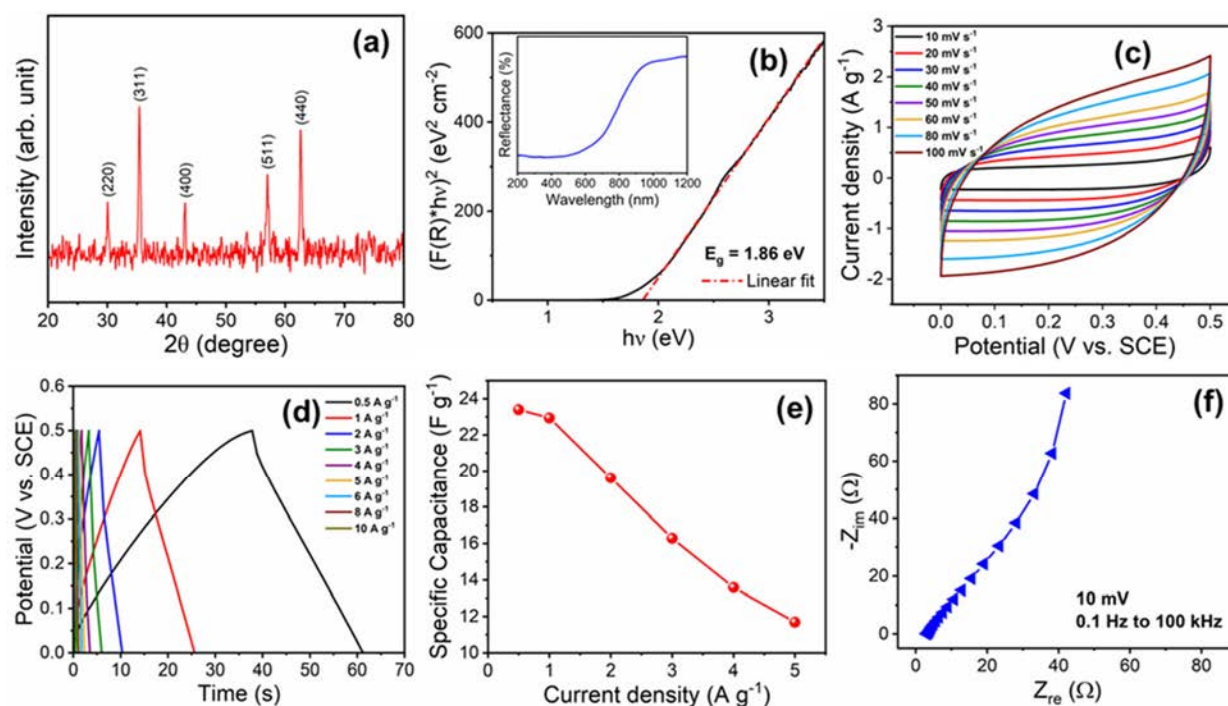


FIGURE 1. (a) XRD pattern of the synthesized sample, (b) Tauc plot; the inset shows reflectance spectra of the sample, (c) CV curves, and (d) GCD curves of the working electrode, (e) Variation of specific capacitance with current density, (f) Nyquist plot.

The CV curves depicted in Fig. 1(c) exhibit nearly rectangular shapes, indicating a combination of electric double-layer capacitance and pseudocapacitive behavior^{8,10}. The increase in current density with scan rate suggests fast charge transfer and limited diffusion time, resulting in predominantly surface-controlled processes. The CV curves also demonstrate good repeatability, reversibility, and capacitive characteristics.

Figure 1(d) depicts the GCD curves at current densities of 0.5–10 A g⁻¹ exhibiting nearly triangular shapes, with small IR drops, confirming good capacitive behavior and low internal resistance^{11,12}. Figure 1(e) corresponds to the specific capacitance (C_{sp}) of the electrode, calculated using the equation,

$$C_{sp} = \frac{I \cdot \Delta t}{m \cdot \Delta V} \quad (2)$$

where I , Δt , m , ΔV are the current (A), the discharge time, weight (g), and potential range (V) during the discharge process, respectively¹³. A maximum specific capacitance of 23.4 F g⁻¹ was observed at a current density of 0.5 A g⁻¹. The specific capacitance decreased with increasing current density.

The internal resistance of a SC has its origin from various sources¹³ and is collectively referred to as equivalent series resistance (ESR). Figure 1(f) shows a Nyquist plot drawn from EIS measurements. The absence of a distinct semicircle in the high-frequency region indicates low charge-transfer resistance, while the inclined line in the low-frequency region suggests ion diffusion within the electrode^{14,15}. Overall, these results demonstrate efficient charge transport, favorable ion diffusion, and dominant surface-controlled capacitive behavior.

CONCLUSIONS

Mg_{0.7}Co_{0.3}Fe₂O₄ nanoparticles were synthesized using the coprecipitation method. The structural and optical analyses confirmed the formation of a single-phase cubic spinel structure with a direct optical band gap. The electrochemical studies revealed dominant surface-controlled capacitive behavior with pseudocapacitive contributions and good reversibility. A maximum specific capacitance of 23.4 F g⁻¹ was achieved at a current density of 0.5 A g⁻¹. The EIS results indicate low charge-transfer resistance and efficient ion transport. Overall, the electrochemical performance of Mg_{0.7}Co_{0.3}Fe₂O₄ nanoparticles suggests that the material is a promising candidate for SC electrode applications.

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Trimetallic MnCoFeO₄ Nanostructures as Advanced Electrode Materials for Pseudocapacitive Energy Storage

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Abstract. The increasing demand for sustainable energy storage has driven the need for efficient electrode active materials with high redox activity and conductivity. In this study, MnCoFeO₄ spinel ferrite nanoparticles were synthesized via the co-precipitation method and investigated as a pseudocapacitive cathode material. Structural characterization by XRD confirmed the successful formation of the MnCoFeO₄ spinel phase, while FESEM analysis showed uniformly distributed size of the particles around ~29 nm. Electrochemical analysis using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) in a three-electrode setup exhibited excellent specific capacitances of 720.29 F g⁻¹ at 2 mV/s and 767.23 F g⁻¹ at 1.5 A/g, respectively. The superior performance is attributed to the synergistic redox activity of Mn, Co, and Fe ions within the spinel lattice, which enables fast kinetics and efficient ion diffusion. These results highlight MnCoFeO₄ as a promising candidate for next-generation supercapacitor cathodes.

INTRODUCTION

The growing demand for economical and environmentally friendly energy storage options has increased interest in supercapacitors for their fast charging and discharging capability, high-power density, and long cycling life. Spinel ferrites (AB₂O₄) have drawn attention as a potential candidate for pseudo-capacitor electrode materials due to their abundant redox-active sites, tunable composition, and excellent chemical stability.¹ Trimetallic spinel ferrites such as MnCoFeO₄ have generated widespread interest due to their ability to integrate the redox properties of Mn, Co, and Fe ions within a single-phase structure, providing the potential for improved charge storage capacity and structural stability. The coexistence of multiple oxidation states (Mn²⁺/Mn³⁺, Co²⁺/Co³⁺ and Fe²⁺/Fe³⁺) encourages efficient redox transitions, thereby enhancing pseudocapacitive performance. However, comprehensive electrochemical analysis of trimetallic spinel ferrites for energy storage remains limited. Here, we have synthesized MnCoFeO₄ nanoparticles using a simple co-precipitation method followed by thermal annealing. Electrochemical performance was investigated through CV and GCD in a three-electrode setup with aqueous 3 M KOH electrolyte solutions.

EXPERIMENTAL

• Synthesis of MnCoFeO₄ Nanoparticles

Stoichiometric ratios of Manganese (II) chloride tetrahydrate (MnCl₂·4H₂O), Cobalt (II) chloride hexahydrate (CoCl₂·6H₂O), and Iron (III) chloride (anhydrous) (FeCl₃) were dissolved in aqueous solution and mixed under continuous magnetic stirring at 40 °C. The pH was adjusted to 10 by adding 0.8 M NaOH solution dropwise. After continuous stirring, a black precipitate was formed, which was cleaned multiple times with ethanol and DI water, and subsequently dried at 100 °C. The dried product was finally calcined at 600 °C for 3 h in a tube furnace.

• Characterization Techniques and Electrochemical Measurements

X-ray diffraction (XRD) of the synthesized material was carried out using Cu K_α radiation ($\lambda = 1.54\text{\AA}$) in the 2 θ range of 15°–90°. The morphology of the material was evaluated using Field Emission Scanning Electron Microscopy (FE-SEM). The working electrode was prepared by mixing MnCoFeO₄ powder, activated charcoal, and PVDF binder in an 8:1:1 ratio using N-methyl-2-pyrrolidone (NMP) as the solvent, and coated onto nickel foam. The electrochemical performance was investigated using a three-electrode cell configuration. An Ag/AgCl electrode served as the reference electrode, while a platinum mesh was used as the counter electrode. All electrochemical measurements were conducted in 3 M KOH electrolyte using an electrochemical workstation.

RESULTS AND DISCUSSIONS

• Structural and Morphological Analysis

Figure 1(a) illustrates the XRD pattern of MnCoFeO₄ nanoparticle, confirming the formation of a cubic spinel structure with space group $Fd\bar{3}m$, (JCPDS No.#22–1086). The average size (D) and microstrain (ϵ) of MnCoFeO₄ nanoparticles were calculated by using the Williamson-Hall modified Scherrer equation²:

$$\beta \cos \theta = \left(\frac{0.9\lambda}{D} \right) + 2\epsilon \sin \theta \quad (1)$$

The inset of Figure 1(a) shows the $\beta \cos \theta$ vs. $4 \sin \theta$ plot (Williamson-Hall plot), which infers the average crystallite size of MnCoFeO₄ nanoparticles as 25 nm. The FESEM image as shown in Figure 1(b) illustrates the agglomerated MnCoFeO₄ nanoparticles. Particle size distribution as in Figure 1(b) inset, showing maximum number of particles having size ~29 nm, validates the enhancement of the surface area and thus offers numerous active sites for efficient redox reactions.

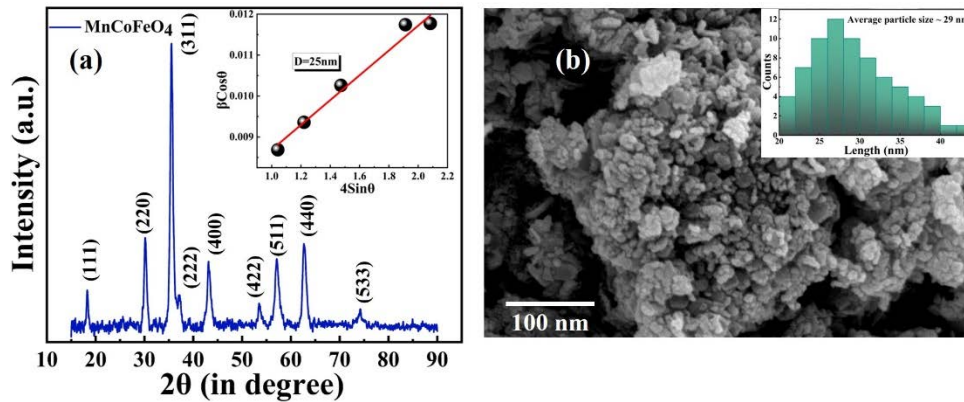


FIGURE 1: (a) XRD pattern and (b) FESEM images of MnCoFeO₄. Inset (a) W-H plot, inset (b) particle size distribution of MnCoFeO₄ nanoparticles

• Electrochemical analysis

Figure 2(a) represents the CV curves at different scan rates ranging from 2 mV/s to 100 mV/s within the potential window of 0.00–0.75 V. The presence of broad and overlapping redox peaks indicates faradaic pseudocapacitive behavior, attributed to reversible redox transitions involving Mn²⁺/Mn³⁺, Co²⁺/Co³⁺ and Fe²⁺/Fe³⁺. The specific capacitance (C) was calculated from the CV and GCD measurement using equations (2) and (3),³ respectively:

$$C = \frac{\oint I dV}{m \Delta V} \quad (2)$$

$$C = \frac{I \Delta t}{m \Delta V} \quad (3)$$

Where I , v , m , ΔV , Δt represents response current (A), scan rate (mV/s), mass of active material (g), potential window (V), and discharge time (s), respectively.

The maximum specific capacitance value obtained from CV was 720.29 F g⁻¹ at 2 mV/s scan rate. The inset of Figure 2(a) clearly shows that the specific capacitance decreases gradually with increasing scan rate, which is a typical characteristic of pseudocapacitive materials. This decline is associated with limited diffusion of ions at higher scan rates, where only surface or near-surface redox sites are employed, resulting in reduced charge storage. In contrast, lower scan rates allow electrolyte ions to penetrate deeper into the electrode matrix, enhancing ion adsorption and storage, and thus delivering higher capacitance.

To determine the dominant charge storage mechanism in MnCoFeO₄, the power-law relationship $i_p = a v^b$ was used, where v , i_p represent scan rate and peak current, respectively, and b indicates the charge storage type. The value of b , obtained from the slope of the $\log(i_p)$ vs. $\log(v)$ plot, as shown in Figure 2(b), is 0.64. According to literature, $b \approx 0.5$ suggests a diffusion-controlled (EDLC) process, while $b \approx 1$ indicates pseudocapacitive behaviour, whereas, intermediate b values ($0.5 < b < 1$) signify a hybrid charge storage mechanism involving both diffusion and capacitive contributions.⁴ Here, the estimated b value (~0.64) indicates a hybrid charge storage mechanism which may be predominantly pseudocapacitive in nature.

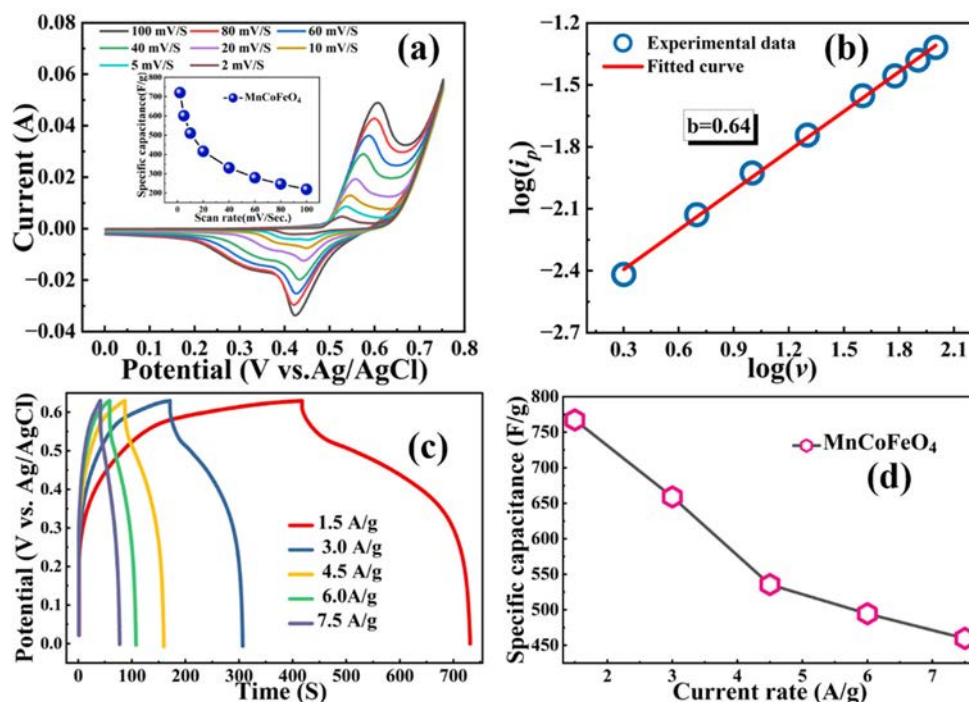


FIGURE 2: (a) CV curves, (b) $\log(i_p)$ vs. $\log(v)$ plot, (c) GCD data, (d) capacitance vs various current insrz rate plot

Figure 2(c) shows quasi-triangular GCD curves of MnCoFeO₄ (three electrode system) across current densities from 1.5 to 7.5 A/g within a 0.00–0.62 V potential window, confirming the pseudocapacitive behavior of MnCoFeO₄. From GCD measurement, the highest specific capacitance value of 767.23 F g⁻¹ is recorded at 1.5 A/g. Further, in Figure 2(d), the specific capacitance was measured at different current rates.

CONCLUSION

The synergistic features highlight the significant potential of MnCoFeO₄ as a promising next-generation electrode material for high-performance supercapacitors.

ACKNOWLEDGMENTS

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Effect of Co-catalyst and growth temperature during Graphene synthesis by PECVD method – analysed using Raman Spectroscopy

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Abstract. This study presents vibrational spectroscopic studies on graphene films synthesized by plasma enhanced chemical vapor deposition with cobalt catalyst. The grown films were characterized by Raman spectroscopy to assess the effects of catalyst sputtering time and growth temperature on structural quality, including defect density and estimation of number of layers. Optimal PECVD conditions were determined as 6 minutes of cobalt sputtering followed by growth at 800 °C to synthesize few-layer graphene with minimal defects.

INTRODUCTION

Graphene is a two-dim. form of carbon that has sp² hybridized carbon atoms in a hexagonal arrangement. It has exceptional properties like high electrical conductivity, mechanical strength, and optical transparency, which make it useful for high-frequency electronics, transparent conductors, sensors, and energy storage devices¹. But in order for graphene-based technologies to work in real life, we need to be able to make graphene with controlled structural quality, layer thickness, and defect characteristics over large areas. Chemical vapor deposition (CVD) techniques are often used to grow thin films because mechanical exfoliation methods don't work well on a large scale. But traditional thermal CVD needs high temperatures, which makes it less compatible with some substrates^{2,3}.

This limitation is overcome by plasma-enhanced CVD (PECVD), which permits growth at comparatively lower temperatures⁴. This lowers thermal burden, enhances substrate compatibility, and offers more control via reactive species produced by plasma. However, competing processes including increased nucleation, defect formation, and etching are introduced by the presence of energetic ions and radicals, complicating the growth mechanism⁵. The growth behaviour of graphene is significantly influenced by the catalyst selection. Because transition metals like cobalt are more carbon soluble than copper, a dissolution–precipitation mechanism usually produces few-layer graphene with varying thicknesses⁶. Carbon diffusion, nucleation, and film morphology are therefore greatly influenced by factors like sputtering time and growth temperature⁷.

In this study, we investigate the effect of cobalt catalyst sputtering time and PECVD growth temperature on the structural characteristics of graphene. The analysis focuses on understanding how these parameters influence layer formation, defect characteristics, and overall film quality, considering the presence of competing growth mechanisms under plasma conditions

PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION

In RF-PECVD, plasma generated by radio-frequency power creates reactive species, including ions, radicals, and electrons, which facilitate precursor dissociation and film deposition. Besides chemical reactions, ion bombardment at the substrate surface affects nucleation, surface diffusion, and the structural development of the growing film.

As a result, graphene formation is governed by the combined effects of plasma-assisted deposition and ion-induced modification processes. Cobalt was chosen as the metal catalyst due to its moderate carbon solubility which supports graphene formation through bulk modulated growth process forming few layers graphene.

Graphene was synthesized on alumina substrates using RF-PECVD in three main steps. First, cobalt was sputtered onto the substrate for 2, 4, and 6 minutes to vary the catalyst thickness. In the second step, the surface was pre-treated at 600 °C using 200 W RF plasma in an argon atmosphere (10 ccm) at 0.2 mbar for 15 minutes, with a 2 cm substrate-to-electrode distance. Finally, graphene growth was performed at 600 °C, 700 °C, and 800 °C using a gas mixture of acetylene and hydrogen (both at 20 ccm), under 0.5 mbar pressure and 200 W plasma for 30 minutes.

RAMAN SPECTROSCOPY SETUP

Raman measurements were performed using a CCD-based Andor spectrometer equipped with a 532 nm Nd:YAG laser as the excitation source. The laser power was maintained at 25 mW, with a slit width of 150 microns and a diffraction grating of 600 lines/mm for spectral dispersion. The setup follows a U-shaped optical path that includes four main sections: excitation, beam steering, signal collection, and detection. The laser beam was expanded and directed using mirrors and lenses, then focused onto the sample. The scattered light from the sample was collected in a backscattering geometry and passed through an edge filter to remove Rayleigh scattering. The filtered Raman signal was then dispersed by the grating and finally recorded by a CCD detector. The collected Raman spectra were then processed and analyzed using Origin software for baseline correction, peak fitting, and extraction of key parameters.

Results and Discussion

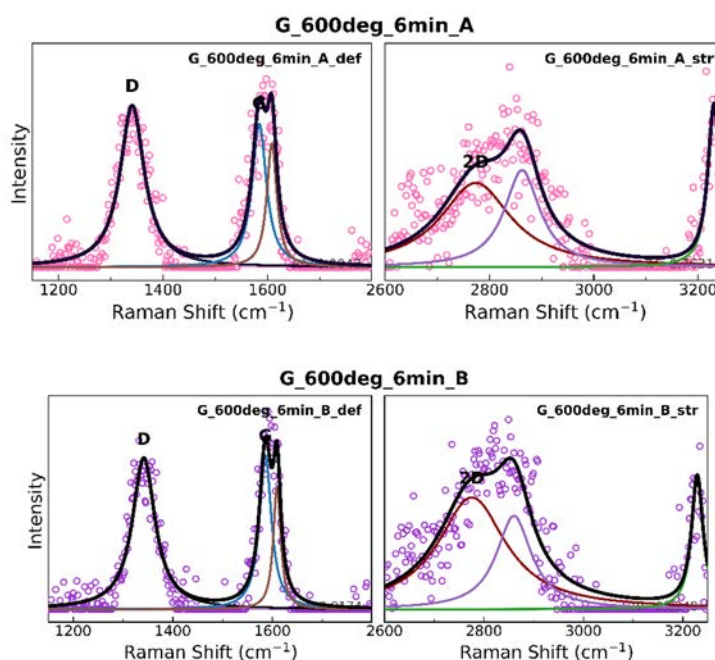


Fig 1. Raman spectra of PECVD Graphene films with Co deposition time 6 min and growth temperature 600°C on Alumina substrate

Figures 1–3 show the Raman spectra of PECVD graphene thin films synthesized with different cobalt catalyst sputtering times and growth temperatures, on both rough and smooth surfaces of alumina substrates. In total, a matrix of sputtering durations (2, 4, and 6 min), growth temperatures (600, 700, and 800 °C), and substrate surface morphologies (rough and smooth) was explored; only conditions yielding spectrally distinct and analytically meaningful results are discussed here. Intermediate conditions (4 min sputtering and 700 °C growth) did not show significant improvements over adjacent parameter points and hence are not discussed further.

Each spectrum is resolved into two spectral windows: the deformation region (1150–1800 cm^{-1}), comprising the D, G, and D' bands, and the overtone/combination region (2600–3300 cm^{-1}), comprising the 2D, D+D', and 2D' bands. The key Raman bands include the D band ($\sim 1350 \text{ cm}^{-1}$), which arises from defect-activated intervalley scattering in sp^2 domains; the G band ($\sim 1580 \text{ cm}^{-1}$), from in-plane vibrations of sp^2 carbon atoms serving as a marker of graphitization; and the 2D band ($\sim 2700 \text{ cm}^{-1}$), a second-order overtone sensitive to layer number and stacking order^{8, 9}.

As shown in Fig. 1, films grown on smooth substrates exhibit better spectral quality and signal-to-noise ratio than those on rough substrates for all conditions. The rough-surface sample (G_600°C_6min_A) shows $\text{D/G} = 1.12$ and $\text{I2D/IG} = 0.99$, while the smooth-surface sample (G_600°C_6min_B) gives $\text{D/G} = 0.98$ and $\text{I2D/IG} = 1.31$. The smoother substrate yields a more prominent 2D band with lesser broadening compared to the rough counterpart, indicating larger graphitic domains and lower disorder³. The improved spectral quality on smooth substrates links to uniform Co film deposition and more homogeneous carbon precipitation during growth, leading to larger graphitic domains and reduced boundary-related disorder^{4, 6}.

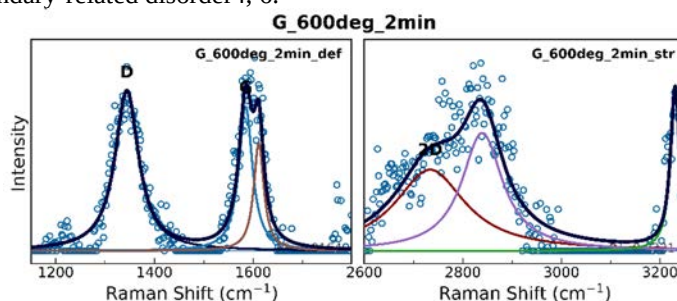


Fig 2. Raman spectrum of PECVD Graphene films with Co deposition time 2 min and growth temperature 600°C on Alumina substrate

For the 2 min sputtering at 600 °C (Fig. 2), the spectra show a prominent D band and weak 2D response, characteristic of high disorder and small domain sizes. Increase of sputtering time to 4 minutes also did not yield significant improvement in spectral quality in the overtone region. Increasing sputtering time to 6 min (Fig. 1) enhances the 2D band intensity and symmetry, particularly on smooth substrates. The ID/IG ratio decreases from ~ 1.11 (2 min) to ~ 0.98 (6 min smooth, site B), confirming reduced defect density with thicker, more uniform catalyst films that promote homogeneous carbon precipitation by reducing the density of non-graphitic nucleation sites^{6, 7}.

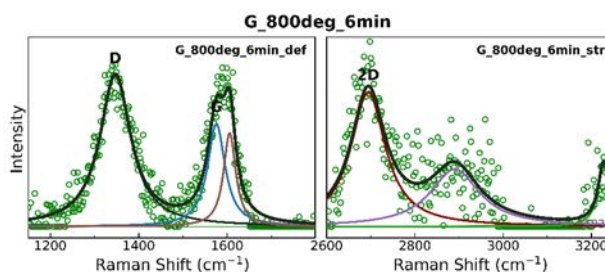


Fig 3. Raman spectrum of PECVD Graphene films with Co deposition time 6 min and growth temperature 800°C on Alumina substrate.

Raising the growth temperature to 800 °C with 6 min sputtering (Fig. 3) produces the sharpest 2D band (FWHM 95 cm^{-1}) and highest I2D/IG (~ 1.76), with the 2D position shifting to $\sim 2694 \text{ cm}^{-1}$ closer to few-layer graphene⁸. This indicates improved crystallinity, larger domains, and reduced layer count relative to 600 °C films. It is consistent with enhanced carbon diffusion and selective etching of amorphous carbon at higher temperature⁴. Although ID/IG (~ 1.47) is higher than at 600 °C smooth, the superior signal-to-noise and 2D ratios confirm overall better quality. Fitted parameters for all key samples are given in Table 1. Results shows smooth substrates and 6 min sputtering minimize defects at 600 °C, while 800 °C further enhances order and reduces effective layers. An increase in 2D/G ratio, in addition to enhanced signal to noise ratio, symmetry and sharpness of 2D band, from 600 to 800oC indicates better quality fewer layer films at higher temperatures. Further analysis is being carried out and will be presented.

TABLE 1. List of peak position, FWHM and other fitted parameters of various graphene films for D, G, D', 2D, D+D' and 2D' peaks. Also listed here are the 2D/G and D/G ratio used for characterizing the quality of films.

		Sample Name	G_600deg_2min	G_600deg_6min_A	G_600deg_6min_B	G_800deg_6min
DEFORMATION	Peak 1 (D)	Position (cm ⁻¹)	1344.00	1340.97	1341.57	1346.97
		Width	57.84	56.33	55.17	83.92
		Height	2610.6	1228.6	1083.3	642.23
	Peak 2 (G)	Position (cm ⁻¹)	1584.85	1584.22	1585.91	1575.58
		Width	33.2	33.35	29.3	48.07
		Height	2358.68	1093.82	1106.63	435.51
	Peak 3 (D ^{''})	Position (cm ⁻¹)	1611.38	1608.22	1609.18	1605.62
		Width	25.07	23.32	18.3	33.36
		Height	1759.09	942.25	875.31	397.0
STRETCHING	Peak 1 (2D)	Position (cm ⁻¹)	2733.76	2773.81	2775.76	2694.24
		Width	173.51	164.55	167.7	95.0
		Height	2236.45	1086.45	1448.78	767.03
	Peak 2 (D+D ^{''})	Position (cm ⁻¹)	2839.43	2862.72	2860.0	2890.48
		Width	1011.15	83.62	86.66	136.06
		Height	3230.14	1242.31	1209.03	327.43
	Peak 3 (2D ^{''})	Position (cm ⁻¹)	2230.84	3230.76	3229.9	3228.14
		Width	22.84	28.69	28.17	30.88
		Height	4396.65	2054.31	1677.74	354.14
Ratio – 2D/G		0.94	0.99	1.31	1.76	
Ratio – D/G		1.11	1.12	0.98	1.47	

CONCLUSION

The effect of Co catalyst sputtering time and growth temperature was analyzed for graphene film synthesized on alumina substrates, using Raman spectroscopy. All samples exhibit the characteristic Raman signatures of graphitic carbon, but their spectral shape, changes noticeably with cobalt sputtering time and growth temperature.

Increasing Co sputter time from 2 min to 6 min improves the 2D/G ratio in smooth samples, indicating that a thicker, uniform Co film promotes formation of graphene with larger crystalline domains. Rough morphology yields poorer layer formation and higher disorder. Raising the growth temperature to 800 °C on a 6-min smooth Co catalyst greatly improves graphene quality by increasing domain size (narrower 2D peak FWHM 95 cm⁻¹), enhancing layer order (I2D/IG ~1.76) and S/N ratio. The 600 °C, 6-min smooth sample shows the minimum ID/IG (~0.98) and lowest defects among low-temperature conditions, while 800 °C yields the overall best Raman signatures of improved crystallinity. High I2D/IG and narrowed 2D band at 800 °C suggest formation of few-layer (2–4 layer) graphene under these conditions. These results highlight that both catalyst thickness and temperature are critical in optimizing PECVD graphene growth.

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Correlation Effects in Coupled Quantum Wires using the Single Loop Random Phase Approximation

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Abstract. The dynamical response theory is used to calculate the static structure factors, pair correlation functions, and correlation energies of an electron-electron quantum wires of confinement width b using the single loop random phase approximation. This study emphasis on how intra- and inter-wire correlations influences the structural properties. The intra-wire static structure factor and pair correlation function show minimal variation, whereas the inter-wire observables exhibit strong sensitivity to interwire separation d , with pronounced correlations emerging at small separations. Also, the correlation energy reveals a significant enhancement as d decreases, driven by strong inter-wire electron interactions. This behavior exhibits the enhanced role of inter-wire coupling d , highlighting the importance of spatial confinement in shaping many-body correlation effects in low-dimensional systems.

INTRODUCTION

The one-dimensional electron gas has fascinating properties with diverse technological application [1]. When it comes to describing the behavior of interacting fermions in higher dimensions (2D and 3D), Landau's theory of Fermi liquid has been remarkably successful. However, the particles (electrons) confined in one spatial dimension deviates from the Landau's Fermi liquid paradigm and give rise to various exotic quantum phenomena [2]. These one-dimensional systems are of great importance in both experimental [3] and theoretical aspects of the field because of its unique quantum behavior. The Tomonaga-Luttinger (TL) liquid is a standard model that facilitates the understanding of these enhanced correlations in one dimensional system [4]. There have been a lot of comprehensive computational and theoretical studies to understand the correlations between the electrons in low dimensional systems. The effect of interactions between electrons in parallel quantum wires embedded in a semiconductor substrate has been of great interest [5-7]. The computational study of the ground-state properties of parallel, infinitely thin electron-electron biwire using variational monte carlo have been done by Sharma et al. [8] for several electron densities n_s and inter-wire separations d . The inclusion of finite width b in the model of quantum wires introduces significant changes to the interaction and confinement properties [9]. In this work we report the single loop random phase approximation (RPA) results for static structure factors (SSFs), pair-correlation functions (PCFs) and correlation energies (E_c) of quantum wires at a particular confinement width b for various values of inter-wire separation d .

THEORETICAL MODEL

We consider a system of two parallel quantum wires, each with width b , separated by d (where $d \geq b$). In this system, both wires are filled with electrons of opposite spins. The quasi-free motion of the carriers are along the wire axis and is constrained along the transverse directions through a strong confinement potential [9],

$$V_{ll'}(Q) = \frac{2e^2}{\epsilon_0} K_0 \left(k_F Q \sqrt{b^2 + (1 - \delta_{ll'})d^2} \right) \quad (1)$$

where K_0 is the modified Bessel function of the second kind, k_F is the fermi wave vector, and $\delta_{ll'}$ is the kronecker delta. The homogeneous electron gas in one-dimension is described by the random phase approximation (RPA), and strongly valid in the high-density limit. The density response function for an electron-electron system $\chi_{ll'}(Q, \Omega)$ is given by

$$\chi_{ll'}(Q, \Omega) = \frac{\chi_0(Q, \Omega) [\delta_{ll'} + (-1)^{\delta_{ll'}} V_{ll'}(Q, \Omega) \chi_0(Q, \Omega)]}{(1 - \chi_0(Q, \Omega) V_{11})^2 - (\chi_0(Q, \Omega) V_{12})^2} \quad (2)$$

where $\chi_0(Q, \Omega)$ is the non-interacting part of the, given by, $\chi_0(Q, \Omega) = \frac{r_s}{\pi^2 Q} \ln \left[\frac{\left(\frac{Q}{2}-1\right)^2 + \Omega^2}{\left(\frac{Q}{2}+1\right)^2 + \Omega^2} \right]$

RESULTS AND DISCUSSIONS

The SSF $S(Q)$ is defined through the fluctuation-dissipation theorem [6] and the PCF $g(r)$ is obtained from the SSF

$$S_{ll'}(Q) = -\frac{\pi}{2r_s} \int_0^\infty \chi_{ll'}(Q, \Omega) Q d\Omega; \quad g_{ll'} = 1 + \int_0^\infty \cos\left(\frac{\pi}{2r_s} Qr\right) [S_{ll'}(Q) - \delta_{ll'}] dQ \quad (3)$$

The correlation energy in terms of the density-density response function is expressed as

$$E_c = -\frac{\pi}{16r_s^2} \sum_{l=1}^2 \sum_{l'=1}^2 \int_0^\infty V_{ll'}(Q) \left[\int_0^\infty (\chi_{ll'}(Q, \Omega) - \chi_0(Q, \Omega)) Q d\Omega \right] dQ \quad (4)$$

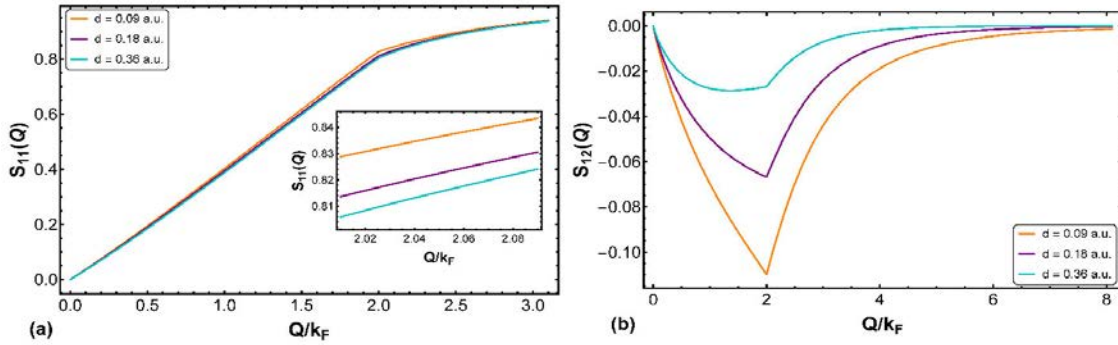


FIGURE 1. SSFs for a coupled quantum wire system with transverse confinement width $b = 0.09$ a.u., $r_s = 0.85$ a.u. plotted as a function of Q/k_F for varying d . (a) Intra-wire SSF $S_{11}(Q)$ with subtle dependence on d highlighted in the inset. (b) Inter-wire SSF $S_{12}(Q)$.

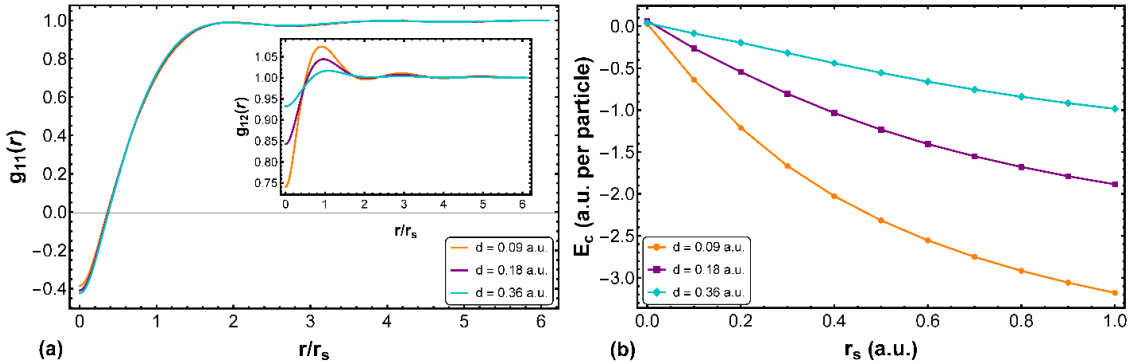


FIGURE 2. (a) PCFs for a coupled quantum wire system with transverse confinement width $b = 0.09$ a.u., $r_s = 0.85$ a.u. plotted as a function of r/r_s for varying inter-wire separations d . The main plot shows Intra-wire PCF $g_{11}(r)$. The inset shows the inter-wire PCF $g_{12}(r)$. (b) Correlation energy per particle E_c as a function of r_s , for various wire separations.

A quantity that can be measured by experiments [3] and contains important information about the structure of the system. Intra- $S_{11}(Q)$ and inter- $S_{12}(Q)$ SSFs obtained from Eq. (3) and are shown in the Fig. 1a and Fig. 1b, respectively evaluated for $r_s = 0.85$ a.u. with a wire width of $b = 0.09$ a.u. at various d . In case of $S_{11}(Q)$, at small Q , all curves exhibit a linear dependence. The slope at low Q remains largely unchanged with increasing inter-wire

separation, indicating that $S_{11}(Q)$ correlations are only weakly perturbed by the presence of the neighboring wire. However, the inset reveals a subtle increase in the amplitude of $S_{11}(Q)$ at $Q = 2k_F$ as d decreases with the highest peak at $d = 0.09$ a.u. and the lowest at $d = 0.36$ a.u., suggesting reduced screening as the wires begin to decouple. Inter $S_{12}(Q)$ shows pronounced negative dip for small values of d again highest at $d = 0.09$ a.u., reflecting strong correlations between carriers in adjacent wires-indicative of repulsive inter-wire interactions. As d increases, the peak shifts from $2k_F$ indicating a crossover from a strongly coupled to a decouple behavior. Fig. 2a shows both the intra- $g_{11}(r)$ and inter-wire $g_{12}(r)$, PCFs evaluated from the Eq. (3). The main plot demonstrates that there is no significant change in $g_{11}(r)$, indicating a very weak sensitivity of intra-wire correlations to the inter-wire separation, even at a smaller d . This implies that the $g_{11}(r)$ structure is primarily governed by same-wire interactions and remains largely unaffected by inter-wire coupling at a particular r_s , also we see that the artifact of RPA which leads to the known negative values of PCFs at small distances since the exchange (vertex) corrections are not included. On the other hand, the $g_{12}(r)$, shown in the inset, exhibits pronounced changes with decreasing d , with a strong peak at $r = r_s$ for $d = 0.09$ a.u and its value shifting towards zero at $r = 0$ because of strong repulsion between electrons. As the wire separation increases to $d = 0.36$ a.u., the oscillatory behavior broadens, indicating the wires are far apart. Figure 2b presents the variation of the correlation energy per particle E_c as a function of the density parameter r_s for different d and is expressed in Eq. (4). It is observed that E_c becomes increasingly negative as r_s increases, highlighting the enhanced role of correlation effects in the low-density regime. Furthermore, at any fixed r_s , smaller values of d result in significantly lower (more negative) correlation energy, indicating stronger inter-wire interactions. Conversely, for larger separations such as $d = 0.36$ a.u., the correlation energy is correspondingly less negative.

CONCLUSION

We studied correlation effects in coupled quantum wires using the single loop RPA, focusing on how inter-wire separation d influences structural properties. While intra-wire quantities $S_{11}(Q)$ and $g_{11}(r)$ show minimal variation, inter-wire observables $S_{12}(Q)$ and $g_{12}(r)$ exhibit strong sensitivity to d , with pronounced correlations emerging at small separations. The correlation energy E_c reveal a significant enhancement in magnitude as d decreases, driven by stronger inter-wire interactions. This behavior underscores the enhanced role of inter-wire coupling at lower d , highlighting the importance of spatial confinement in shaping many-body behavior in low-dimensional systems.

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Correlation Energies of Quasi-One-Dimensional Ferromagnetic Electron Gas

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Abstract. We study the correlation energies of quasi-one-dimensional ferromagnetic electron gas for harmonic-delta confinement in the transverse directions. The singularity of the one-dimensional Coulomb potential at zero inter-particle distance is regularized by confining the motion of electrons in the transverse plane by a harmonic-delta potential. The first-order random phase approximation, including self and exchange-energy contributions, which provides ground-state structure beyond random phase approximation, is used to numerically compute the ground state properties, i.e. correlation and ground state energies. The correlation energy significantly depends on pragmatic widths b and density parameters r_s . For the ultrathin wire in the high-density limit, the correlation energy converges to $-\pi^2/360$ a.u. for the harmonic-delta potential, in agreement with the exact results.

INTRODUCTION

The quasi-one-dimensional (1D) homogeneous electron gas is the simplest model that is crucial for studying many-body interactions in fermionic systems. The system is rendered electrically neutral by the presence of a uniform background of positive charge, referred to as a jellium model [1]. This theoretical framework allows for the study of fundamental electronic properties without the complexities introduced by discrete ion cores. The concept of an infinitely thin wire is an idealization used for theoretical calculations and modeling, but it cannot be fabricated experimentally. In practice, we study quasi-1D systems such as carbon nanotubes [2] and semiconductor nanowires [3]. Our present work mainly focuses on ferromagnetic quantum wire, in which electrons are free to move along the axis of a finite-width wire, while strongly confined in the transverse directions using an external potential. These systems have been studied at zero and finite temperatures in the high-density regime for harmonic and cylindrical-potential models of transverse confinement [4-8]. Our calculations are confined to the extreme quantum limit, an approximation valid for atomic-scale metallic wires [7,8]. In this regime, electrons are assumed to occupy only the lowest energy subband associated with transverse confinement. The correlation energy is a key parameter that quantifies the error introduced by the mean-field approximation of the Hartree-Fock method, which treats electron-electron repulsion in an averaged way. We use first-order random phase approximation (FRPA), including self and exchange-energy contributions, to calculate the correlation and ground state energies.

THEORETICAL FORMALISM

A. Confinement Model

Firstly, we consider a two-dimensional electron gas confined to the xy -plane with a zero thickness so that the motion of electrons can be neglected in the z -direction. Within this system, electrons move freely along the x -axis (wire axis), while a harmonic potential provides confinement in the y -direction. Because the motion of electrons in the z -direction is neglected and all electrons occupy the lowest subband of the harmonic potential, the system effectively behaves as a quasi-one-dimensional system. The analytic form of this effective electron-electron interaction potential in reciprocal space is [7],

$$V(q) = \exp(q^2 b^2 / 4) K_0(q^2 b^2 / 4). \quad (1)$$

Where K_0 denotes the zeroth-order modified Bessel function of the second kind and b is wire width of the quantum wire.

Density Response Function

The density response function characterizes how the electron density of a system changes in response to an applied external potential. This can be formally expressed as [6,8],

$$\chi(q, \omega) = \frac{\chi_0(q, \omega) + \lambda\{\chi_1^{se}(q, \omega) + \chi_1^{ex}(q, \omega)\}}{1 - \lambda V(q)[\chi_0(q, \omega) + \lambda\{\chi_1^{se}(q, \omega) + \chi_1^{ex}(q, \omega)\}]}, \quad (2)$$

where $V(q)$ is the effective interaction potential in reciprocal space and λ signifies the order of the potential, while $\chi_1^{se}(q, \omega)$ and $\chi_1^{ex}(q, \omega)$ denote the first-order self-energy and exchange corrections to the polarizability, respectively. In the high-density limit, Eq. (2) simplifies to a first-order approximation as,

$$\chi(q, i\omega) \approx \chi_0(q, i\omega) + \lambda V(q)\chi_0^2(q, i\omega) + \lambda\{\chi_1^{se}(q, i\omega) + \chi_1^{ex}(q, i\omega)\}. \quad (3)$$

RESULTS AND DISCUSSIONS

Using FRPA, the accurate calculation of correlation energy is given by [6,8],

$$E_c = \frac{n}{2} \sum_{q \neq 0} V(q) \left[-\frac{1}{n\pi} \int_0^1 d\lambda \int_0^\infty \{\lambda V(q)\chi_0^2(q, i\omega) + \lambda\chi_1^{se}(q, i\omega) + \lambda\chi_1^{ex}(q, i\omega)\} d\omega \right], \quad (4)$$

where $n = 1/2r_s$ is the electron number density, and the correlation energy per electron is [6],

$$\varepsilon_c = \frac{1}{4\pi} \int_0^\infty V(q) S_1(q) dq. \quad (5)$$

Where $V(q)$ represents the harmonic-delta potential, and $S_1(q) = S_1^d(q) + S_1^{se}(q) + S_1^{ex}(q)$, denotes the first-order static structure factor (SSF), which includes contributions from direct, exchange and self-energy terms.

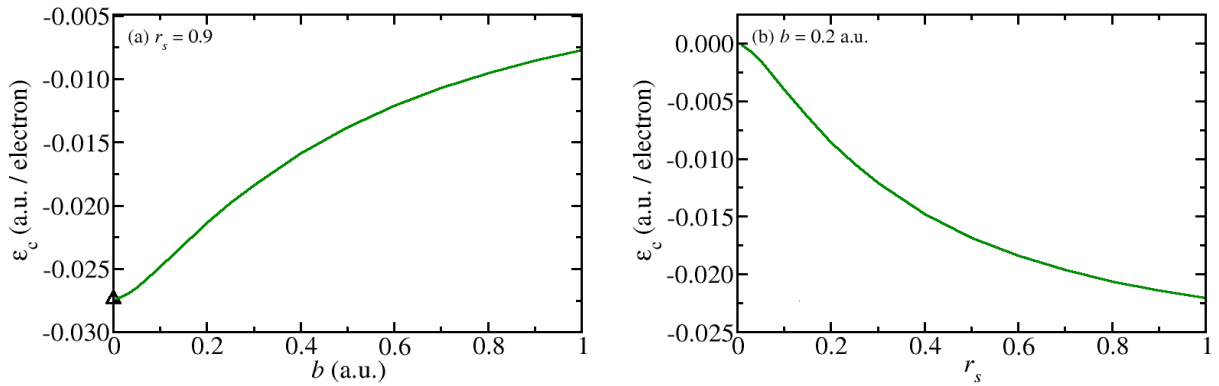


FIGURE 1. Correlation energy per electron (ε_c) is plotted as a function of wire width (b) and density parameter (r_s) at fixed $r_s = 0.9$ and $b = 0.2$ a.u., respectively. The triangle symbol (Δ) indicates the correlation energy $\varepsilon_c = -\pi^2/360$ a.u. at high density limit as $b \rightarrow 0$.

In Fig. 1, correlation energy per electron is plotted as a function of wire width (b) and density parameter (r_s) at fixed r_s and b , respectively. In Fig. 1(a), as the wire width (b) decreases, the correlation energy becomes more negative at fixed $r_s = 0.9$; a smaller b signifies that an increased strength of the confining forces electrons closer together,

enhancing their mutual Coulomb interaction. The correlation energy converges to $-\pi^2/360$ a.u. as b approaches zero, in agreement within high-density limit for ultrathin wire [6,9].

Figure 1(b) illustrates the dependence of the correlation energy on density parameter (r_s) at $b = 0.2$ a.u. At fixed b , a larger r_s value indicates a lower electron density, which intensifies electron-electron interactions and the correlation energy decreases. This concludes that a smaller wire width (b) produces the same effect on electron-electron correlations as a larger density parameter (r_s) impact.

CONCLUSION

We have examined the correlation effects on the correlation energies of a ferromagnetic quasi-one-dimensional electron gas. The correlation energy is highly sensitive to both the wire width b and density parameter r_s . For the ultrathin wire in this limit, the correlation energy converges to $-\pi^2/360$ a.u. as $b \rightarrow 0$ for harmonic-delta potential, and our findings are in agreement with the high-density exact results [6,9].

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Quantum Correlation Effects of 1D Trapped Electrons Confined in the Transverse Plane by Infinite Square-Well and a Triangular Potential

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Abstract. We study the ground-state properties (static structure factor, pair correlation function, ground state energy, and correlation energy) of quasi-one-dimensional electron gas. The electrons are confined in the yz -plane by transverse confinement of infinite square-well and a triangular potential. Within this framework we employ the first order random phase approximation including self and exchange contribution to compute the ground state properties at high density r_s . Our results demonstrate that the confinement geometry significantly modifies effective electron interactions in one-dimensional (1D) systems. The static structure factor and pair correlation function reveal enhanced density correlations and spatial ordering, particularly signified by a pronounced $2k_F$ peak in the static structure factor and oscillatory behavior of period $2r_s$ in the pair correlation function. As $b \rightarrow 0$, the system approaches the idealized 1D system, where interactions dominate resulting in the most negative energies which reflects the stronger correlation effects.

INTRODUCTION

In low-dimensional systems, strong Coulomb interactions lead to behavior that deviates significantly from the predictions of Landau-Fermi liquid theory [1]. In particular, one-dimensional (1D) electron systems exhibit enhanced correlations and collective excitations characteristic of Luttinger liquids, motivating extensive theoretical and experimental research. The infinitely thin and finite width quantum wires under harmonic and cylindrical confinements have been examined by Vinod et.al. [2-5]. In this work, we study a quasi-one-dimensional electron system in which electrons are confined in the yz -plane by transverse confinement. This confinement is defined by an infinite square well along the y -direction, and by a triangular quantum well in the z -direction, described by a linear potential $V(z) = kz$ for $z > 0$, where k is a positive constant with hard-wall boundary conditions at $z = 0$ [6]. This leads to an effective electron-electron interaction potential $V(q)$. We use this framework to calculate ground-state properties such as the static structure factor (SSF), pair correlation function (PCF), ground state energy, and correlation energy at high density r_s , revealing how confinement geometry alters effective interactions in 1D systems.

THEORETICAL FORMALISM

The average electron-electron interaction potential in reciprocal space can be formulated as [6],

$$V(q) = \frac{2\beta^6}{a^2} \int_0^a dy' \int_0^a dy'' \sin^2\left(\frac{\pi y'}{a}\right) \sin^2\left(\frac{\pi y''}{a}\right) \int_0^a dz' \int_0^a dz'' z'^2 z''^2 e^{-\beta(z+z'')} K_0(qR). \quad (1)$$

Where K_0 is the zeroth-order modified Bessel function of the second kind.

The ground-state properties of a one-dimensional (1D) homogeneous electron gas have been determined through the application of the density response function and fluctuation-dissipation theorem. The density response function is given as [3-5],

$$\chi(q, \omega) = \frac{\chi_0(q, \omega) + \lambda \{\chi_1^{se}(q, \omega) + \chi_1^{ex}(q, \omega)\}}{1 - \lambda V(q) [\chi_0(q, \omega) + \lambda \{\chi_1^{se}(q, \omega) + \chi_1^{ex}(q, \omega)\}]}, \quad (2)$$

where λ denotes the order of the potential $V(q)$, while $\chi_1^{se}(q, \omega)$ and $\chi_1^{ex}(q, \omega)$ signify the first-order self-energy

and exchange corrections to the polarizability, respectively. The first-order approximation of Eq. (2), which is valid in the high-density limit, is expressed as,

$$\chi(q, \omega) \approx \chi_0(q, \omega) + \lambda V(q) \chi_0^2(q, \omega) + \lambda \{ \chi_1^{se}(q, \omega) + \chi_1^{se}(q, \omega) \}. \quad (3)$$

RESULTS AND DISCUSSIONS

The static structure factor is defined as,

$$S(q) = -\frac{1}{n\pi} \int_0^\infty \chi(q, i\omega) d\omega. \quad (4)$$

The pair correlation function is the inverse Fourier transform of static structure factor as,

$$g(r) = 1 - \frac{1}{2n\pi} \int_{-\infty}^{+\infty} [1 - S(q)] \exp(iqr) dq. \quad (5)$$

The correlation energy per electron is given by [4,5],

$$\varepsilon_c = \frac{1}{4\pi} \int_0^\infty V(q) S_1(q) dq. \quad (6)$$

Where $S_1(q) = S_1^d(q) + S_1^{se}(q) + S_1^{ex}(q)$, denotes the first-order SSF, which includes contributions from exchange and direct terms of SSF as the self-interaction term vanishes.

The ground-state energy can be evaluated as [4,5],

$$E_g = E_0 + \frac{n}{2} \sum_{q \neq 0} V(q) [S_0(q) - 1] + \frac{n}{4} \sum_{q \neq 0} V(q) [S_1(q)]. \quad (7)$$

Where $E_0 = \pi^2/24r_s^2$, is kinetic energy and $S_0(q)$ denotes non-interacting SSF.

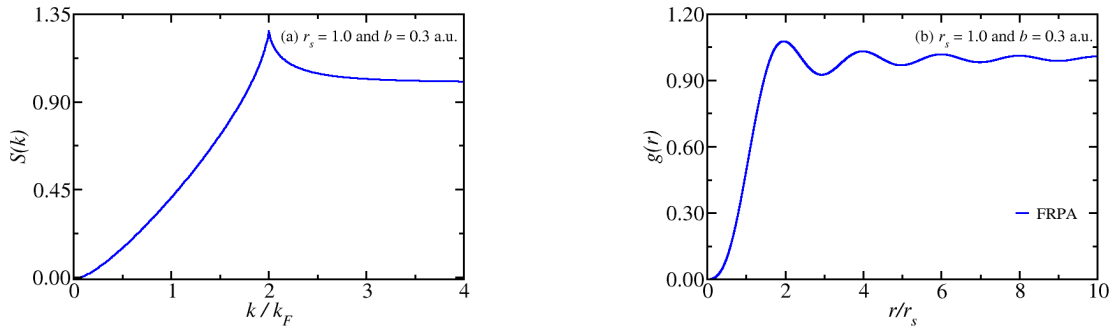


FIGURE 1. Static structure factor $S(k)$ plotted as a function of k/k_F in Fig. 1(a) and pair-correlation function $g(r)$ plotted as a function of r/r_s with periodic oscillations of $2r_s$ in Fig. 1(b).

Figure 1(a) shows the variation of $S(k)$ as a function of k/k_F for a quasi-1D wire of $b = 0.3$ a.u. and electron density of $r_s = 1.0$. At small k , $S(k)$ increases nearly linearly; however, a pronounced peak is observed near $k = 2k_F$, which signals the presence of strong density correlations. Figure 1(b) presents the pair correlation function $g(r)$, which provides real-space information about electronic correlations. The function starts from zero at $r = 0$, satisfying the Pauli exclusion principle, and then rapidly increases, reaching a maximum near $r/r_s \approx 2.0$. The depth and periodicity of the oscillations highlight the influence of the confinement-induced interaction profile embedded in $V(q)$.

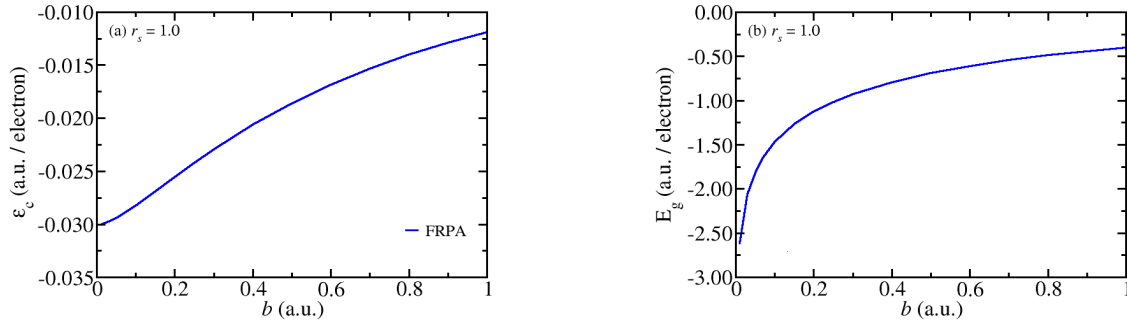


FIGURE 2. Correlation energy E_c plotted as a function of width b in Fig. 2(a) and ground state energy E_g plotted as a function of width b in Fig. 2(b) at a particular electron density $r_s = 1.0$.

Figure 2(a) depicts the variation of the correlation energy per electron ϵ_c as a function of the wire width b at a fixed density $r_s = 1.0$. The correlation energy becomes progressively less negative with increasing b , indicating a reduction in the strength of electron–electron correlations as the wire broadens. In the limit $b \rightarrow 0$, corresponding to an idealized 1D system, the correlation energy reaches its minimum, reflecting the pronounced role of correlations in one-dimensional systems. Figure 2(b) shows the total ground-state energy per electron E_g , as a function of b for the same electron density. Similar to ϵ_c , the ground-state energy increases (becomes less negative) with increasing b . Notably, the increase is nonlinear, with a steep slope as $b \rightarrow 0$, signifying the dominant influence of strong confinement in the quasi-1D limit.

CONCLUSION

Our results highlight the crucial role of dimensional confinement in shaping the ground-state properties of quasi-one-dimensional electron systems. The static structure factor and pair correlation function reveal enhanced density correlations and spatial ordering, particularly signified by a pronounced $2k_F$ peak in SSF and oscillatory behavior of period $2r_s$ in PCF. In addition, the variation of the correlation energy ϵ_c and ground-state energy E_g with the confinement width b demonstrates that electron–electron correlations are suppressed with increasing b , as indicated by the less negative energies. As $b \rightarrow 0$, the system approaches the idealized 1D system, where interactions dominate resulting in the most negative energies which reflects the stronger correlation effects. These findings reveal how our confinement model influences the ground-state properties of quasi-1D systems.

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Systematic Growth of Layered Metallic 1T–VS₂ using Chemical Vapor Deposition

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Abstract. In this work, the systematic growth of large-area 1T-VS₂ flakes via atmospheric pressure chemical vapor deposition (APCVD) is achieved, with lateral sizes in the range of 15 – 30 μm . The formation of the predominant 1T-phase is evident with the strong amorphous background, along with the presence of minor V_5S_8 as a secondary phase. Electrical characterization reveals linear I–V behavior, validating the metallic nature of the material, with a measured sheet resistance $\sim 20\text{ k}\Omega$. The resistivity, independently evaluated using both geometrical and analytical models, was consistently found in the range of 20 – 40 $\mu\Omega\text{m}$. These results demonstrate the growth of crystalline 1T-VS₂, with robust metallic electrical performance.

INTRODUCTION

Over the past decade, two-dimensional (2D) materials have garnered immense attention because of their remarkable mechanical, electronic, and optical properties, offering significant potential for next-generation technological applications. Among these, metallic transition metal dichalcogenides (MTMDCs) have emerged as particularly attractive candidates owing to their high electrical conductivity and the recent observation of room-temperature ferromagnetism, which opens new opportunities in electronics, spintronics, and energy-related devices [1], [2].

Among the various transition metal dichalcogenides, Vanadium Disulfide (VS₂) has demonstrated promising magnetic and electronic properties. Magnetic hysteresis at 300 K has been reported in exfoliated VS₂ nanosheets, while temperature-dependent ferromagnetism has also been observed in hydrothermally synthesized, vacuum-cleaved, and powdered VS₂ systems [3]. In this work, 1T-VS₂ flakes were synthesized via atmospheric pressure chemical vapor deposition (APCVD), exhibiting metallic behavior with a measured sheet resistance of approximately 20 k Ω .

RESULT AND DISCUSSION

Structural analysis

Figure 1(a) displays the optical microscope image of the synthesized 1T-VS₂ flakes. The observed flakes exhibit a well-defined hexagonal morphology with a typical lateral dimension in the range of 15–20 μm . The background of the black dots represents the multiple nucleation sites within the substrates, which are of the order of a few tens of nanometres. The corresponding field-emission scanning electron microscopy (FESEM) image, shown in Figure 1(b), further confirms the hexagonal geometry, along with the presence of grains within the flakes. The FESEM image also reveals the nucleation sites, which appeared to be black dots in the optical microscope image. Image analysis using

ImageJ software reveals an average lateral size of approximately $15\ \mu\text{m}$, with the largest measured flake reaching up to $31\ \mu\text{m}$.

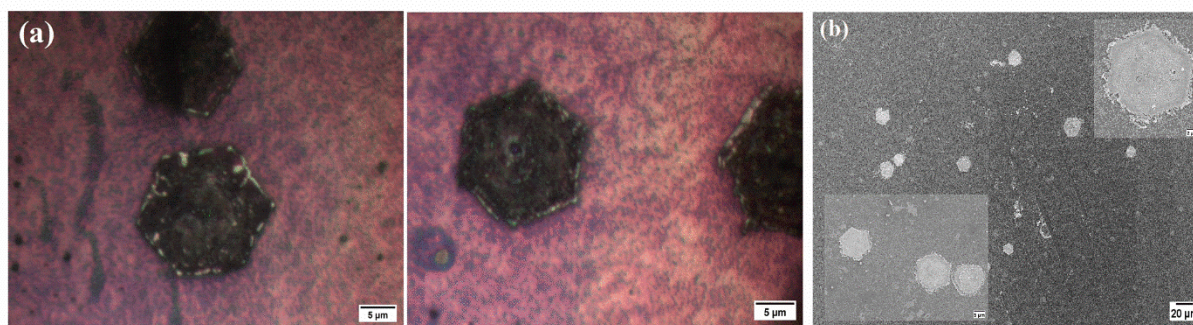


Figure 1. (a) Optical microscope image, (b) FESEM micrograph of the prepared 1T-(VS₂).

X-ray diffraction (XRD) analysis, Figure 2(a), reveals that the synthesized material primarily crystallizes in the 1T-VS₂ phase, with a minor presence of V₅S₈ as a secondary phase. The phase identification is based on JCPDS card No. 00-036-1139 for VS₂ and No. 00-029-1381 for V₅S₈ [3]. The indexing of the obtained peaks, intense enough in the XRD pattern, can be done based on the mentioned JCPDS cards, where peaks around 32° , 36° , 45° , 47° , and 58° corresponds to the (hkl) planes as (002), (101), (102), (003), and (110) of VS₂ as quoted in Figure 2(a) with red coloured text. Those planes (222) and (040) around 42° and 55° are of V₅S₈ quoted in Figure 2(a) with blue text. Complementary Raman spectroscopy Figure 2(b) exhibits well-defined peaks around 141 , 191 , 283 , and $406\ \text{cm}^{-1}$ which correspond to the rocking and stretching vibrations of V-S bonds or their combination. Peaks around 141 and $283\ \text{cm}^{-1}$, correspond to the in-plane E_{1g} and E_{2g} vibrational modes, respectively, along with a prominent A_{1g} out-of-plane mode at $406\ \text{cm}^{-1}$, consistent with the 1T-VS₂ phase [1], [2]. The sharpness of the Raman features confirms high crystallinity, supporting the predominance of the 1T-VS₂ phase despite minor off-stoichiometry detected in XRD.

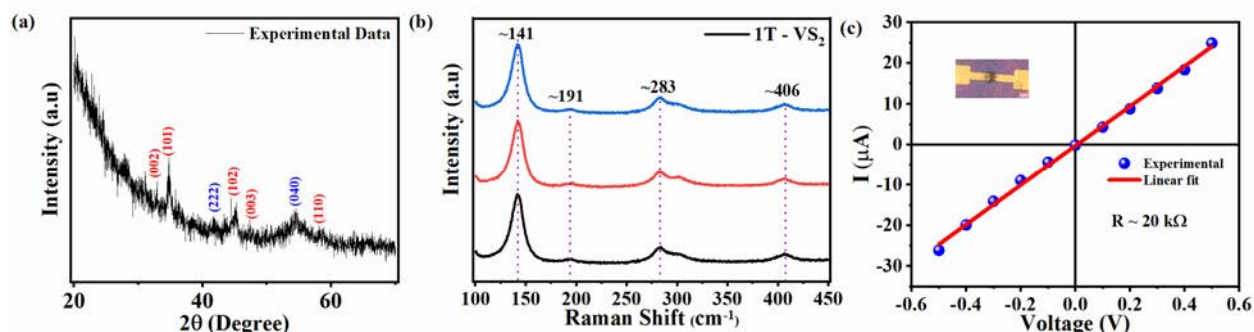


FIGURE 2. (a) XRD pattern, (b) Raman spectrum of CVD grown 1T-(VS₂) and (c) I-V characteristics of the obtained hexagonal flakes measured for a two-terminal device as shown in the inset.

I-V Characteristics

Figure 2(c) presents the room temperature current–voltage (I–V) characteristics of the fabricated two-terminal device (inset, Figure 2(c)), patterned via standard photolithography, along with the deposition of the gold electrodes via thermal evaporation on the large VS₂ flakes of lateral size of the order of $31\ \mu\text{m}$. The distance between the two electrodes is approximately $12\ \mu\text{m}$. The linear I–V characteristics of the prepared device indicate ohmic behaviour, confirming the metallic nature of the synthesized material. A linear fit to the experimental data yields a device resistance on the order of $\sim 20\ \text{k}\Omega$ [3]. Comparatively, the resistance value measured by Littlejohn *et. al*[3] is of the order of $\sim 22\ \Omega$. This relatively high resistance can be attributed to the partial oxidation of the flakes during the fabrication or measurement process. The resistivity of the sample can be evaluated by the methods mentioned by

Littlejohn *et al.* [3] which assumes that the sample has a rectangular shape of width W , length L , and thickness t . So, the resistance is defined as $R = \left(\frac{\rho L}{Wt}\right) = \frac{R_s L}{W}$, where $R_s = \rho/t$ is the sheet resistance. Assuming the thickness of the flakes to be approximately 100 nm, the value of resistivity, $\rho \sim 20 \mu\Omega m$. Another method for calculating sheet resistance of two two-dimensional rectangular samples using two probes is to fit the experimental I-V data by the equation [3], [4] given as

$$V = \frac{IR_s}{\pi} \left[\frac{e^{-\left(\frac{2\pi s}{W}\right)} - 1}{\left(1 + e^{-\left(\frac{2\pi L}{W}\right)}\right)} + \frac{\pi s}{W} + \ln \left(1 - e^{-\left(\frac{4\pi s}{W}\right)}\right) - \ln \left(1 - e^{-\left(\frac{2\pi s}{W}\right)}\right) \right] \quad [1]$$

where s – distance between the electrodes, and then evaluating ρ similarly as before, which gives $\rho \sim 37.5 \mu\Omega m$ almost similar to that obtained by the first method.

CONCLUSION

In summary, large-area 1T-VS₂ flakes were systematically grown via APCVD, yielding well-defined hexagonal domains with predominantly metallic 1T-phase characteristics. XRD and Raman analyses confirmed the formation of crystalline VS₂, with minor contributions from secondary phases. The observed linear I-V characteristics and low resistivity further establish the metallic transport behaviour of the synthesized flakes, underscoring their potential for future electronic and spintronic devices.

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Fe Impurity-Driven Magnetism in 2D-1T'-MoX₂ Monolayers: A First-Principles Study

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Abstract: Since the isolation of single-layer graphene, 2D van der Waals (vdW) materials especially polymorphic transition metal dichalcogenides (TMDs) have gained significant attention for their tunable electronic structures and quantum properties. Using first-principles calculations, we prove that Fe atoms prefer interstitial sites only the in ditellurides but not the disulfides and diselenides counterparts, under Te-poor conditions. Such interstitial Fe atom induces strong magnetism ($2\mu_B$) and highlighting the potential of defect engineering for spintronic, quantum, and energy-related applications.

INTRODUCTION

The isolation of single-layer graphene has driven significant interest in exploring two-dimensional van der Waals (2D-vdW) materials, owing to their remarkable and unconventional properties. In this category, transition metal dichalcogenides (TMDs) [1–4] are particularly notable for their wide variety of electronic band structures and fascinating quantum phenomena, which differ substantially from those present in their bulk counterparts. Monolayer (1L) of MoX₂ exhibits intriguing semiconductor-to-metal transition [5] with unique electronic structures, enabling novel quantum phenomena. By the density functional theory (DFT) calculations, we have investigated its post-growth deposition of Fe atoms in 1T' phase of 1L-MoX. Overall, this theoretical study of Fe doping leads to site-dependent structural and magnetic variations in 1T' phase of 1L-MoTe₂ [1].

COMPUTATIONAL METHODS

The spin-polarized DFT studies are carried out by optimized 1T' phase of 1L-MoX₂ structure for different atop configurations using the pseudopotential-based projector-augmented wave method of generalized-gradient approximation (GGA) by Perdew-Burke-Ernzerhof exchange-correlation (PBE) functional as given in Vienna ab initio simulation package (VASP) [6]. A 2×4×1 rectangular supercell is modeled for doping concentration. The wavefunctions are converged to 10⁻⁶ eV with 500 eV plane wave cutoff, and atomic forces are relaxed below 0.01 eV/Å without any symmetry constraints, using Monkhorst-Pack k-mesh sampling including spin-orbit coupling (SOC). The phonon dispersion calculation performs using the Phonopy code. The spin resolved band structures generated by VASPkit along the high-symmetry paths of Brillouin zone are plotted using PYPROCAR code. The phonon dispersion calculations are done by finite displacement method as mentioned in VASP. The optimized ball-and-stick models are shown using VESTA software.

RESULTS AND DISCUSSION

The top and side views of selected area of optimized atomic structures of Fe in distinct adatom configurations such as Te-top, H-top, Mo-top inside, interstitial (Int) site and Mo-substitutional site (Sub) for 1T' phase of 1L-MoX₂ is shown in Fig 1(a-f). The Mo–Te bond length (2.77 Å) is noticeably larger than that in pristine MoX₂ systems, where Mo–S and Mo–Se bonds are shorter (≈2.44 Å), reflecting the larger atomic size of Te compared to S and Se. The Fe atom is unstable at the X-top site, whereas the H-top becomes the most stable surface adatom configuration in all the dichalcogenides. Most interestingly, the Int site becomes the most stable configuration compared adatom sites only in the 1L-MoTe₂ monolayer. The Int configurations are not stable in disulfides and di selenides. In 1L-MoTe₂, the Int configuration is 0.8 eV/Fe higher stable than the H-top [1], inducing strong magnetism with 2 μ_B . Whereas the

Int site exhibit a higher value of $2\mu_B$ compared to the Sub with $1.08 \mu_B$. Overall, Fe doping in the 1T' phase of 1L-MoTe₂ modifies the local bond lengths and induces significant magnetism, with the magnetic moment varying strongly depending on the adsorption site.

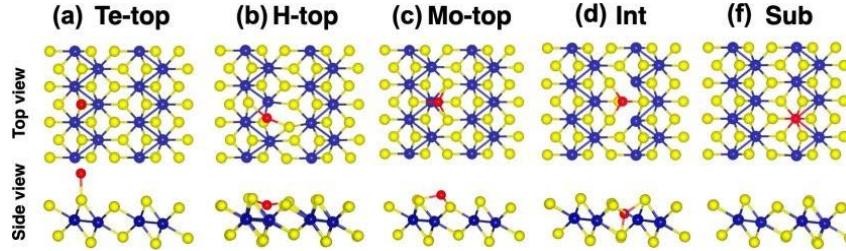


FIGURE 1. Top and side views of Fe in various adatom configurations Te-top, H-top, Mo-top, interstitial (Int) site and Mo-substitutional site (Sub) in 1T' (a-f) phases of MoX₂ (X = S, Se and Te). The blue, yellow, and red colored balls represent the Mo, Te, and Fe atoms, respectively.

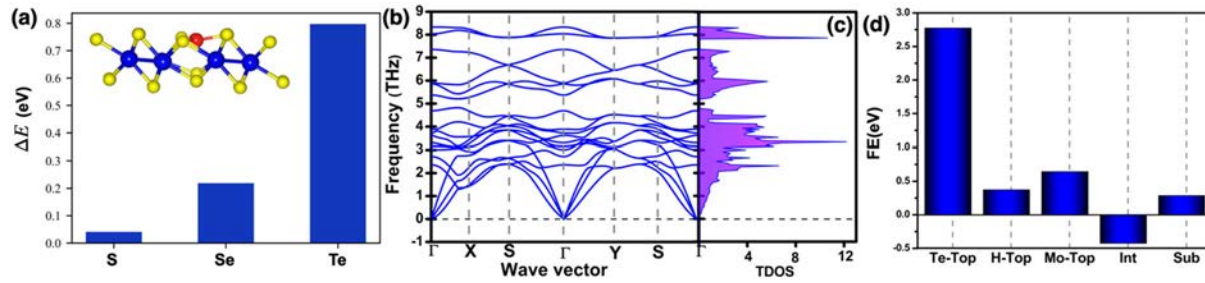


FIGURE 2. (a) E_{diff} (eV) represents the energy difference between the stable surface adatoms H-top to interstitial site (Int) for 1T'-MoX₂ (X = S, Se, Te); (b) Phonon dispersion spectrum and (c) phonon density of states of 1T'-MoTe₂ along high-symmetry paths without any imaginary modes throughout the Brillouin zone (d) Formation energy (FE) per Fe of different impurity configurations in 1T' phase of MoTe₂.

The E_{diff} signifies the energy difference between the H-top and Int-site for different TMD like MoX₂ (X = S, Se, Te). For other chalcogen like S and Se the Fe impurity does not even go in Int site, it is only bind in the plane of the chalcogen layer as shown by the inset Fig 2(a). The Int-site is only stable for MoTe₂ as shown by the higher energy difference as shown in Fig 2(a). The phonon dispersion curves along selected high-symmetry directions depicted by Fig 2(b) confirms the dynamic stability due to the absence of any imaginary modes throughout the Brillouin zone for the pristine MoTe₂. The total phonon DOS (TDOS) as given in Fig (c) further supports the mechanical robustness this, showing forbidden regions between 5.0-5.8 THz and 7.4-7.8 THz, likely arise due to atomic mass or bonding contrast, which can potentially impact in thermal transport. To compare their formation stability, we calculate their formation energy (FE) using eq. (1), where $E(L+Fe)$, $E(L)$ and $\mu(Fe)$ are total energies of Fe added MoTe₂ layer, pristine MoTe₂ layer and chemical potential of Fe(110) monolayer, respectively. The strong negative FE prominently shows that the Fe atom preferentially occupy the Int site of 1T'-MoTe₂ in compared to the other configuration as shown in Fig 2(d).

The $\mu(Mo)$ is only considered for the Fe-substituted MoTe₂ layer, as eq. (2), where $E(Fe-MoTe_2+Mo)$ and $E(Fe-MoTe_2)$ represent the total energies of Fe-substituted 1T' phase of 1L-MoTe₂ with and without Mo atom, respectively.

$$FE = E(L + Fe) - E(L) - \mu(Fe) + \mu(Mo) \quad (1)$$

$$\mu(Mo) = E(Fe - MoTe_2 + Mo) - E(Fe - MoTe_2) \quad (2)$$

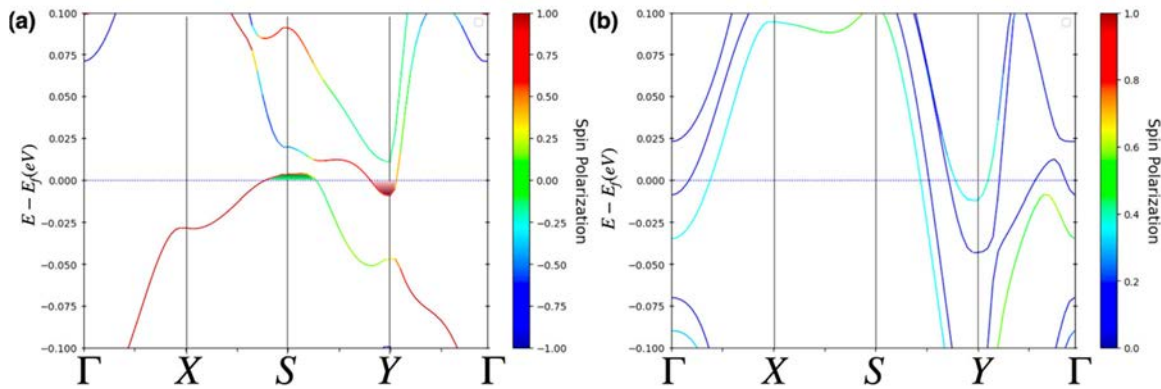


FIGURE 3. The spin-polarized band structures with spin-orbit coupling (SOC) for Fe-doped MoTe₂ at (a) Int and (b) Sub sites. The color bar denotes spin polarization, where +1 and -1 represents the approximate eigenstates of the spin projection operator for up-spin and down-spin states, respectively. "Adapted with permission from [1] copyright {2025} American Chemical Society."

The band crossings near the Fermi level (E_f) at high-symmetry points between S, and Y in the band structure in Fig 3 (a) signifies the minimal overlap between conduction and valence bands in momentum space by creating the hole packet (green) and electron packet (red) shadows near the E_f level. Which suggest not a conventional metal but rather an electron-hole compensated semimetal [1]. While the prominent band crossing represents the metallic nature as shown in Fig 3(b) for sub case. The origin of the metallic behavior of Sub case highly dispersive bands arises from strong hybridization with the d-orbitals of Fe and Mo within zigzag chain.

CONCLUSIONS

Our investigation into Fe doping in 1T' phase of 1L-MoX₂ reveals a preference for Int sites for 1L-MoTe₂ under Te-poor conditions, inducing strong magnetism and showcasing the potential of defect engineering for spintronic and quantum device applications in 1T' phase of 1L-MoTe₂.

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Role of Electron Correlation in the Surface Electronic Structure of type-II Dirac Semimetal NiTe₂

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Abstract: We investigate the electronic structure of NiTe₂ using angle-resolved photoemission spectroscopy and theoretical approaches. While the bulk as well as surface Fermi surface is well described within mean-field approaches, an accurate description of the topological surface state appearing much below the Fermi level necessitates the consideration of strong surface electronic correlation effects. Our study highlights the critical role of many-body interactions in determining the topological surface states in NiTe₂, advancing the understanding of electron correlation effects in topological quantum materials.

INTRODUCTION

Two-dimensional van der Waals transition metal dichalcogenides, 1T-MX₂ (M = Ni, Pd, Pt; X = Te) have emerged as promising platforms for realizing type-II Dirac Fermions, characterized by strongly tilted Dirac cones, where the coexistence of electron and hole pockets at the Dirac point results in a finite density of states [1-3]. The nontrivial band topology of NiTe₂ gives rise to type-II bulk Dirac point in the vicinity of Fermi level (E_F), as well as various topological surface states, offering promising prospects for next-generation electronic and spintronic devices [3,4]. Notably, two prominent surface states have been the focus of extensive experimental and theoretical investigations, one near E_F along the $\bar{\Gamma} - \bar{M}$ (SS0) and another forming a Dirac-like conical crossing at the $\bar{\Gamma}$ (SS2), located far below the E_F [3,4]. While density functional theory (DFT) captures the bulk electronic structure accurately, it shows clear discrepancies in predicting the energy position of the topological surface states, SS2 [3-5]. Electron correlation significantly influences band topology and topological surface states in various transition metal compounds [6,7]. Including GW-level correlations reveal that correlation effects drive PtSe₂ and PtTe₂ into trivial metallic states, whereas NiTe₂ retains a strongly tilted type-II Dirac cone [6]. These findings, together with discrepancies in the topological surface state position, suggest that electron correlations effects are important to describe the surface electronic structure of NiTe₂. Here, we investigate the electronic structure of NiTe₂ using angle-resolved photoemission spectroscopy (ARPES) combined with DFT. We demonstrate that an accurate treatment of surface electronic correlation is essential for correctly describing the band topology and topological surface states in NiTe₂.

METHODOLOGY

Photoemission measurements were performed on *in situ* cleaved NiTe₂ single crystals [8] at 30 K, with total instrumental resolutions of ~10 meV for ARPES using He I radiation ($h\nu = 21.2$ eV). DFT calculations were performed using projector augmented wave method as implemented in VASP [9] with a 500 eV energy cutoff and Γ -centered $18 \times 18 \times 10$ k -mesh, employing the GGA-PBE functional [10]. Surface band structure was calculated using a Te-terminated slab of ten primitive unit cells along [001] direction with 10 Å vacuum. Spin-orbit coupling was included in all calculations.

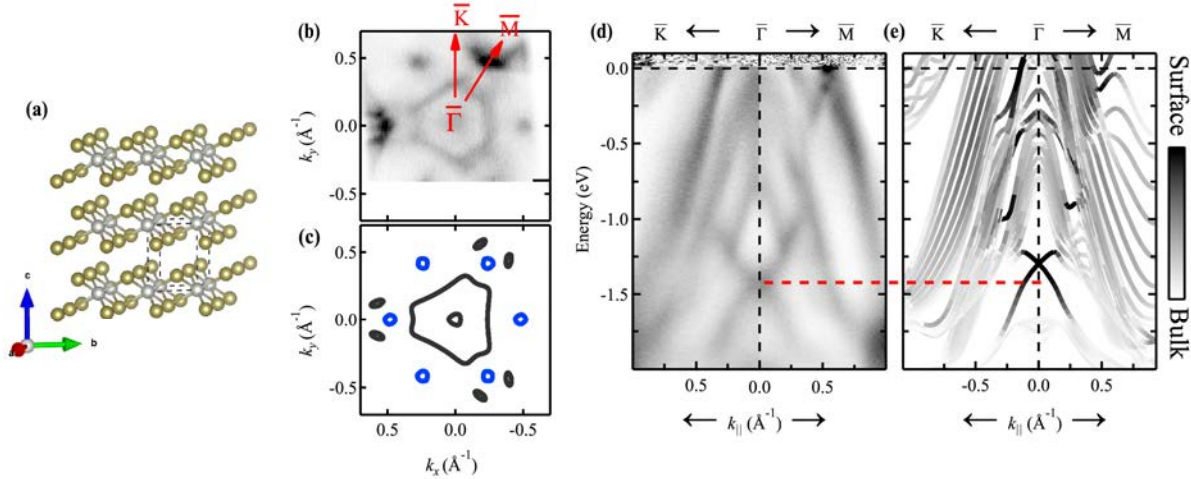


FIGURE 20. (a) Crystal structure of NiTe₂, where grey and golden spheres represent Ni and Te atoms respectively. FS map of NiTe₂ obtained from (b) ARPES and, (c) DFT calculation (black and blue show the bulk and surface FS). Band dispersion along $\bar{K} - \bar{\Gamma} - \bar{M}$ from (d) ARPES and, (e) DFT calculation. Red dashed line indicates SS2 position.

RESULTS AND DISCUSSION

NiTe₂ crystallizes in the trigonal structure with the space group $P\bar{3}m1$, comprising a Ni layer sandwiched between two Te layers, as shown in Fig. 1(a). The weak van der Waals interaction between adjacent Te layers render the Te-terminated plane the natural cleavage surface. To investigate its surface electronic structure, we show the Fermi surface (FS) mapped using ARPES measurements with He I radiation in Fig. 1(b). The FS exhibits a three-fold symmetry, featuring a small triangular pocket and an irregular hexagon-shaped contour centred at $\bar{\Gamma}$. Additionally, arc-shaped and circular features appear along alternate $\bar{\Gamma} - \bar{M}$ directions. The arc-shaped feature consists of three small electron pockets. Despite its layered structure, NiTe₂ exhibits strong out of plane (k_z) dispersion and thus the symmetry and shape of ARPES FS strongly depends on the photon energy [3-5]. In the present case 21.2 eV photon energy probes the $k_z = 0.34 c^*$ plane of the Brillouin zone [4]. Thus, we show the DFT calculated FS for the k_z value of $0.34 c^*$ in Fig 1(c). The calculated bulk FS (black) well replicate the features in ARPES FS except for six-fold symmetric circular features along $\bar{\Gamma} - \bar{M}$ directions. It is important to note here that NiTe₂ hosts various surface states, including a parabolic band that crosses the E_F , giving rise to electron pockets [3,4]. We calculated the surface FS using slab configuration within DFT (shown by blue lines in the Fig. 1(c)), which exhibits six-fold symmetric circular electron pockets along $\bar{\Gamma} - \bar{M}$. The overall experimental FS aligns excellently well with the DFT calculated FS indicating a three-fold symmetry of bulk and six-fold symmetry of surface state. These results suggests that the electron correlation may not be important in describing the bulk FS.

The ARPES spectra along $\bar{K} - \bar{\Gamma} - \bar{M}$ direction (highlighted by red in Fig. 1(b)) have been shown in Fig. 1(d). The surface states (SS0) along $\bar{\Gamma} - \bar{M}$ crosses the E_F forming electron pockets. Another topological surface state (SS2) forms a Dirac-like conical crossing at Γ within the parity-inverted bulk gap. The surface state, SS2 is formed by the crossing of linearly dispersing band at ~ -1.42 eV. We show the DFT calculated surface band structure using slab configuration in Fig. 1(e) along $\bar{K} - \bar{\Gamma} - \bar{M}$ direction. The DFT calculated band dispersion nicely captures all the surface state but exhibits a discrepancy in the position of SS2 (As shown by red dashed line), locating it at a position of -1.30 eV. This discrepancy has also been consistently reported in various studies, where the experimentally observed Dirac crossing always appears at lower energy than the DFT obtained results [3-5]. The surface state SS2 is formed within the parity inverted band gap formed by the bands having hybridized Ni 3d and Te 5p states [3,4]. However, the electron correlation effects in the bulk are reported to be weak, allowing the bulk electronic structure to be accurately described within conventional DFT [3,8].

Electron correlation effects are significantly enhanced at the surface, where the effective correlation strength is expected to be larger as a result of significantly smaller screening and coordination number [11]. Thus, we calculate the surface band structure of NiTe₂ within DFT+U (U = Hubbard parameter) method, with $U = 5$ eV applied to the

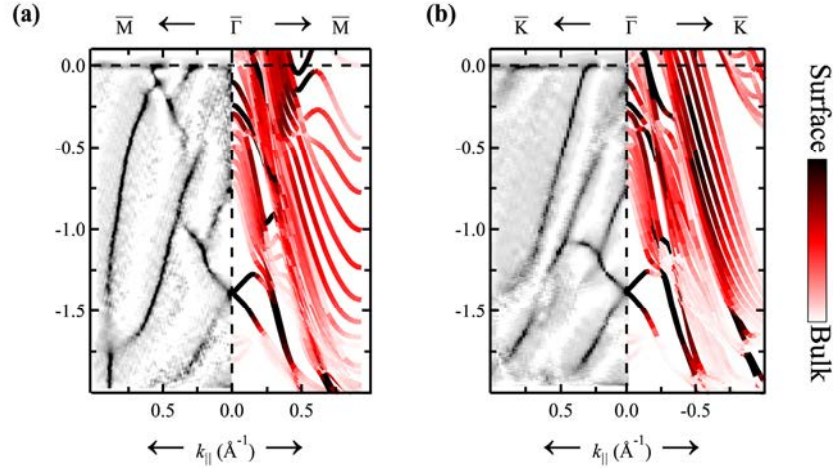


Figure 21. Comparison of 2D curvature plot of ARPES spectra (left) and DFT+ U results along (a) $\bar{\Gamma} - \bar{M}$ and (b) $\bar{\Gamma} - \bar{K}$.

surface Ni atoms only and compare the results with ARPES spectra in Figs. 2(a) and 2(b). The left halves of the Figs. 2(a) and 2(b) show the 2D curvature plot of the ARPES spectra (shown in Fig. 1(d)), used to suppress background intensity and enhance the contrast and sharpness of dispersive band features, while the right halves show the DFT+ U calculated surface band structure. The striking similarity between the experimental spectra and theoretical results regarding the energy dispersions and positions of surface state SS2 and various other surface state is clearly evident. These results suggest that the energy position of Ni-3d and Te-5p hybridized surface state SS2 can only be described by inclusion of the enhanced surface electronic correlations.

CONCLUSION

In summary, we highlighted the role of electron correlation in the surface electronic structure of NiTe₂ using photoemission spectroscopy and band structure calculation within DFT and DFT+ U method. The experimental Fermi surface can be well captured within the DFT framework. The enhanced electron correlation effects at the surface results in electron correlation induced shifting of the topological surface states. Our study demonstrates that inclusion of the surface electronic correlation is essential for accurately determining the topological surface state of NiTe₂.

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Electron-Hole Plasma Optical Gain in Metal Halide Perovskites Quantum Dots

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Abstract. Metal halide perovskites (MHP) quantum dots (QDs) are a promising platform for the lasing and optoelectronic applications due to their exceptional properties. Despite various demonstrations of optical gain in MHP QDs, the role of electron-hole plasma (EHP) phase remains largely unexplored. Here, we investigate the role of EHP state in amplified spontaneous emission (ASE) in CsPbBr₃ QDs by using temperature and fluence dependent photoluminescence and transient absorption measurements. At 5 K, two ASE bands with the threshold fluences of 25 and 100 $\mu\text{J}/\text{cm}^2$ corresponding to excitonic and EHP phase are demonstrated respectively. The EHP driven ASE produces a broadband optical gain of ~ 150 meV, indication of strong many body interactions. This dual-band behaviour persists for up to 200 K and disappears at room temperature due to the enhanced non-radiative recombination, phonon populations and a higher Mott density threshold. This work demonstrates the potential of EHP to be a practical platform for studying macroscopic quantum phenomena and developing optoelectronic devices.

INTRODUCTION

. Metal halide perovskites (MHP) quantum dots (QDs) have emerged as a promising material for optical amplification and lasing application due to their exceptional properties such as strong light-matter interaction, near unity photoluminescence (PL) quantum yield (QY), narrow emission linewidth and high defect tolerance nature [1-3]. Recently, in 2015, amplified spontaneous emission (ASE) from CsPbBr₃ QDs demonstrated, but the gain mechanism, particularly role of electron-hole plasma (EHP) phase is not explored too much [4]. At high carrier density, coulomb screening weakens the excitonic interactions and drive transition from bound excitons to correlated EHP state. The lasing action through EHP has been reported in ZnO nanostructures and organometallics perovskites [5,6]. However, its role in colloidal perovskite quantum dots remains largely unexplored. In this work, we have demonstrated that ASE through EHP state in CsPbBr₃ QDs by using fluence and temperature dependent photoluminescence and transient absorption measurements.

RESULT AND DISCUSSION

To demonstrate our study, we have synthesized uniform, spheroidal-shaped, monodispersed and high-quality CsPbBr₃ quantum dots (QDs) by using a room temperature synthesis technique [7]. The ground-state optical absorption of synthesized spheroidal CsPbBr₃ QDs for 5 K, demonstrates two sharp excitonic absorption peaks, see Fig. 1 (a). To investigate the ASE, we have used the femtoseconds Photoluminescence (PL) spectroscopy by exciting the CsPbBr₃ QDs with a pulse of photons of 120 fs whose energy is 3.1 eV.

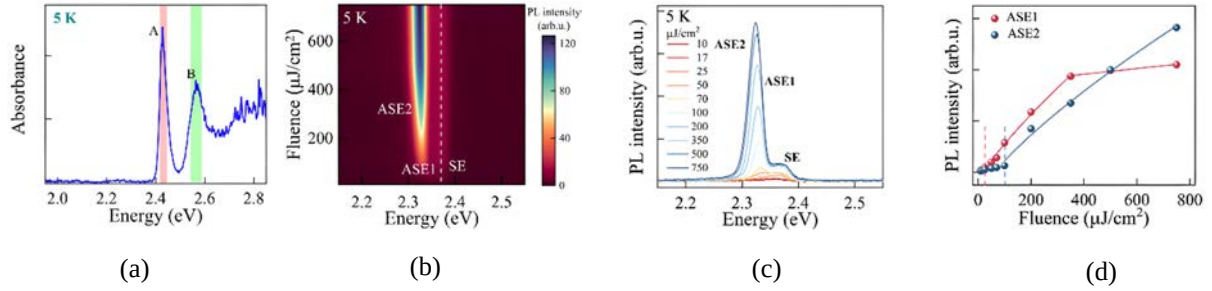


FIGURE 1. (a) Optical absorption spectra of CsPbBr₃ QDs. (b) 2D color plot of fluence dependent photoluminescence (PL) spectra. (c) PL spectral profile at selected fluences (d) Variation of PL intensity as a function of excitation fluence.

Figure 1 (b) shows the 2D color plot of fluence dependent PL spectra and Fig. 1 (c) represents the spectral profiles at 5 K. It is clear from Fig. 1(b) and 1(c), at low excitation fluence ($10 - 25 \mu\text{J}/\text{cm}^2$), a broad spontaneous emission (SE) peak emerges at $\sim 2.359 \text{ eV}$ with a linewidth of $\sim 45 \pm 4 \text{ meV}$. As the excitation fluences surpassed $25 \mu\text{J}/\text{cm}^2$, a sharp and narrow peak emerged towards lower energy at $\sim 2.333 \text{ eV}$, exhibit a linewidth of $\sim 23 \text{ meV}$ and a superlinear fluence-dependent behaviour indicative of ASE (see Fig. 1 (c)), labelled as ASE1. With further increasing the excitation fluence beyond $\sim 100 \mu\text{J}/\text{cm}^2$, the ASE1 undergoes an unusual redshift and broadening, indicating the onset of another ASE band at $\sim 2.315 \text{ eV}$, (Fig. 1(c)). The threshold behaviour of both ASE peak is summarized in Fig. 1 (d).

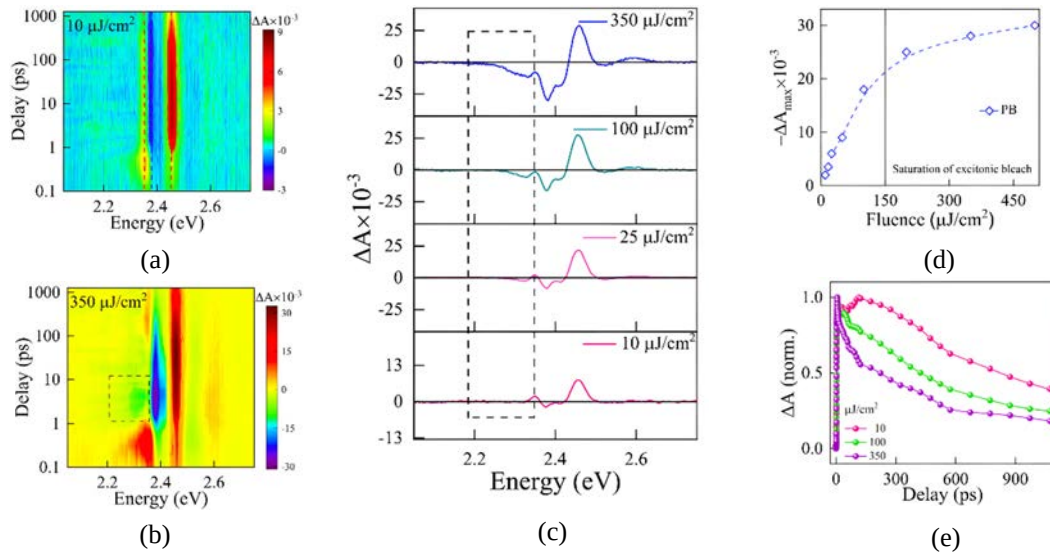


FIGURE 2 (a) 2D contour plot of TA spectra at $10 \mu\text{J}/\text{cm}^2$. (b) 2D contour plot of TA spectra at an excitation fluence of $350 \mu\text{J}/\text{cm}^2$. (c) Fluence dependent TA spectral profile (d) Variation of magnitude of excitonic bleach probed at 2.38 eV . (e) Kinetic profile of excitonic bleach A probed at $\sim 2.38 \text{ eV}$ at selected excitation fluences.

To find the nature of the electronic states underlying ASE1 and ASE2 process, we employed transient absorption (TA) measurements and change in absorbance (ΔA), reflecting the difference between excited and ground-state absorption, was monitored. Figure 2 (a) and 2 (b) represents the 2D color plot of TA spectra at 10 and $350 \mu\text{J}/\text{cm}^2$. At low excitation fluence (excitonic phase), the TA spectrum consist photobleach corresponding to excitonic position and absorption feature, similar to previous studies [8]. As we cross the Mott density regime (See Figs. 2 (b) and 2 (c)), the excitonic position experienced a blueshift and a broadening towards lower energy side of $\sim 150 \text{ meV}$, with onset at $\sim 2.22 \text{ eV}$. Such spectral evolution is characteristic of exciton ionization driven by strong Coulomb screening,

marking the emergence of a EHP state. Transition from excitonic to EHP phase is further evidenced by saturated behaviour of ΔA at higher excitation fluences (Fig. 2d) [8]. Figure 2(e) showing fluence dependent kinetic profile of bleach probed at ~ 2.38 eV, showing transition from monoexponential profile to biexponential behaviour.

Figure 3 (a) reveals the temperature dependent behaviour of ASE. As the temperature increased, due to more phonon populations and non-radiative losses, the FWHM of ASE peak increased and intensity decreased. Furthermore, it enhanced the threshold fluence of excitonic ASE (Fig. 3 (b)). Due to increased nonradiative losses at 300 K, the mott density is increases by ~ 60 times, so the EHP state will not form at room temperature.

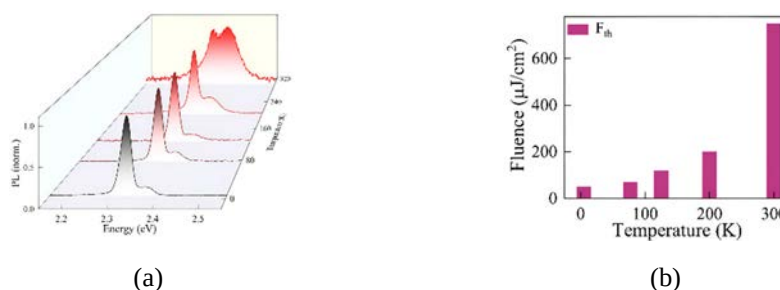


FIGURE 3 (a) PL spectral profile various temperatures at a constant excitation fluence of $\sim 750 \mu\text{J}/\text{cm}^2$. (b) Variation of ASE threshold as a function of temperature.

CONCLUSION

In summary, we have studied the electron-hole plasma induced optical gain in CsPbBr_3 quantum dots, highlighting EHP as a practical platform for studying macroscopic quantum phenomena and developing optoelectronic devices.

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Effect of Dimension Reduction on superconducting properties of Aluminum: Ab initio investigation

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Abstract. Aluminum (Al) is a well-known superconductor with a superconducting transition temperature of 1.2K in its bulk state. It is a workhorse material for fabrication of superconducting Qubits. Many experimental studies show that dimension reduction from 3D to 2D can extremely change the superconducting properties due to inclusion of Quantum effects. For aluminum it is experimentally observed that in the thin film structures the transition temperature and superconducting gap at fermi level have tendency to increase. In this study, by employing the first principal approaches like density functional theory (DFT) and Density functional perturbation theory (DFPT) we have calculated the superconducting properties of Aluminum in its bulk and monolayer state using Quantum ESPRESSO and EPW (Electron-Phonon coupling using Wannier functions) code. We have calculated the electron-phonon coupling constant (λ), Eliashberg spectral function ($\alpha^2F(\omega)$), superconducting transition temperature (T_c), superconducting gap (Δ). Our calculation showed that bulk state transition temperature (T_c) 1.2K is enhanced to around 7.5K in the monolayer state, which is in good agreement with experimental studies.

INTRODUCTION

Aluminum is "special" in quantum computing because of its exceptionally clean oxide, low decoherence, and ease of nanofabrication. These advantages make it an ideal material for building high-coherence superconducting qubits. Although it has a lower T_c than other superconductors, but its advantages in material quality and reproducibility outweigh this limitation in most quantum computing contexts. It is a simple metal with good electronic structure understanding along with superconductivity arising from conventional electron phonon coupling (EPC) mechanism, which makes it an ideal for validating first-principal approaches in the study of conventional superconductivity.

Ginzburg suggestion [1] has motivated many experimental research towards the investigation of effect of dimension reduction on the superconducting properties. For a 2D layer of a material superconducting properties and behavior can be drastically different from bulk state. It can enhance [2] as well as reduce [3-4] the superconductivity. This unexpected or complex behavior of superconductivity can be within both unconventional and conventional superconductors [5]. A recent experimental study on epitaxially grown aluminum thin films showed extreme enhancement of superconducting transition temperature when it was studied on thin films which are grown near to monolayer limit [6].

Though there are many experimental researches which investigate the effect of dimension reduction on the superconducting properties of aluminum but theoretically the effect is not studied widely. This motivated us to study this system using Quantum ESPRESSO [7] and EPW code [8]. The EPW code (built on top of Quantum ESPRESSO) is a powerful open-source tool designed for doing electron phonon calculations with ab initio approach. It relies on DFPT and maximally localized wannier function (MLWFs), which is used for the fine sampling of the Brillouin Zone (BZ). The code is primarily designed to calculate electron-phonon interactions, superconducting properties, and transport properties. EPW code serves as a powerful and versatile tool for the theoretical investigation of bulk and low-dimensional materials, bridging fundamental quantum mechanical theory and practical materials design.

THEORETICAL METHODOLOGY

Superconductivity in conventional superconductors arises from the pairing of electrons mediated by lattice vibrations (phonons). This interaction is captured through the electron-phonon matrix elements, which are the central quantities in the Migdal-Eliashberg theory. The EPW code implements this theory within the framework of DFT and

DFPT, allowing for the solution of the anisotropic Migdal–Eliashberg equations or, more commonly, the estimation of transition temperature using the isotropic Allen–Dynes modified McMillan formula.

The overall EPW computational workflow involves the following steps:

Ground-State DFT Calculation: Performed using Quantum ESPRESSO to obtain electronic eigenvalues, wavefunctions, and a charge density self-consistent field (SCF) solution on a coarse k-point mesh.

Phonon and EPC Matrix Elements via DFPT: Using the same pseudopotentials and cutoff parameters, DFPT is employed to compute the phonon dynamical matrices and electron-phonon coupling (EPC) matrix elements on a coarse q-point mesh.

Wannierization: The electronic bands near the Fermi level are projected onto maximally localized Wannier functions (MLWFs), using the Wannier90 code. This step enables interpolation of EPC quantities onto dense k- and q-point meshes without the need for costly DFPT calculations at every point.

Wannier Interpolation: EPW performs Wannier interpolation of the electron-phonon matrix elements and phonon properties onto dense Brillouin zone meshes. This step is essential to accurately compute quantities that require fine resolution around the Fermi surface.

Calculation of $\alpha^2F(\omega)$, λ , and T_c :

The Eliashberg spectral function $\alpha^2F(\omega)$ is computed using:

$$\alpha^2F(\omega) = \frac{1}{N(\varepsilon_F)} \sum_{q,v} \delta(\omega - \omega_{qv}) \sum_{k,n,m} |g_{k,n;k+q,m}^v|^2 \delta(\varepsilon_{k,n} - \varepsilon_F) \delta(\varepsilon_{k+q,m} - \varepsilon_F)$$

Where: $N(\varepsilon_F)$ is electronic density of states at the Fermi level, ω_{qv} is phonon frequency, $g_{k,n;k+q,m}^v$ are electron-phonon matrix elements, and $\varepsilon_{k,n}$ is the electronic energy for wavevector k and band n.

The electron-phonon coupling constant λ is calculated as:

$$\lambda = 2 \int_0^\infty \frac{\alpha^2F(\omega)}{\omega} d\omega$$

The logarithmic average phonon frequency is computed as:

$$\omega_{log} = \exp\left(\frac{2}{\lambda} \int_0^\infty \frac{\alpha^2F(\omega) \ln(\omega)}{\omega} d\omega\right)$$

The superconducting critical temperature is estimated using the Allen–Dynes modified McMillan equation:

$$T_c = \frac{\omega_{log}}{1.2} \exp\left(-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right)$$

Where: μ^* is the Coulomb pseudopotential.

In this work, superconducting parameters were calculated for both bulk and monolayer state (modeled using a (1×1) surface unit cell). For Density Functional Theory (DFT) calculations plain-wave pseudopotentials and general gradient approximation (GGA-PBE) exchange-correlation energy functional are used, with cutoff value of 240 Ry and 30 Ry for charge density and wavefunction respectively. Geometry optimization was carried out using the BFGS algorithm for both atomic positions and lattice parameters. For accounting van der Waals interaction Grimme's D2 dispersion correction scheme was used along with a 2D slab geometry for monolayer calculations. The Brillouin zone was sampled using a Monkhorst-Pack k-point mesh of $6 \times 6 \times 1$ and $6 \times 6 \times 6$ for monolayer and bulk state respectively. For avoiding periodic interaction perpendicular to the monolayer, a vacuum layer of thickness ~ 20 Å was added. Using the same pseudopotentials and cutoff parameters, DFPT is employed to compute the phonon dynamical matrices and electron-phonon coupling (EPC) matrix elements on a coarse q-point mesh.

For Wannierization sp^3 and sp^2 projections were used for bulk and monolayer respectively, along with the disentanglement window of 10eV above and below the fermi energy. For performing superconducting parameter calculations using electron-phonon wannier interpolations 60×60 k and q points grids were used. The grid is enough dense to ensure the convergence of the electron phonon coupling constant (λ) and Eliashberg spectral function $\alpha^2F(\omega)$. The calculations are done for different values of μ_c parameter starting from 0.1 to 0.16. Convergence threshold used for iterative calculation for isotropic Eliashberg calculations was 1×10^{-8} .

RESULTS AND DISCUSSION

Calculated superconducting parameters for bulk and monolayer aluminum (1×1 plane) are shown in below figure.

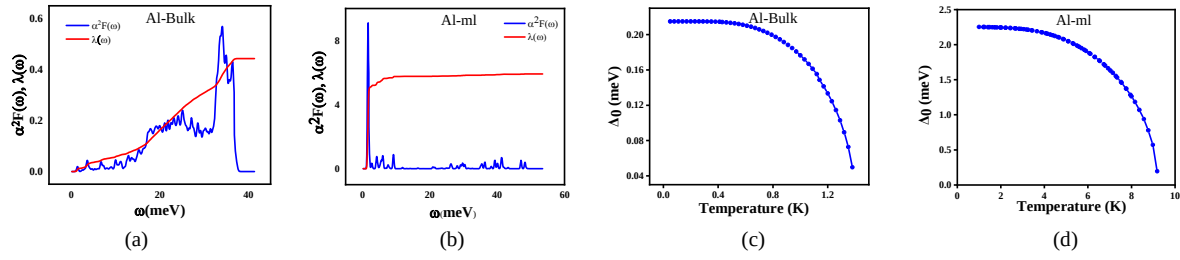


FIGURE 1. Eliashberg spectral function and electron phonon coupling constant (left), variation of superconducting gap with temperature (right) for bulk and monolayer aluminum.

For bulk state of Aluminum, we have done the calculation for μ_c value starting from 0.10 to 0.16. Increasing the μ_c value was leading to decrement in the value of transition temperature. The value $\mu_c=1.4$ showed good agreement of transition temperature of bulk state of Aluminum with experimental values which is equal to 1.2K. For bulk state of aluminum, the calculated superconducting transition temperature at $\mu_c=1.4$ is around 1.2K and superconducting gap is around 0.21eV, which is very near to the experimentally measured value ~ 0.18 eV. This good agreement with experimental values confirms the accuracy for our computational approach used for calculations. We have also done the anisotropic Migdal-Eliashberg calculation, in these calculations the superconducting gap is distributed in single energy range, which shows that aluminum is not a multiple gap superconductor. Calculation for monolayer showed that the superconducting transition temperature for 1 x 1 monolayer is increased to around 7.5K from 1.2K. This is in the agreement with the other experimental researches. The transition temperature around 5K has been measured experimentally for the thin films of aluminum.

Our studies highlight that superconductivity in aluminum arises from weak-coupling BCS-type mechanisms, with electron-phonon interactions being the primary driver. The spectral analysis reveals that low-frequency phonon modes contribute significantly to the coupling, consistent with the behavior expected in simple metals. The contribution is much higher in the monolayer form as comparable to the bulk state. Also, the electron phonon coupling constant is highly enhanced in the form of thin films. These results validate the use of QE and EPW as robust tools for studying conventional superconductors and establish a methodological foundation for future investigations of more complex superconducting systems.

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Many Body Correlation Effects in The Cylindrical Confinement of Quasi-One-Dimensional Quantum Wire

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Abstract. The many body correlation plays a crucial role in determining the physical properties of quantum materials. Their contribution has critical effect on the strength of the electron-electron coupling parameter r_s , which is a characteristic property of the emergent quantum materials. In this work, the electrons are confined in quasi-one dimension by the cylindrical potential. We use dynamical first-order random phase approximation which includes self and exchange-energy contributions to calculate the ground-state properties of quasi-one-dimensional ferromagnetic quantum wire at various wire widths b and density parameters r_s . We numerically calculated the pair-correlation function, static structure factor, and correlation energy at high-density. The pair-correlation function shows oscillatory behaviour for different r_s with the highest peak at higher value of coupling parameter. The $2k_F$ peak height of the static structure factor grows as r_s increases, indicating increased electron-electron correlation. We have also observed that the correlation energy converges to $-\pi^2/360$ for ultra-thin wire in the high-density regime ($r_s \leq 1$), which is in agreement with the exact high-density theory and quantum monte Carlo simulation.

INTRODUCTION

The systems consisting of interacting fermions has been successfully explained by Landau's Fermi Liquid Theory [1,2] for higher dimensional systems such as 2D and 3D, but it eventually breaks down in one-dimensional (1D) systems. In particular, this theory legitimizes the free electron model based on weakly interacting quasiparticles picture. The strong correlation occurring in 1D ensures that the excitations are collective in nature rather than like quasiparticles. The physical properties of 1D interacting systems can be described by Tomonaga-Luttinger (TL) liquid model [3,4]. The non-Fermi-liquid features has given a large impetus to both theoretical [6-11] and experimental [5] research on 1D materials. In this paper, we use a theoretical approach of first-order Random Phase Approximation (FRPA) to study the ground-state properties (i.e. pair-correlation function (PCF), static structure factor (SSF), and correlation energy) of quasi-1D quantum wire in a cylindrical confinement. We study the wire width (b) dependence of various ground state properties of interacting homogeneous electron gas (HEG) in the high-density regime using FRPA which includes exchange and self-energy contributions. We use Hartree atomic units ($\hbar = |e| = m_e = 4\pi\epsilon_0 = 1$) throughout this article.

THEORETICAL MODEL

We have considered a softened coulomb potential in cylindrical confinement of the form in the real space as [9,11]

$$V(x) \approx 1/\sqrt{x^2 + b^2}, \quad (1)$$

where b is the transverse width parameter of the cylindrical wire.

The Fourier transform of this potential is, $V(q) = 2K_0(bq)$, where K_0 is the modified Bessel function of the 2nd kind. The density response function is defined as [9,11]

$$\chi(q, \omega) = \frac{\chi_0(q, \omega) + \lambda \chi_1(q, \omega)}{1 - \lambda V(q) [\chi_0(q, \omega) + \lambda \chi_1(q, \omega)]}, \quad (2)$$

where λ indicates the order of the potential, $\chi_0(q, \omega)$ is noninteracting polarizability and $\chi_1(q, \omega) = \chi_1^{se}(q, \omega) + \chi_1^{ex}(q, \omega)$ is the first order correction to the polarizability with exchange and self-energy contributions.

RESULTS AND DISCUSSIONS

The SSF is defined using density response function as [9,11]

$$S(q) = -\frac{1}{\pi\rho} \int_0^\infty d\omega \chi(q, i\omega). \quad (3)$$

The PCF $g(r)$ is obtained from the SSF $S(q)$ as,

$$g(r) = 1 - \frac{1}{2\pi\rho} \int_{-\infty}^\infty dq e^{iqr} [1 - S(q)]. \quad (4)$$

The correlation energy per electron ϵ_c is given by [9,11],

$$\epsilon_c = \frac{1}{4\pi} \int_0^\infty V(q) [S_1^d(q) + S_1^{se}(q) + S_1^{ex}(q)] dq, \quad (5)$$

where $S_1^d(q)$, $S_1^{se}(q)$, and $S_1^{ex}(q)$ are direct, self, and exchange interaction terms, respectively.

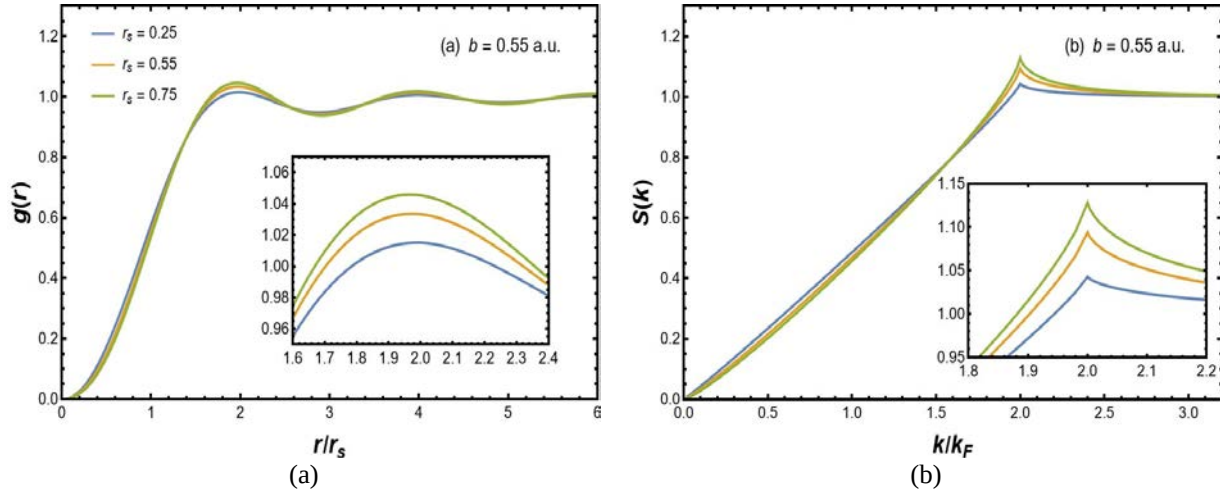


FIGURE 1. Pair correlation function $g(r)$ plotted as a function of r/r_s in Fig. 1(a) and static structure factor $S(k)$ is plotted as a function of k/k_F in Fig. 1(b), whereas the inset shows the zoomed-in view, respectively.

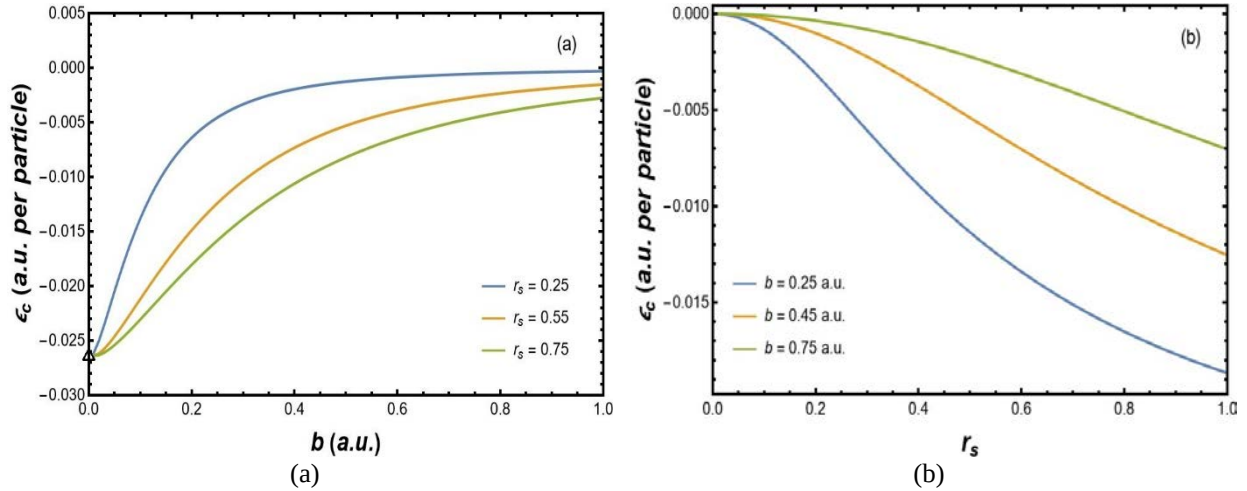


FIGURE 2. Correlation energy per particle plotted as a function of wire width b for fixed density parameters r_s in Fig. 2(a) and Fig. 2(b) shows the r_s dependence of correlation energy per particle at fixed wire widths b .

In Fig. 1(a), PCF shows the probability of finding a pair of electrons at various density parameters for fixed wire width $b = 0.55$ a.u. and the inset provides the zoom view of oscillations around $r = 2r_s$ showing the significant difference in PCFs for various density parameters. For high density regime ($r_s \leq 1$), the values of PCF at $2r_s$ increases, exhibiting correlations getting stronger for higher values comparatively lower values of r_s . The same behavior can be

observed in Fig. 1(b), the SSF is plotted against k/k_F at various density parameters for fixed wire width $b = 0.55$ a.u. and the inset shows the zoom view of peaks at $2k_F$.

Figure 2(a) depicts that the correlation energy decreases as b decreases and when $b \rightarrow 0$ the correlation energy is approaching to the high-density limit $-\pi^2/360$ a.u. for various density parameters ($r_s = 0.25, 0.55$ and 0.75). These results are in agreement with exact results [9,12]. In Fig. 2(b), the correlation energies are more negative as the r_s is increasing for fixed wire widths ($b = 0.25, 0.45$ and 0.75 a.u.). The smaller wire width b indicates the stronger confinement.

CONCLUSIONS

For cylindrical confinement, we have studied the wire width and density parameters (b and r_s) dependence of ground-state properties in high density regime using FRPA. The amplitude of oscillations in PCF around $2r_s$, and the $2k_F$ peak heights of SSF, grow as the r_s increases for the fixed value of wire width $b = 0.55$ a.u. which signifies more strong correlations for higher value of r_s . We have also observed as wire width $b \rightarrow 0$, the correlation energy approaches to the high-density limit $-\pi^2/360$ a.u. for various density parameters ($r_s = 0.25, 0.55$ and 0.75), which is in agreement with exact high density theory and quantum monte Carlo simulations [9,12]. The quantum Monte Carlo (QMC) simulations for quasi-1D wire for this cylindrical confinement can be explored in future on the basis of theoretical predictions for applications in nano devices.

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Exploring Spin Texture and Modulating Spin-Splitting in Layered Perovskites: A First-Principles Computational Approach

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Abstract. Spin-orbit coupling in non-centrosymmetric materials can lock carrier spins into a uniform momentum-space pattern—persistent spin texture (PST)—which supports ultralong spin lifetimes and is highly attractive for spintronic applications. Here, using density functional theory and a symmetry-based $\mathbf{k}\cdot\mathbf{p}$ model, we demonstrate PST in the conduction band minimum and Dresselhaus-type spin splitting in the valence band maximum of the layered hybrid perovskite (BrBA)₂PbBr₄ (space group $P2_1$). We extract spin splitting coefficient of $2.85 \text{ eV}\cdot\text{\AA}$ in the conduction band and $0.48 \text{ eV}\cdot\text{\AA}$ in the valence band and confirm these values through fitting to a minimal two-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian.

INTRODUCTION

In crystals with strong spin-orbit coupling (SOC) and broken inversion symmetry, Kramers' degeneracy is lifted away from time-reversal invariant momenta, enabling momentum-dependent spin splitting. The Dresselhaus mechanism produces spin splitting linear in $\mathbf{k}$ [1], and under suitable symmetry conditions can give rise to a PST [2] with spins locked in a uniform direction. PST suppresses spin dephasing, enabling long spin lifetimes desirable for spintronic applications. Such behaviour requires the absence of inversion symmetry and a dominant Dresselhaus field along principal crystalline axes, unlike Rashba systems with in-plane spin winding that do not support PST.

Hybrid organic-inorganic perovskites (HOIPs) are promising platforms for SOC phenomena due to the presence of heavy elements like lead, structural tunability, and broken inversion symmetry [3,4]. The monoclinic perovskite (BrBA)₂PbBr₄, where BrBA is 4-bromo-2-butylammonium, crystallizes in the non-centrosymmetric space group $P2_1$ and exhibits the symmetry operations of the C_{2y} point group, yet its spin-orbit coupling driven spin textures have not been fully characterized. In this work, we employ first-principles density functional theory (DFT) and a symmetry-constrained $\mathbf{k}\cdot\mathbf{p}$ model to reveal that (BrBA)₂PbBr₄ hosts PST in its conduction band minimum and conventional Dresselhaus splitting in its valence band maximum.

COMPUTATIONAL METHODS

All DFT [5,6] calculations were carried out using the Vienna Ab initio Simulation Package (VASP) [7,8] with projector augmented wave pseudopotentials and the PBEsol exchange-correlation functional [9]. Structural relaxations proceeded until residual forces fell below $0.01 \text{ eV}/\text{\AA}$, using a Γ -centered $6\times 6\times 2$ k -points. Spin-orbit coupling was included in noncollinear single-point calculations after structural optimization. Band structures and spin textures were extracted by projecting the Kohn-Sham wavefunctions onto Pauli matrices using the *p4vasp* and *Vasprun Tools* packages. To validate and interpret the DFT results, we constructed a minimal two-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian consistent with the $P2_1$ point-group symmetry, retaining only terms linear in $\mathbf{k}$ and fitting the parameters to the computed spin splitting near the band extrema. To account for van der Waals interactions critical in layered systems, Grimme's D3 dispersion correction was included [10].

RESULTS AND DISCUSSION

The optimized crystal structure of (BrBA)₂PbBr₄ confirms a monoclinic distortion that breaks inversion symmetry. The system crystallizes in the space group $P2_1$, with a two-fold screw rotation (C_{2y}) as its only point

symmetry operation. This absence of inversion, along with the low symmetry, permits spin–orbit-coupling-induced spin splitting and nontrivial spin textures.

Figure 1a shows the layered structure consisting of corner-sharing PbBr_6 octahedra and organic BrBA cations. The spin-projected band structure (Fig. 1b–d) reveals a direct band gap of about 2.3 eV at the Gamma point. Orbital analysis indicates that the CBM is dominated by Pb p-states, while the VBM originates mainly from Br p-states. A spontaneous polarization of 2.4 C/cm² further confirms the polar nature of the system.

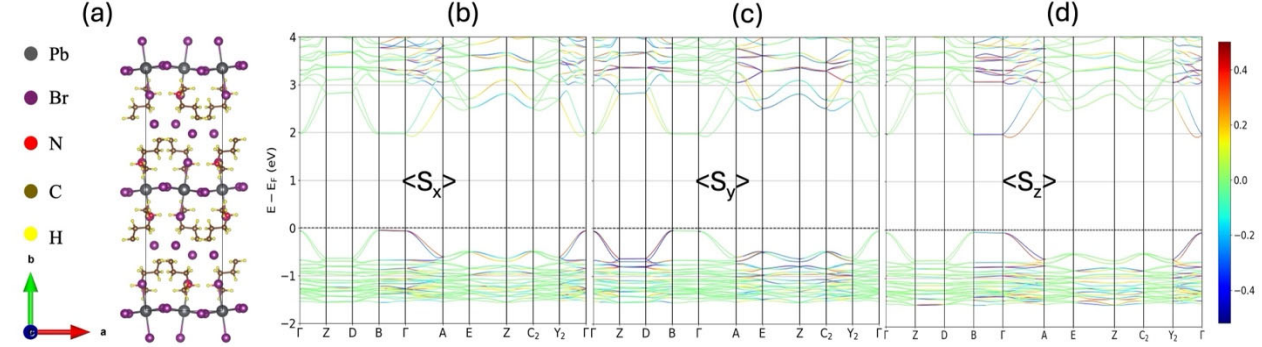


FIGURE 1. (a) Crystal structure of $(\text{BrBA})_2\text{PbBr}_4$. The layered geometry and lack of inversion symmetry are evident from the distorted monoclinic configuration. (b–d) Spin-projected electronic band structures. The contributions from different spin components (S_x , S_y , S_z) are highlighted for selected bands. The Fermi energy is set to zero.

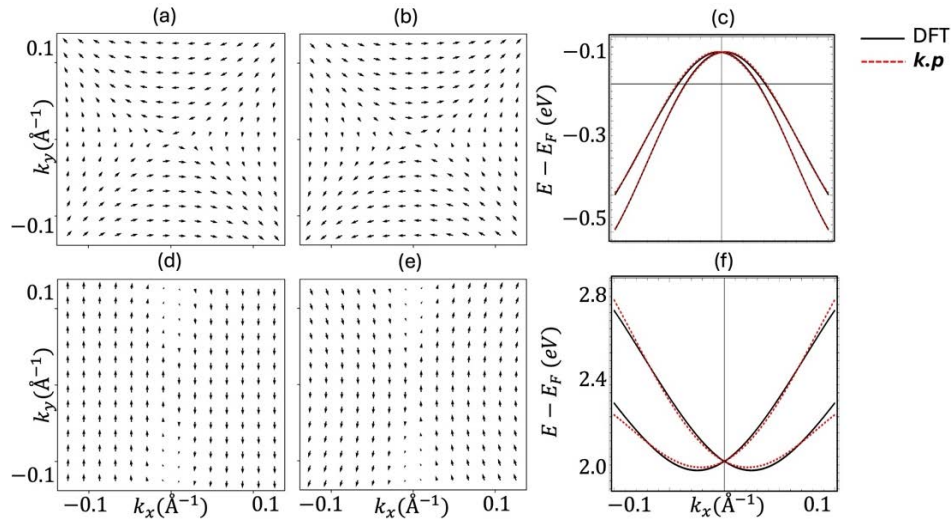


FIGURE 2. (a–b) Spin texture of the VBM (inner and outer branches) over the k_x – k_y plane showing symmetric winding in the S_y – S_z components. (c) Spin splitting along k_x at the VBM with DFT and $\mathbf{k}\cdot\mathbf{p}$ fit. (d–e) Spin texture of the CBM (inner and outer branches) showing nearly uniform spin orientation in the S_y – S_z plane. (f) Spin splitting along k_x at the CBM from DFT and $\mathbf{k}\cdot\mathbf{p}$ model. The VBM shows Dresselhaus-type spin texture, while the CBM exhibits PST with spins aligned along a fixed direction.

The spin texture was mapped over a uniform k_x – k_y grid in the Brillouin zone. Figures 2a and 2b show the VBM spin texture for the inner and outer branches, exhibiting symmetric spin winding characteristic of Dresselhaus-type splitting. In contrast, Figures 2d and 2e show the CBM spin texture, where spins lie in the S_y – S_z plane and remain nearly uniform, indicating a persistent spin texture (PST).

Spin splitting was quantified by calculating energy differences between spin-split bands along the k_x direction. Figures 2c (VBM) and 2f (CBM) show the DFT results along with $\mathbf{k}\cdot\mathbf{p}$ fits. The CBM exhibits larger splitting with linear k_x dependence, consistent with PST, while the VBM shows smaller asymmetric splitting due to competing SOC terms.

To corroborate these findings, we employed a two-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian for $k_z=0$ plane of the form

$$H(\mathbf{k}) = H_0(\mathbf{k}) + \alpha k_x \sigma_x + \beta k_x \sigma_z + \gamma k_y \sigma_y$$

Where $H_0(k) = E_0 + ak_x^2 + bk_y^2$. Here, k_x and k_y are the Cartesian component of the crystal momentum in the plane around Gamma point, and σ are the Pauli matrices which describes the spin degrees of freedom.

The extracted spin-orbit coupling coefficients are summarized in Table 1. For the conduction band, $\alpha = 0.17 \text{ eV}\cdot\text{\AA}$, $\beta = 2.85 \text{ eV}\cdot\text{\AA}$, and $\gamma = 0.15 \text{ eV}\cdot\text{\AA}$. The small value of α , γ and dominant β term indicate that the spin orientation is primarily along the out-of-plane σ_z direction, which is consistent with PST. For the valence band, $\alpha = 0.01 \text{ eV}\cdot\text{\AA}$, $\beta = 0.48 \text{ eV}\cdot\text{\AA}$, and $\gamma = 0.22 \text{ eV}\cdot\text{\AA}$, showing smaller but finite splitting with symmetric winding characteristic of Dresselhaus-type spin texture.

TABLE 1. Fitted $\mathbf{k}\cdot\mathbf{p}$ model parameters for conduction and valence band.

	a (eV·Å ²)	b (eV·Å ²)	α (eV·Å)	β (eV·Å)	γ (eV·Å)
CB	85.30	23.01	0.17	2.85	0.15
VB	64.05	10.78	0.01	0.48	0.22

This symmetry-resolved analysis shows that (BrBA)₂PbBr₄ hosts both PST and Dresselhaus-type spin textures in different energy regions. Its low-symmetry, non-centrosymmetric structure enables momentum-dependent spin splitting and symmetry-protected PST, making it a promising platform for spintronic applications. External perturbations such as electric fields or strain may further tune its spin properties.

CONCLUSION

In this work, we investigated spin-orbit coupling-induced spin splitting and spin textures in the non-centrosymmetric halide perovskite (BrBA)₂PbBr₄, which crystallizes in the monoclinic space group P2₁ with only a C_{2y} screw axis. First-principles calculations reveal a Dresselhaus-type spin texture at the valence band maximum and a persistent spin texture (PST) at the conduction band minimum, both arising purely from crystal symmetry and spin-orbit interaction. Symmetry-constrained $\mathbf{k}\cdot\mathbf{p}$ modeling shows that the valence band features complex spin winding from comparable β , and γ terms, while the conduction band is dominated by β , resulting in uniform out-of-plane spin alignment. This coexistence of Dresselhaus and PST regimes highlights (BrBA)₂PbBr₄ as a promising platform for spintronic devices such as spin filters and long-lived spin channels. Future work could explore external tunability via strain or electric fields to further engineer its spin properties.

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Behavior of Interacting Electrons in an AB Ring with Correlated Disorder: A Mean Field Study

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Abstract. We investigate the role of on-site Hubbard interaction on persistent current in an isolated quantum ring with Aubry-type quasi-periodic disorder in the half-filled band regime, using a Hartree-Fock mean-field approach. We construct the Hamiltonian within a tight-binding framework and numerically investigate the combined effect of correlated disorder and on-site interaction. Our results reveal that the Hubbard interaction enhances the current when disorder is introduced in the on-site energies while the hopping remains uniform. In contrast, introducing disorder in the hopping suppresses the current with increasing interaction, and this suppression becomes more pronounced at higher disorder strength. When both on-site and hopping disorders are present, the current increases with interaction, with stronger enhancement observed when on-site disorder dominates; the rate of enhancement diminishes as the disorder strengths are comparable

I. INTRODUCTION

In the modern era, key technological breakthroughs trace their origins to fundamental quantum-mechanical phenomena, wave-particle duality, energy quantization, and many-body electronic correlations. To observe such effects experimentally, one must operate in the mesoscopic regime, where the system size (L) is small enough that the single-particle level spacing (δ_E) is comparable to or exceeds the thermal energy ($K_B T$). At a low temperature presence of two interesting features in this regime- first, the phase-coherence length (L_ϕ) becomes of order L , and second, the discreteness of the energy spectrum is directly accessible, catch the researchers' attention. A paradigmatic example is the persistent current (PC)¹⁻³ in a quantum metallic ring threaded by magnetic flux (φ). The presence of Aharonov-Bohm (AB) flux⁴ breaks the time reversal symmetry (TRS) of the electrons, resulting in accumulation of a quantum mechanical phase $\theta = 2\pi\varphi/\varphi_0$ ($\varphi_0 = h/e$, is the flux quantum) while traversing the circumference of the ring and renders the ground state (GS) energy flux-dependent, giving rise to a non-dissipative current known as persistent current. First predicted by Hund and later confirmed by Lévy *et al.*, this phenomenon has been extensively studied in noninteracting, uncorrelated-disorder systems. However, the interplay of electron-electron interaction and correlated disorder-deterministic, nonperiodic modulations lacking translational symmetry yet exhibiting long-range order-remains underexplored. Here, we employ the Aubry-André-Harper (AAH)^{5,6} model to introduce three disorder scenarios: (i) diagonal AAH (on-site modulation, but uniform hopping), (ii) off-diagonal AAH (hopping modulation, but uniform on-site energy), and (iii) generalized AAH (simultaneous on-site and hopping modulation).

Within a tight-binding (TB) formalism augmented by an on-site Hubbard^{7,8} interaction, we solve the model self-consistently by the Hartree-Fock (HF)^{9,10} mean-field approximation. The paper is organized as follows: Section II presents the theoretical framework and numerical methods; Section III discusses our results for all three disorder classes; and Section IV summarizes our essential findings.

II. THEORETICAL FRAMEWORK

TB Hamiltonian. Let, us consider a N -site ring threaded by an AB flux φ . Under TB, the Hamiltonian looks like

$$H = \sum_{i,\sigma} \epsilon_i C_{i,\sigma}^\dagger C_{i,\sigma} + \sum_i U C_{i,\uparrow}^\dagger C_{i,\uparrow} C_{i,\downarrow}^\dagger C_{i,\downarrow} + \sum_{i,\sigma} t_i (C_{i,\sigma}^\dagger C_{i+1,\sigma} e^{j\theta} + h.c.) \quad (1)$$

where, $\epsilon_i = W_0 \cos(2\pi b i)$ and $t_i = t (1 + W_h \cos(2\pi b i))$ are the on-site potential and the hopping strength respectively. W_0, W_h are the disorder strengths and $b = (1 + \sqrt{5})/2$. In presence of φ an electron gains a phase which is $\theta = 2\pi\varphi/N\varphi_0$. U is the Hubbard interaction strength, $C_{i,\sigma}^\dagger, C_{i,\sigma}$ are the fermionic operators.

MF decoupling. Using the MF decoupling scheme, we reduce the interacting Hamiltonian to effective single-particle Hamiltonians for spin-up ($H_\uparrow$) and spin-down ($H_\downarrow$) electrons. The resulting decoupled Hamiltonian takes the form:

$$H = H_\uparrow + H_\downarrow - \sum_i U \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle; H_{\uparrow(\downarrow)} = \sum_{i,\uparrow(\downarrow)} \epsilon_{i,\uparrow(\downarrow)}^{eff} C_{i,\uparrow(\downarrow)}^\dagger C_{i,\uparrow(\downarrow)} + \sum_{i,\sigma} t_i (C_{i,\sigma}^\dagger C_{i+1,\sigma} e^{j\theta} + h.c.). \quad (2)$$

Here, $\epsilon_{i,\uparrow(\downarrow)}^{eff} = W_o \cos(2\pi bi) + U \langle n_{i\uparrow(\downarrow)} \rangle$ is the effective on-site potential energy term.

GS energy and PC. At temperature $T = 0K$, achieving the self-consistent solution we obtain the GS energy (E_g) and PC (I) using these formulae:

$$E_g = \sum_{p=1}^{N_\uparrow} E_{p\uparrow} + \sum_{p=1}^{N_\downarrow} E_{p\downarrow} - \sum_i U \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle; I = -\frac{\partial E_g}{\partial \varphi}. \quad (3)$$

Where, $N_{\uparrow(\downarrow)}$ is the number of up (down)-spin electrons present in the system and $E_{p\uparrow(\downarrow)}$ is the single particle energy eigenvalue of the p^{th} state obtained from solving $H_{\uparrow(\downarrow)}$, arranged in ascending order of magnitude.

III. NUMERICAL RESULTS AND DISCUSSION

Based on the above theoretical prescription, we calculate E_g in eV and PC in μA . The current is scaled by a factor of h/e and computed for a 40-site half-filled ($N_\uparrow = N_\downarrow = 20$) ring with $t = 1eV$. Other required parameters are mentioned in appropriate places.

Diagonal AAH. Figures 1(a)-(b) show that, for correlated on-site disorder of strength $W_o = 1$, with increasing U from 0 to 1, the magnitude and rate of change of E_g with flux φ increases, which further reflects through the PC variation in Fig. 1(c). Enhancement in magnitude of E_g can easily be interpreted from Eq. (1), where in the Hamiltonian, the Hubbard term is in additive form. The present disorder makes some of the selective site energies negative, which tries to trap the electrons there and the repulsive U -term tries to hop those electrons to attain the energy minimization condition, resulting in enhancement of hopping probability and consequence of which PC get increased. We further explore the phenomena for $W_o = 1.5$ for same values of U , obtain similarity in enhancement of current but with low magnitude, supports the robustness of the phenomena against the disorder strength.

Off-diagonal AAH. In contrary with the on-site disorder, we see from Figs. 1(d)-(e), increase of U from 0 to 1 for $W_h = 0.2$, the magnitude of E_g increases but the rate of change with φ decreases and the same is reflected by reduction of PC in Fig.1(f) under same input condition. Hopping disorder breaks translational symmetry (TS), enhancing electronic scattering and reducing PC. At half-filling, the on-site interaction U further restricts hopping by (i) not allowing double occupancy and (ii) favoring alternating spins on adjacent sites. These effects become more pronounced at higher $W_h=0.4$, where the TS is already broken, and even a small U significantly amplifies localization.

Generalized AAH. Finally, the disorder is introduced both in on-site potential and hopping term, and the crucial interplay between U , W_o and W_h is shown in the last row of Fig. 1. We obtain the magnitude and slope change of E_g with φ is increased from $U = 0$ to 0.4, setting $W_o = 1$ and $W_h = 0.2$, that is further reflected in PC change in Fig. 1(f). Here both disorders try to localize the electrons, and suppress the current. However, the role of U is different for both disordered case as discussed earlier. It supports the electrons to hop more freely when trapped by on-site disorder and the same U term supports localization for hopping disorder. As W_o is higher than W_h , the delocalization effect of U increases the current. We further check for $W_o = W_h = 0.2$ in Fig. 1(i), there we find that current still gets increased with U , but the rate of enhancement is smaller as the competition become more severe here.

IV. CLOSING REMARKS

Our analysis unfolds that the current can be modulated by means of disorder and interaction. Our work may be usef-

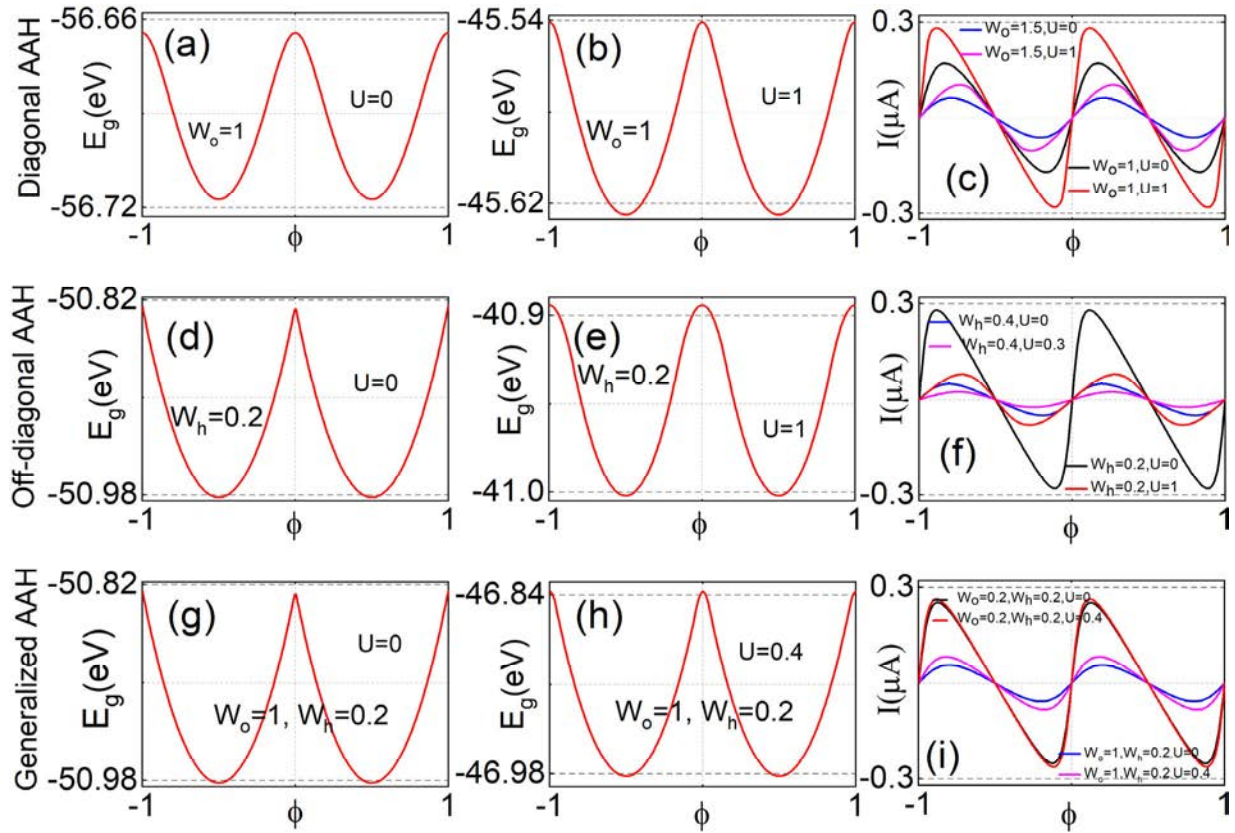


FIGURE1. The first, second, and third rows illustrate the ground-state energy and circular current variations with flux under diagonal, off-diagonal, and generalized AAH conditions, respectively. In subfigure (c), the black and red lines represent the case $W_o = 1$ with $U = 0, 1$ respectively, while the blue and magenta lines correspond to $W_o = 1.5$ for same U values. Sub-figure (f) shows black and red line for disorder strength $W_h = 0.2$ and U values 0, 1 respectively, whereas blue and magenta curves stand for $W_h = 0.4$ and U values 0 and 0.3. Black and red line shows the variation for $U = 0, 0.4$ when $W_o = 0.2$, $W_h = 0.2$ respectively and blue, magenta shows the same variation for same U inputs when W_o is set to 1 keeping W_h same as previous in subfigure (i).

-ul in understanding the electronic behavior in any correlated system and can be further be expanded to non-zero temperature expecting some novel features.

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Anomalous Circular Currents and Drude Weight in an SSH Ring with Higher-Order Hopping and Disorder

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Abstract. This work investigates flux-induced circulating charge current in a Su-Schrieffer-Heeger (SSH) ring in presence of higher order electron hopping within a non-interacting electron picture. Illustrating the system using a tight-binding framework, the circular current is calculated using well-known derivative method. In presence of higher order hopping, several anomalous signatures are found that are studied critically. We also inspect the conducting behavior by analyzing Drude weight as a function of disorder.

INTRODUCTION

The flux-induced circulating current in a quantum ring arising from the Aharonov-Bohm (AB) effect is a novel phenomenon, and has been explored more than two decades ago¹⁻³. A significant amount of research has focused on investigating several crucial features, but most of the studies are restricted to the model based on the nearest-neighbor hopping (NNH). In this work, we study a specific quantum ring where second-neighbor hopping (SNH) is included along with the NNH one. The NNH integrals are dimerized in the form of SSH model. The inclusion of SNH drastically modifies the flux-dependent energy levels, which leads to several anomalous signatures of current depending on electron filling. Along with current, we also explore Drude weight, a quantity that measures conducting properties of the system. With the inclusion of SNH, the conductivity gets significantly modified and exhibit unusual variation with disorder.

MODEL AND THEORETICAL FRAMEWORK

We illustrate the ring within tight-binding (TB) formalism which offers a simple and straightforward representation. The TB Hamiltonian reads as,

$$H = \sum_i \epsilon_i c_i^\dagger c_i + \sum_i (t_\alpha e^{j\theta} c_i^\dagger c_{i+1} + h.c.) + \sum_i (t_3 e^{2j\theta} c_i^\dagger c_{i+2} + h.c.), \quad (1)$$

where t_α ($\alpha = 1, 2$) is the NNH strengths, alternates between t_1 and t_2 , to form the SSH ring, t_3 is the SNH strength, θ represents the phase factor associated with the flux ϕ and is expressed as $\theta = 2\pi\phi/N\phi_0$ (ϕ_0 is the flux quantum), and, ϵ_i denotes the on-site potential at site i . The site energies are chosen according to the Aubry-André-Harper (AAH) model i.e. $\epsilon_i = \lambda \cos(2\pi b i)$. Where λ is the strength of the AAH modulation and $b = (1 + \sqrt{5})/2$ is the golden mean.

The flux-induced circular charge current is determined by the relation^{4,5}

$$I_c = -c \frac{\partial E_g}{\partial \phi}, \quad (2)$$

where E_g , the ground-state energy for a given filling factor with N_e electrons, is obtained by summing the lowest N_e energy levels at absolute zero temperature.

Finally, the Drude weight (D) that measured the conductivity is computed via the relation⁶

$$D = \left(\frac{N}{4\pi^2} \frac{\partial^2 E_g}{\partial \phi^2} \right)_{\phi \rightarrow 0^+}, \quad (3)$$

where N stands for the total number of lattice sites in the quantum ring.

RESULTS AND DISCUSSION

In the following, we report our numerical findings, including flux-dependent energy eigenvalues, current, and the conducting behavior in terms of the Drude weight. Our central focus is to explore the interplay among the dimerized NNH, SNH, and the correlated disorder included in different lattice sites.

Let us start with Fig. 1, which illustrates how the discrete energy eigenvalues vary with the applied flux for three different sets of hopping parameters. In the absence of SNH ($t_3 = 0$), when both the NNH strengths are identical (viz, $t_1 = t_2$), we get intersecting parabolas and the spectrum is uniform across the centre of the energy band ($E = 0$) (see Fig. 1(a)). This behavior is well-known for a one-dimensional TB AB ring. The band spectrum gets modified significantly in the presence of SNH and dimerized hopping, as clearly seen from Figs. 1(b) and (c). Two different dimerized conditions are considered, and in both the cases, the energy levels near the lower energy band edge are denser than the other energy regions, and this effect becomes more prominent when $t_2 < t_1$. This is solely due to the inclusion of higher order electron hopping in the system.

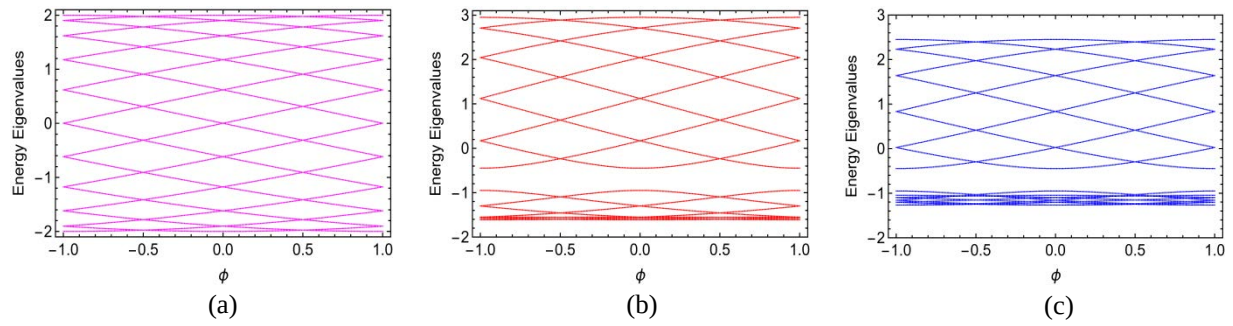


FIGURE 1. Variation of the discrete energy levels of the system with AB flux under three distinct conditions: (a) $t_2 = 1$, $t_3 = 0$, (b) $t_2 = 1.25$, $t_3 = 0.35$, and (c) $t_2 = 0.75$, $t_3 = 0.35$. Here, we set $N = 20$ and $t_1 = 1$.

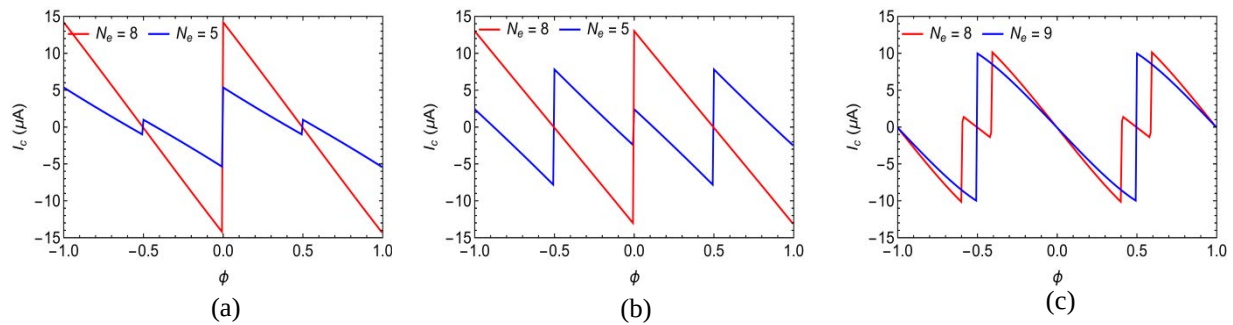


FIGURE 2. Flux dependence of persistent current for three different hopping configurations: (a) $t_2 = 1.25$, (b) $t_2 = 1$, and (c) $t_2 = 0.75$. Here, we take $N = 20$, $t_1 = 1$, and $t_3 = 0.35$.

Following the energy band spectra shown in Fig. 1, the key features of flux-induced circular currents in the ring, presented in Fig. 2, can be easily understood. The results are presented for three distinct hopping conditions in the presence of SNH. Quite interestingly we find that, even in this strictly 1D non-interacting ring (i.e., without considering electron-electron interaction), we can have kink-like structure in the current depending on the filling factor, which is in complete contrast to the conventional NNH ring. This atypical kink-like behavior appears from the

additional crossing of the energy levels near the bottom edge of the energy band. When the filling factor is fixed to a specific value such that the highest occupied energy levels lies within these energy levels, a kink appears. Once we cross this zone, the kink vanishes, and usual saw-tooth like nature of current is obtained. In all these cases, the current exhibits periodicity of one flux-quantum.

Finally, we focus on the variation of Drude weight, which reflects the conducting behavior of the ring. Figure 3 shows D versus the disorder strength λ for three distinct hopping configurations. When SNH strength is set to zero, we get the usual dependence of D with disorder. It decreases gradually with λ . But, the unusual behavior is obtained

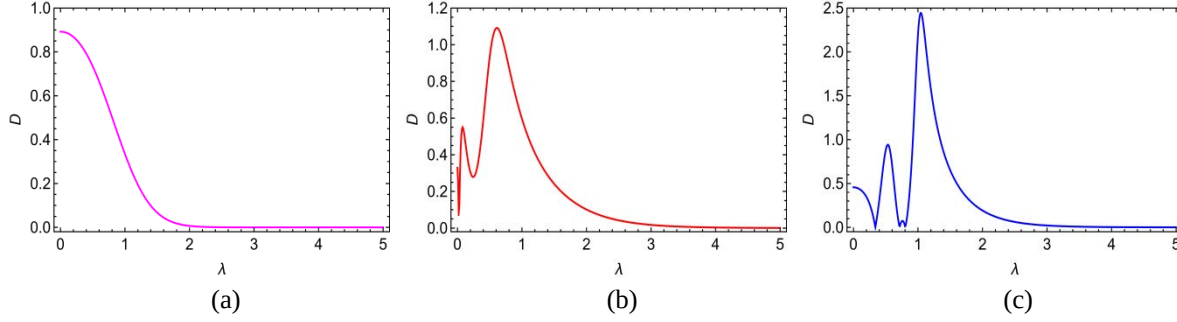


FIGURE 3. Dependence of the Drude weight (measured in units of $N/4\pi^2$) on disorder strength for three different cases: (a) $t_2 = 1, t_3 = 0$, (b) $t_2 = 1.5, t_3 = 0.6$, and (c) $t_2 = 0.75, t_3 = 0.6$. Here, $N = 20$, $N_e = 5$, and $t_1 = 1$.

once we include SNH. Instead of gradual reduction, we find enhancement of D with disorder and that even occurs at multiple values of λ . This is entirely due to the combined effect of disorder and higher order hopping, and might be quite interesting.

SUMMARY

The interplay between the second-neighbor and dimerized nearest-neighbor hopping integrals on magnetic response in a one-dimensional TB ring has been investigated within a non-interacting electron picture. Both flux-driven circular charge current and Drude weight have been explored under different input conditions. Several atypical features have been obtained in the presence of SNH, depending of the filling factor.

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Spin-selective Electronic Specific Heat in a Magnetic System

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Abstract. We explore spin-specific electronic specific heat (ESH) in a magnetic chain under a tight-binding formulation. A significant enhancement of ESH is observed with increasing the spin-resolved scattering amplitude. Determining up and down spin ESHs, we also estimate spin polarization (SP), and find a high degree of SP in a wide range of electro-chemical potential. Our analysis provides a new route of estimating thermal response in different magnetic systems.

INTRODUCTION

The study of electronic specific heat (ESH) has been one of the promising phenomena in low-dimensional systems, and researchers have been working on it over the past many years. From the measurement of ESH, the thermal behavior can be clearly estimated which is highly required especially in device designing. The available works are mostly involved in spinless systems, and a very limited progress has been done so far considering spin-dependent ones. In this work, we consider a one-dimensional ferromagnetic (FM) chain, a simplistic example where spin-dependent scattering factor¹ can be seen and investigate spin-specific ESH from a tight-binding perspective. For the FM system, the total Hamiltonian can be expressed in terms of separate up and down spin sub-Hamiltonians, and therefore, we can easily compute ESHs for both spin components, and hence the net ESH. Because of the scattering, the net ESH increases significantly which holds significant relevance and importance as well. From the components of ESHs we also calculate spin polarization (SP), another tool of estimating SP. Our numerical results show that a high degree of SP can be obtained for a broad range of electro-chemical potential.

THEORETICAL FORMULATION

The ferromagnetic chain is described by the following TB Hamiltonian²

$$H = \sum_n c_n^\dagger (\epsilon_n - \mathbf{h}_n \cdot \boldsymbol{\sigma}) c_n + \sum_n (c_{n+1}^\dagger \mathbf{t} c_n + h.c.), \quad (1)$$

where $c_n^\dagger = (c_{n\uparrow}^\dagger, c_{n\downarrow}^\dagger)$, $(c_{n\uparrow}, c_{n\downarrow})$, $(c_{n\uparrow}^\dagger, c_{n\downarrow}^\dagger)$ are the usual fermionic operators at site n , $\boldsymbol{\sigma}$ is the usual Pauli matrices, $\epsilon_n = \text{diag}(\epsilon_{n\uparrow}, \epsilon_{n\downarrow})$ where $\epsilon_{n\sigma}$ $\sigma = (\uparrow, \downarrow)$ is the on-site potential, and $\mathbf{h}_n$ characterizes the spin-selective scattering amplitude at n th site. $\mathbf{t} = \text{diag}(t, t)$ is the hopping matrix where t is the hopping amplitude.

Under the spin-dependent scattering conditions, there are two different types of ESH, associated with up and down spin electrons³. To find them, we need to compute average energies in the two spin sub-spaces. They are defined as⁴

$$\langle U_\sigma \rangle = \sum_{i=1}^N (E_{i\sigma} - \mu) f(E_{i\sigma}) \quad (2)$$

Here, $E_{i\sigma}$'s are the eigenvalues found by diagonalizing the Hamiltonian matrix of the system, μ represents the electro-chemical potential, $f(E_i)$ is the Fermi-Dirac distribution, k_B represents the Boltzmann factor, and T is the absolute temperature.

The spin-dependent ESH, $C_{v\sigma}$ is defined as

$$C_{v\sigma} = \frac{d\langle U_\sigma \rangle}{dT}. \quad (3)$$

Following some algebraic calculations, we reach to the expression of $C_{v\sigma}$ as

$$C_{v\sigma} = \frac{1}{k_B T^2} (E_{i\sigma} - \mu)^2 f(E_{i\sigma}) (1 - f(E_{i\sigma})). \quad (4)$$

The total ESH, C_v is obtained by adding the contributions of both up and down spin electrons. Thus, $C_v = C_{v\downarrow} + C_{v\uparrow}$. Finally, we define spin polarization (SP) as

$$SP = \frac{|C_{v\uparrow} - C_{v\downarrow}|}{C_{v\uparrow} + C_{v\downarrow}} \quad (5)$$

NUMERICAL RESULTS AND DISCUSSION

Before discussing the results, let us mention the common parameter values. We choose $\epsilon_{n\uparrow} = \epsilon_{n\downarrow} = 0$ and strength $t = 0.1$. All the results are computed for a 200-site FM chain with $h_n = h \forall n$. All the energies are reported in eV.

Figure 1 shows the dependence of total ESH, C_v , as a function of μ at three separate values of h , where each sub-figure contains the results for three separate temperatures. The results are very interesting and important as well.

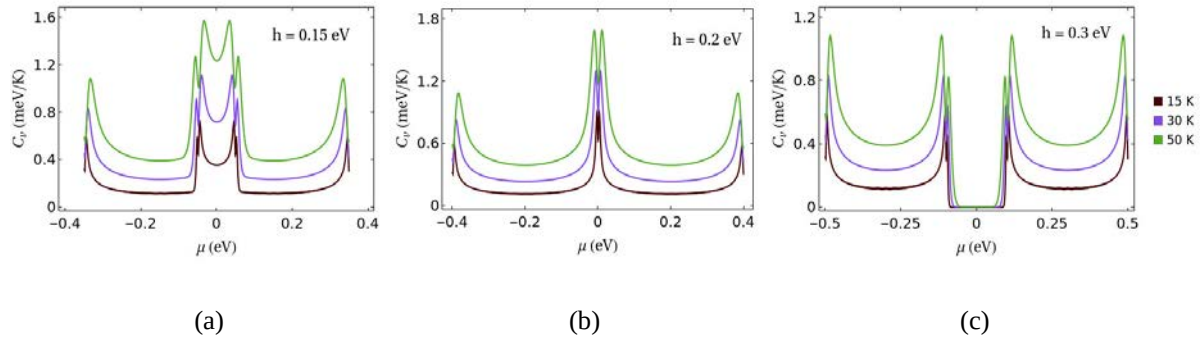


FIGURE 1: ESH– μ curves at three distinct temperatures, where (a) $h = 0.15$, (b) $h = 0.2$, and (c) $h = 0.3$.

Depending on h , ESH obtains different values and it becomes maximum at $h = 0.2$. The variation of total C_v entirely depends on the available up and down spin energy channels. At $h = 0.3$, a large gap across $\mu = 0$ appears due to finite separation between the two spin sub-bands. The ESH gradually increases with the rise of temperature, and this is fully consistent with the previous studies⁵ in the low-temperature limit.

To inspect the critical role of h on total C_v , in Fig. 2, we present the characteristic variation of C_v by changing h , considering $T = 20\text{K}$. The ESH shows a gradual enhancement with h , exactly corroborating the behavior of density of states (DOS) (not shown here in the figure).

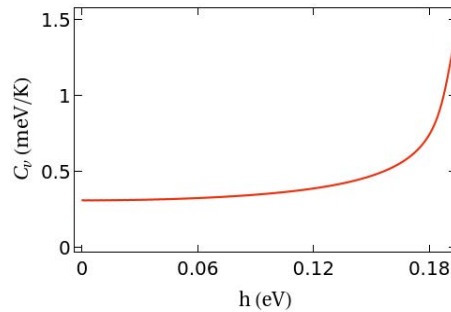


FIGURE 2: Variation of total ESH with h when T is set at 20K. Here $\mu = 0$.

From the behavior of individual components of ESH, we can estimate the degree of spin polarization. For illustrative example, in Fig. 3, we present the results of SP at three distinct values of h , setting the temperature constant. For low h ($h < 2t$), around $\mu = 0$, there is an energy window ($\sim -0.05 < E < \sim 0.05$) where SP is moderate, whereas across this region a cent percent SP is obtained (Fig. 3(a)).

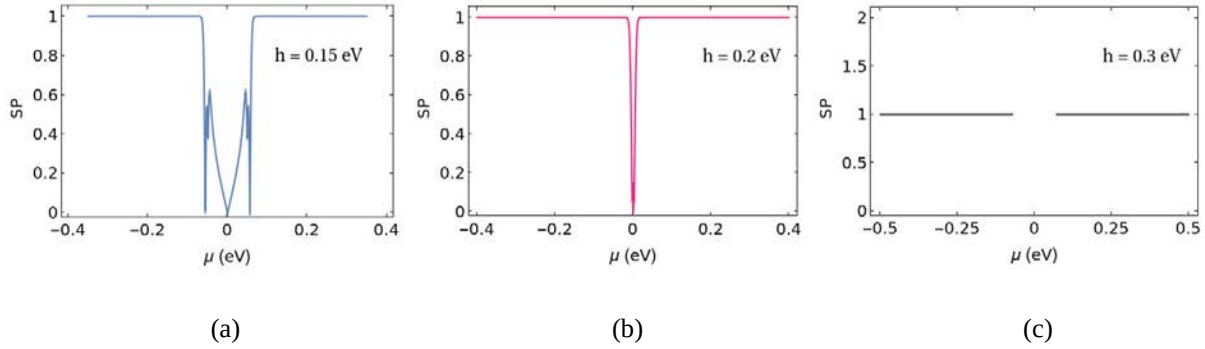


FIGURE 3: SP as a function of μ at 15K, where (a), (b), and (c) correspond to $h = 0.15$, 0.2 , and 0.3 eV, respectively.

These features are directly associated with the contributing up and down spin energy bands. With increasing h , the overlap between the two spin energy bands gradually decreases, and eventually for large h they get separated. Accordingly, the high degree of spin polarization is achieved for broader energy regions, that is clearly reflected from Figs. 3(b) and (c). The large gap in SP around $\mu = 0$ in Fig. 3(c) is connected to the finite separation between up and down spin bands for the high value of h . This gap progressively diminishes with increasing the temperature.

SUMMARY

This work investigates spin-selective ESH and spin polarization in a magnetic system treated within a tight-binding scheme. Considering spin-dependent scattering effects, a finite mismatch appears among the spin-up and spin-down energy channels. Adjusting the electro-chemical potential selectively we can achieve a reasonably large net ESH and also the spin polarization. More interesting phenomena might be expected in the presence of spin flipping and disorder, and we will focus on that in our forthcoming work.

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Dual-Gate Bias Driven Tuning of Electrical Behaviour of MoS₂ FET

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Abstract. Controlling charge carrier transport in Molybdenum Disulfide (MoS₂) field-effect transistors (FETs) is crucial for enabling their integration into next-generation 2D based nanoelectronics devices. Here, we demonstrate effective transport control using a dual-gated FET with sputter deposited SiO₂ as top gate dielectric. To evaluate, we first analyse the back-gated performance of FET under various fixed top gate biases (V_{tg}). As V_{tg} increases from 0 to 3 V, threshold voltage (V_{th}) changes from 19 to 3.6 V and on state current (I_{on}) increases from 3.85×10^{-6} to 1.07×10^{-5} A, indicating tuning of V_{th} and enhanced channel conductivity. Conversely, the top-gated performance of FET is analysed under various fixed back gate biases (V_{bg}). As V_{bg} increases from 0 to 3 V, V_{th} changes from 2.27 to 1.91 V, I_{on} increases from 1.25×10^{-6} to 2.17×10^{-6} A. These results confirm efficient electrostatic coupling between the top and back gates, offering dynamic control over channel conduction and demonstrates the promise of dual-gated architectures for threshold-voltage tuning and improved electrical performance through higher drive currents.

INTRODUCTION

The continued miniaturization of semiconductor devices as predicted by Moore's law has led to increasing limitations in traditional silicon-based devices due to short-channel effects, high leakage currents and degraded electrostatic control at nanoscale dimensions [1]. In this context, transition metal dichalcogenides (TMDs) have emerged as promising alternatives due to their atomic thickness, tunable band gap (~ 1.2 - 1.8 eV), superior electrical performance, optoelectronic properties, mechanical flexibility and chemical stability [2]. Among these MoS₂ has been extensively studied for field-effect transistors (FETs) applications owing to its high carrier mobility and large I_{on}/I_{off} ratio [3]. For practical device implementation, precise threshold voltage (V_{th}) control and enhanced gate electrostatics are essential to achieve low power consumption and to fully harness the intrinsic capabilities of MoS₂. However, conventional single-gated FET often exhibit limited electrostatic control, particularly in multilayer MoS₂, where the gate field is unable to effectively modulate carriers in the upper layers. This results in partial channel depletion and degraded conductivity [4]. To overcome these limitations, dual-gated architectures employing both top and back gates have been explored as a means to enhance electrostatic control [5]. In this work, we investigate the electrical characteristics of dual-gated MoS₂ FETs under simultaneous biasing of both gates. The electrical behaviour of one gate can be modulated via bias applied to the other, thereby offering dynamic control over channel conduction. Such a dual-gating strategy introduces additional degrees of freedom for tuning key FET parameters and represents a promising pathway toward optimizing MoS₂-based transistors for high-performance electronic applications.

FABRICATION AND MEASUREMENT

Molybdenum disulfide (MoS₂) Multilayer flakes were prepared via mechanical exfoliation using an adhesive tape and a polydimethylsiloxane (PDMS) stamp. The flakes were transferred onto a highly p-doped silicon (p++ Si) substrate with a 200 nm thermally grown SiO₂ layer, where p++ Si served as back gate electrode and SiO₂ as back gate dielectric. Device fabrication was carried out in three sequential photolithography and sputtering steps. In the first step, source and drain electrodes were patterned using standard optical photolithography, followed by the sputter deposition of a Ni/Au (30/100 nm) metal stack. In the second step, the top gate area was defined by photolithography followed by 50 nm thick SiO₂ dielectric deposition via sputtering. The third level of photolithography was used to define the top-gate contact, which was formed by sputtering a Ti/Au (30/100 nm) metal stack. Electrical characteristics were measured in ambient condition at room temperature using the Polaris B1500 Agilent Semiconductor Characterization System.

RESULTS AND DISCUSSION

Figure 1(a) and Figure 1(b) represent the 2D and 3D schematic of the fabricated dual-gated MoS₂ field-effect transistor (FET), respectively, while Figure 1(c) shows the representative optical microscopic image of the device. To evaluate the electrostatic control and coupling behaviour, the electrical performance of the device was systematically studied by simultaneously tuning both gates. The channel length and channel width of the device are 3 μm each.

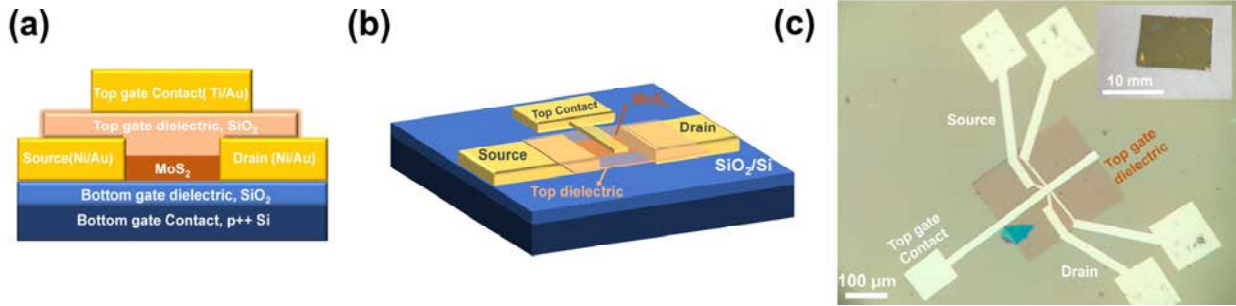
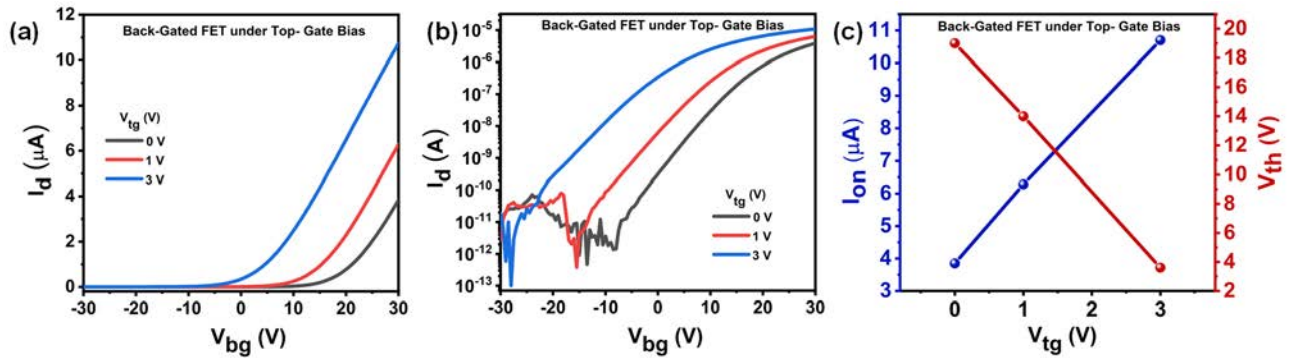


Figure 1. (a) 2D schematic of the dual-gated MoS₂ FET. (b) 3D schematic illustrating the device layout. (c) representative optical image of the fabricated device; inset shows a camera image of the full device.

To evaluate back-gated performance, transfer characteristics (I_d vs. V_{bg} ; $V_d = 1$ V) were recorded at various fixed top gate voltages (V_{tg}) ranging from 0 to 3 V. The device demonstrates typical n-type semiconductor behaviour. As shown in Figure 2(a), applying a more positive top gate voltage led to a noticeable increase in drain current (I_d) and pronounced leftward shift in the threshold voltage (V_{th}). V_{th} was calculated by Extrapolation in the Linear Region (ELR) method [6]. Figure 2(b) displays the transfer characteristics on a logarithmic scale. Figure 2(c) shows the variation of on current (I_{on}) and V_{th} with V_{tg} . I_{on} was determined from the current value at the maximum V_{bg} . This behaviour confirms that the top gate field efficiently modulates carrier concentration in the MoS₂ channel even during back gate operation, demonstrating strong vertical electrostatic coupling between the gates. The improved channel

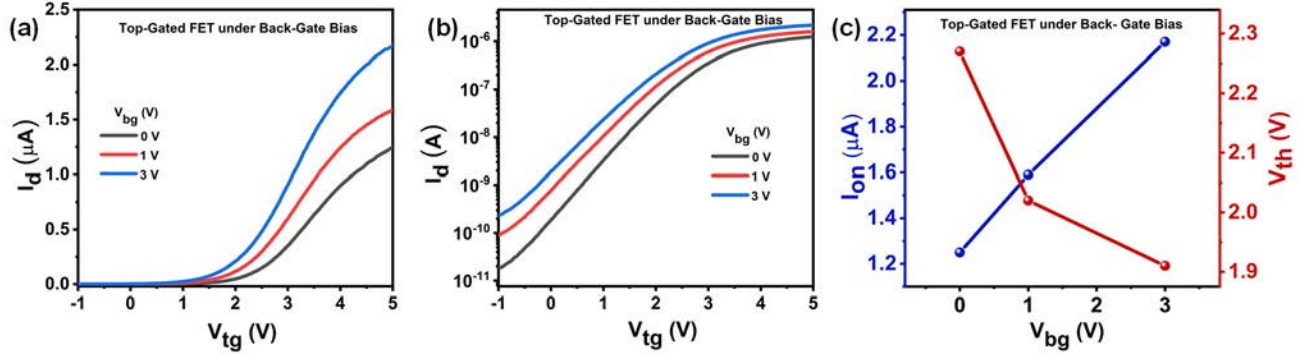


conductivity at higher top gate bias is attributed to enhanced electron accumulation.

Figure 2. Transfer characteristics of the Back-gated MoS₂ FET (I_d vs. V_{bg} ; $V_d = 1$ V) measured at different applied top gate biases ($V_{tg} = 0$ to 3 V): (a) in linear scale, (b) in logarithmic scale and (c) Variation of I_{on} and V_{th} with V_{tg} .

Conversely, the top-gated performance (I_d vs. V_{tg} ; $V_d = 1$ V) was analysed at various fixed V_{bg} ranging from 0 to 3 V). As shown in Figure 3 (a), a similar trend is observed. I_{on} increases and V_{th} shift to leftwards. This again confirms the dual-gate interplay where the electrostatic influence of the back gate extends to modulate the effective field seen by the top gate, enabling more efficient charge carrier transport. Figure 3(b) displays the transfer characteristics on a logarithmic scale. Figure 2(c) shows the variation of I_{on} and V_{th} with V_{bg} . Please note that a complete off-state could not be achieved within the applied voltage range, as V_{tg} was restricted to prevent dielectric breakdown of the top-gate dielectric.

Figure 3: Transfer characteristics of the Top-gated MoS₂ FET (I_d vs. V_{tg} ; $V_d = 1$ V) measured at different applied back gate



biases ($V_{bg} = 0$ to 3 V): (a) in linear scale, (b) in logarithmic scale and (c) Variation of I_{on} and V_{th} with V_{bg} .

These observations demonstrate strong vertical electrostatic coupling in the dual-gated MoS₂ FET, where both gates collaboratively influence the channel conductivity. Precise threshold voltage V_{th} tuning is a critical requirement in semiconductor device engineering. The observed V_{th} modulation confirms that the dynamic onset of current can be effectively controlled through this dual-gate scheme. This work highlights the effectiveness of the dual-gate configuration in achieving electrostatic control.

CONCLUSIONS

In summary, the dual-gated MoS₂ FETs exhibits strong electrostatic coupling between the top and back gates, enabling the performance through one gate to be effectively modulated by the bias applied to the other. This configuration allows precise control over the threshold voltage (V_{th}) and significantly enhances the on-current (I_{on}). Such control is crucial for integrating 2D FETs into next-generation nanoelectronics systems. Hence, this work demonstrates a practical and effective strategy for achieving dynamic electrostatic control in MoS₂ devices.

ACKNOWLEDGEMENT

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First-Principles Study of Kagome metal EuV_3Sb_4

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Abstract. We present the first density functional theory investigation of the *Fmmm* Kagome-lattice compound EuV_3Sb_4 using FPLO-PBE calculations. The structure consists of Eu zigzag layers interleaved with V-Sb networks, where V atoms form a two dimensional Kagome framework. The scalar relativistic band structure reveals a metallic ground state with flat-band like features and Dirac-like crossings from Kagome derived states. The Spin resolved analysis shows distinct majority and minority channels, while the Fermi surface is seen to host quasi-2D cylindrical sheets around the Γ point and hexagonal like pockets around the boundaries. The strong angular variation of extremal orbits highlights pronounced two dimensionality, establishing EuV_3Sb_4 as a promising platform for exploring magnetically driven topological phases.

INTRODUCTION

The term “Kagome”, Japanese for “holes in a basket”, describes a two dimensional network of corner-sharing triangles (and interlaced hexagons), whose geometry has emerged as a versatile platform for realizing a variety of quantum phenomena giving rise to flat bands, Dirac-like crossings, van Hove singularities [1-3] and pronounced magnetic frustration among others. First discussed in the physics literature by Shōji in 1951 [4], in recent years several Kagome compounds have been on the forefront of research among which the AM_3X_4 [5-6] stoichiometry (A: La, Ce, Sm, Ca, Yb, Eu, Gd; M: V, Ti; X: Sb, Bi) has attracted considerable attention for hosting intertwined orders, charge density waves, nontrivial band topology, and unconventional magnetism within a single crystal structure [7-8]. Here, we

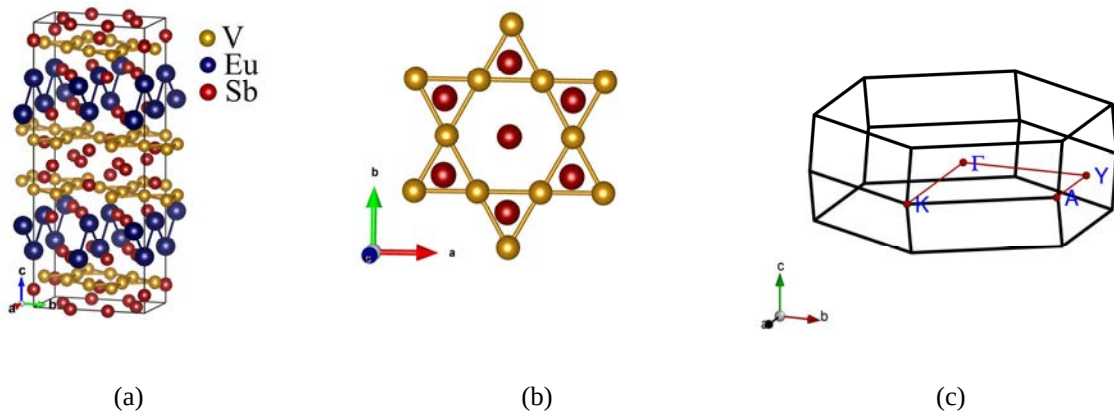


FIGURE 1. (a) Crystal structure of EuV_3Sb_4 , showing the unit cell containing Eu atoms (blue), V atoms (yellow), and Sb atoms (red) (b) Vanadium-based kagome network formed within the structure. (c) Brillouin zone (BZ) with labeled high-symmetry points used for electronic structure calculations.

report a study of EuV_3Sb_4 , a newly discovered member of this family which has limited experimental and DFT work, in which the interplay between the V-derived Kagome electronic bands and the localized Eu^{2+} moments offers a fertile ground for exploring magnetically driven topological phases.

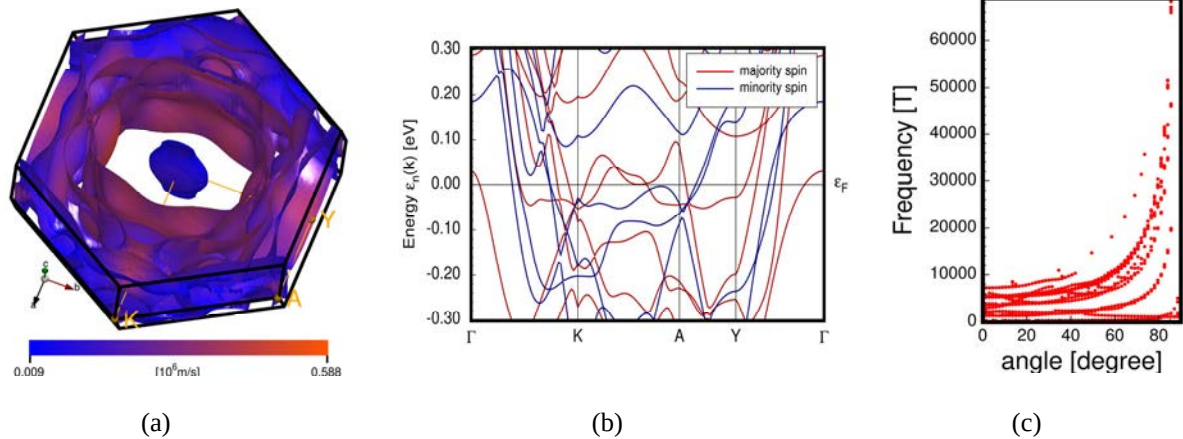


FIGURE 2. (a) Scalar-relativistic electronic band structure, with majority-spin states shown in red and minority-spin states in blue. (b) Fermi surface of EuV₃Sb₄. The bottom scale displays Fermi velocity. (c) Angular variation of the de Haas–van Alphen (dHvA) oscillation frequencies, obtained from the calculated Fermi pockets of EuV₃Sb₄.

COMPUTATIONAL DETAILS

First-principles calculations were carried out with the FPLO full-potential local-orbital code (v22.00-62) [9-10], using the PBE form of the GGA for the exchange correlation[11]. Self-consistency was achieved with convergence thresholds of 10^{-8} for the charge density and 10^{-8} Hartree for the total energy; atomic positions were relaxed until residual forces were below 10^{-3} eV/Å. Brillouin-zone integrals employed the Blöchl-corrected linear tetrahedron method on a $12 \times 12 \times 12$ k-mesh. The Fermi surface was built via iterative isosurface refinement on a $48 \times 48 \times 48$ grid, and dHvA spectra were obtained from these isosurfaces using an angular subdivision 60 with 200 sampling planes.

RESULTS

The crystal structure of EuV₃Sb₄, shown in Figure 1(a), consists of zigzag layers of Eu atoms (blue), while V (yellow) and Sb (red) atoms occupy positions that create a combination of layered stacking with honeycomb like geometry. The Kagome framework originates from the V-atom network, as highlighted in Figure 1(b). The Brillouin zone (BZ) for the orthorhombic *Fmmm* phase, with labeled high symmetry points used in the band structure calculations [12], is shown in Figure 1(c).

The scalar-relativistic electronic band structure, presented in Figure 2(a) indicates a metallic ground state, revealing eight bands crossing the Fermi level. Signatures of flat-band-like dispersion and Dirac-type crossings emerge from the V-derived Kagome states. The majority spin states are shown in red and minority spin states in blue. The resulting Fermi surface shown in Figure 2(b) comprises of multiple pockets, including a prominent quasi-two-dimensional cylindrical sheet centered at Γ and several hexagonal sheet-like features near the BZ boundaries similar to other kagome metals [13-14].

To explore the quantum oscillation behavior, we computed extremal cross-sectional areas of the Fermi surface and extracted the corresponding de Haas–van Alphen (dHvA) frequencies displayed in Figure 2(c). The tilt angle θ is measured from the crystallographic c-axis, where 0° corresponds to the magnetic field aligned along c, and 90° corresponds to the field lying within the ab-plane. The frequencies increase systematically with θ , reaching values up to ~ 60 kT, consistent with the coexistence of 2D cylindrical pockets. This mirrors behavior observed in other Kagome metals [13-14]. This strong angular dependence provides a clear experimental signature for future quantum-oscillation measurements.

CONCLUSION

We have carried out the first-principles study of EuV₃Sb₄, which reveals a metallic ground state with Dirac-like and flat-band features originating from its V-based Kagome network. The calculated Fermi surface hosts quasi-2D

cylindrical and hexagonal pockets, with pronounced angular dependence in dHvA frequencies, indicating strong two-dimensionality. These results provide a theoretical foundation for future experimental exploration of magnetically driven topological phases in this material.

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Structural and Electronic Properties of Gold: An Ab-initio study of Bulk, 2D and 1D Phases.

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Abstract: Gold behaves quite differently at the Nano-scale than its bulk form. While bulk gold is chemically inert, its low-dimensional forms can show high reactivity, even can act as catalysts. We have explored the structural and electronic properties of gold in 3D (bulk), 2D (Goldene and hexagonal-2D monolayer) and 1D (Nano-ribbon) forms. The 1D gold Nano-ribbons demonstrated lower binding energies compared to their bulk and 2D counterparts, indicating higher chemical reactivity and potential for functionalization. Phonon dispersion analysis revealed the absence of imaginary frequencies in all forms indicating the thermally stability of the studied systems. Additionally, the electronic band structures showed no bandgap, which means they exhibit metallic behaviour. Among the 1D nanoribbons, the 8-AuEneNR_y structure exhibited a magnetic moment of around 0.38μB due to spin splitting and edge effects and can be used in spintronic applications. Overall, our findings show that low-dimensional gold structures hold promise for future Nano-electronic and magnetic devices.

INTRODUCTION

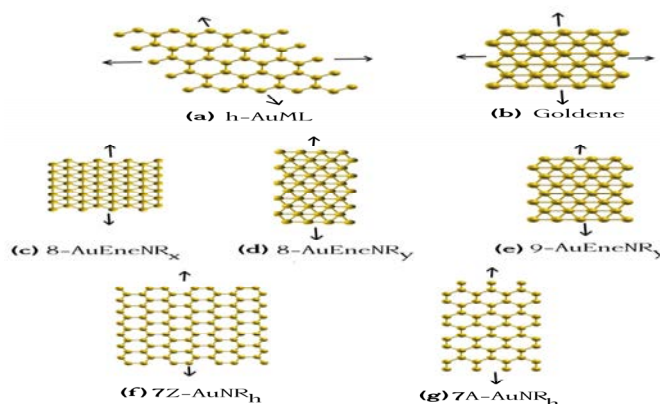


FIGURE 1. Structural configuration of 2D and 1D Gold Nanostructures (a) h-AuML (hexagonal monolayer), (b) Goldene (square lattice), (c) 8-AuEneNR_x (nanoribbon periodic along x-axis with 8 rows), (d) 8-AuEneNR_y (nanoribbon periodic along y-axis with 8 rows), (e) 9-AuEneNR_y, (f) 7Z-AuNR_h (zigzag nanoribbon of h-AuML) and (g) 7A-AuNR_h (armchair nanoribbon of h-AuML).

Gold is a material commonly known for its beauty, corrosion resistance and high electrical conductivity [1]. In recent years, gold has drawn the attention of many researchers due to its remarkable properties that emerge when it is reduced to lower dimensions, particularly at the nanoscale [2]. In its bulk (3D) form, gold crystallizes in an FCC structure and behaves as an excellent conductor of electricity [3]. However, lower-dimensional forms of gold show unique structural and electronic behavior and have even demonstrated catalytic activity in certain chemical reactions [4]. Such properties make them promising candidates for applications in spintronics [5] and hydrogen storage [6]. The various atomic structures of gold in different dimensional forms are illustrated in the FIGURE 1.

COMPUTATIONAL DETAILS

We used SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) code for structural and electronic calculations [7]. Density functional theory (DFT) calculations were performed using relativistic pseudopotentials as implemented in the SIESTA package. The GGA-PBEsol exchange correlation functional with DZP (Double Zeta Polarized) appropriate basis set were employed for electronic structure calculations. A $15 \times 15 \times 15$, $15 \times 15 \times 1$ and $15 \times 1 \times 1$ Monkhorst Pack-grids were used for bulk crystal, 2D and 1D structures. For all the calculations a mesh cut-off of 300 Ry was used. A vacuum of 20 Å is applied in z direction.

RESULTS AND DISCUSSION

We investigate the lattice constants and binding energies of all the structures, as shown in TABLE 1. The optimized lattice constant value of bulk system is 4.237 Å which is consistent with reported data [8], confirming the reliability of our approach. A clear trend arises with dimensional reduction when we are moving from bulk (3D) to Goldene/h-AuML (2D) and lastly to nanoribbons (1D) shows systematic decrease in the magnitude of the binding energy. This occurs due to the reduced atomic coordination and weaker overlapping of Au 5d–6s orbital, increasing reactivity and lowering cohesion. Z-AuNR_h and A-AuNR_h ribbons show the smallest cohesive strengths of –2.214 eV and –2.127 eV per atom respectively, illustrated in TABLE 1, depicting that in such edge-rich geometries, atoms experience a less constrained bonding environment. The lattice parameters for 3D, 2D and 1D systems are displayed in FIGURE 2 and FIGURE 3.

TABLE 1: Lattice Constant and Binding energies of the structures

Structure	Bulk	Goldene	h-AuML	8-AuEne NR _x	8-AuEne NR _y	9-AuEne NR _y	Z-AuNR _h	A-AuNR _h
Lattice constant (Å)	4.237 (4.20) ^[8]	a=2.767, b=4.777	4.656 (4.61) ^[8]	2.754	4.724	4.717	4.571	7.898
Binding Energy (eV/atom)	-3.60 (3.19) ^[9]	-3.049	-2.264	-2.866	-2.692	-2.759	-2.214	-2.127

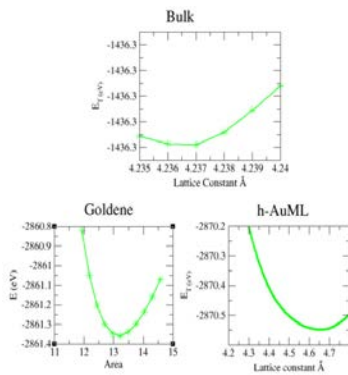


FIGURE 2. Lattice constant or minima (Bulk, Goldene and hexagonal monolayer).

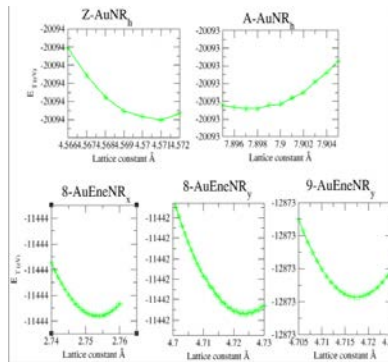


FIGURE 3. Lattice constant or minima of 1D Nano-ribbons.

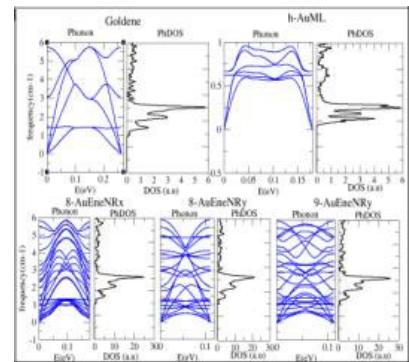


FIGURE 4. Phonon dispersion of different structures of gold.

FIGURE 4 shows no imaginary phonon modes, indicating positive restoring forces for all wavevectors and confirming dynamic stability. FIGURES 5–6 confirm metallic behavior, with the Fermi level crossing dispersive Au 5d–6s bands that enable strong charge delocalization. In FIGURE 7, the 8-AuEneNR_y ribbon exhibits spin-polarized edge states and a net magnetic moment of ~0.38 μB, arising from reduced symmetry and localized edge states where exchange interactions are enhanced.

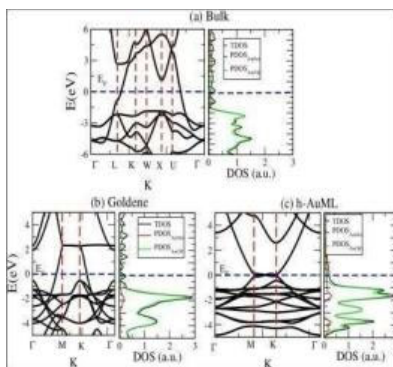


FIGURE 5. Band structures and DOS of bulk (a) and 2D gold(b) and (c).

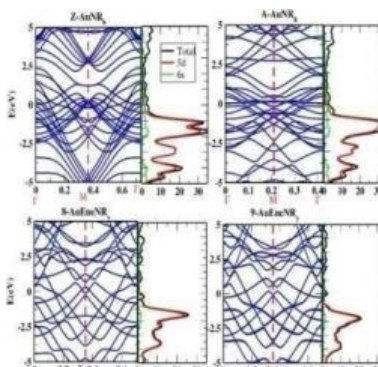


FIGURE 6. Band structure and DOS of 1D Nano-ribbons.

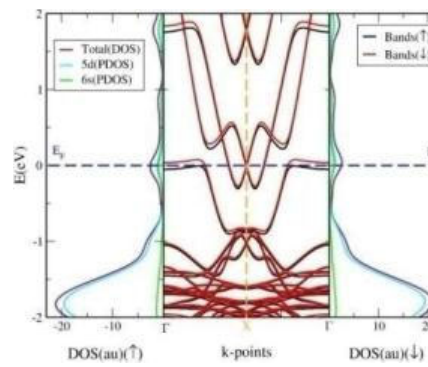


FIGURE 7. Band structure and DOS of 8-AuEneNR_y showing magnetic moment.

CONCLUSION

1D gold Nano-ribbons demonstrated lower binding energies compared to their bulk and 2D counterparts, making this promising for chemical reactivity. Phonon dispersion confirms their thermal stability, while band structures show metallic behavior across all low-dimensional forms. The 8-AuEneNR_y Nano-ribbon also shows a finite magnetic moment ($\sim 0.38\mu_B$), indicating potential in spintronics. Combined with their stability, conductivity, and tunable geometry, these structures are also suited for Nano-electronic interconnects, electrode materials for supercapacitors, sensors and hydrogen storage applications.

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Lattice-Electronic Locking and Disorder-Driven Mott Gap Suppression in 1T-TaS₂

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Abstract. We use low-temperature scanning tunneling microscopy/spectroscopy (STM/S) to investigate the interplay between lattice order, electronic correlations, and disorder in the commensurate charge density wave (CCDW) phase of 1T-TaS₂. Atomically resolved imaging confirms the ($\sqrt{13}\times\sqrt{13}$)R13.9° “Star of David” (SOD) superstructure and a Mott gap of ~0.38 eV. Local structural imperfections in nanoscale induce modulations in the Hubbard peak positions and, in extreme cases, a collapse of the Mott gap and local breakdown of CCDW coherence. Within the Mott gap, 2D local density of states (LDOS) mapping reveals periodic modulations commensurate with the SOD periodicity, providing direct evidence of electronic states inside the gap and further demonstrating that surface imperfections can suppress or even eliminate the gap.

INTRODUCTION

Two-dimensional (2D) materials host diverse electronic phenomena due to their elemental composition and interlayer interactions, such as electron-electron correlations, electron-phonon coupling, orbital hybridization, and van der Waals forces [1-2]. Among them, 1T-TaS₂ is a prototypical 2D correlated system, known for its rich sequence of CDW transitions. Upon cooling it transforms from metallic 1T structure → incommensurate (≤ 550 K) → nearly commensurate (≤ 350 K) → commensurate (≤ 180 K) CCDW phase. In the CCDW phase, Ta atoms form a ($\sqrt{13}\times\sqrt{13}$)R13.9° SOD, with twelve Ta atoms contracting toward a central Ta, distorting the adjacent sulfur atoms, and displaying a periodic lattice modulation [2-4]. This reconstruction leads Ta 5d band into narrow correlation-driven subbands, localizing one unpaired electron per SOD, with strong on-site Coulomb interactions stabilizing a Mott insulating ground state [3-8]. Here, we employ STM/S to investigate the interplay between lattice order, electronic correlations, and disorder in the CCDW phase of 1T-TaS₂. We first characterize the pristine surface structure and Mott gap (Δ_{Mott}), then reveal how structural imperfections induce nanoscale electronic inhomogeneities and local Mott-gap collapse. Momentum-resolved LDOS mapping demonstrates that, despite such disorder, the electronic modulations remain perfectly locked to the CCDW lattice, with their intensity exhibiting strong energy-dependent variation that reflects the dispersion of the underlying states.

EXPERIMENTAL METHODS

STM/S measurements were conducted in a Scienta Omicron GmbH variable-temperature STM system at a base pressure of 6×10^{-11} mbar at 26 K. The crystal was cleaved *in-situ* at room temperature. All the STM measurements are performed in constant current mode using an electrochemically etched W tip. dI/dV spectra were measured using a lock-in amplifier with a modulation voltage and frequency of 10 mV and 1.373 kHz, respectively.

RESULT AND DISCUSSION

Figures 1(A–B) represent a typical STM topography of the 1T-TaS₂ surface in the CCDW phase and the corresponding FFT, respectively. The FFT exhibits well-defined superlattice reflections (magenta circles) associated with the CDW modulation, rotated by 13.9° with respect to the (1×1) Bragg peaks (red circles) of the underlying lattice, thereby confirming the ($\sqrt{13}\times\sqrt{13}$)R13.9° reconstruction. The CDW modulation wavelength, extracted from the reciprocal-space peak positions, is estimated to be 1.3 ± 0.1 nm [4,5]. In atomically resolved image [Fig. 1(C)],

each CDW maximum corresponds to a SOD consisting of a central Ta atom surrounded by three out-of-plane-displaced top-layer S atoms in a trimer arrangement and nine additional S atoms forming an equiangular hexagon [8]. The concentric alignment of hexagon and SOD with the CDW unit cell corners indicates negligible in-plane displacement, consistent with CCDW-lattice locking. In Fig. 1(D), we show measured dI/dV spectrum from a clean region and its parabolic background subtracted spectrum showing two main features: LHB and UHB peak at -0.24 eV and $+0.14$ eV, giving rise a Mott gap of ~ 0.38 eV, a signature of strong on-site Coulomb repulsion [4, 6]. The STM topography in Fig. 1(E) reveals randomly distributed structural imperfections that locally modulate surface corrugation. These defects act as local charge dopants [7,8], perturbing the potential landscape and inducing spatial shifts of the UHB and LHB, thereby renormalizing the local Mott gap. The spatially resolved dI/dV spectra acquired along red dotted arrow in Fig. 1(E), traversing multiple defects, are shown in Fig. 1(F). Spectra exhibit Hubbard peaks with spatial variations and extracted Δ_{Mott} [Fig. 1(G)], showing pronounced modulation, including strong suppression at certain locations, and a near-complete collapse at regions showing enhanced corrugation (gray profile). This indicates a local breakdown of CCDW coherence, possibly due to defect-induced electronic delocalization.

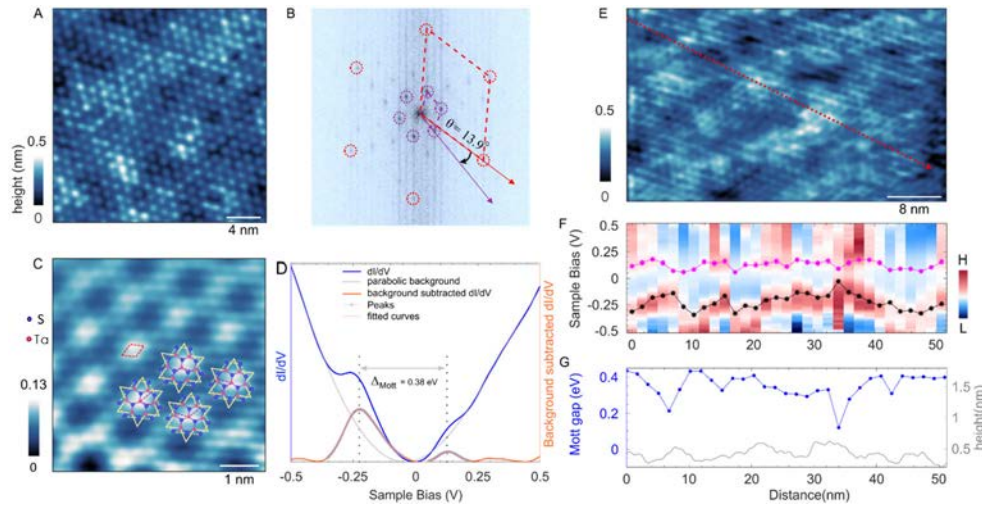


FIGURE 1. (A) STM topography ($V_b = -0.16$ V, $I_t = 0.48$ nA) of the 1T-TaS₂ surface in CCDW phase. (B) Fast Fourier Transform (FFT) highlighting both atomic lattice (red) and CDW wavevectors (magenta). (C) Atomic-resolution topography resolving CDW and (1×1) atomic unit cell with a ball-and-stick model overlayed. (D) dI/dV spectrum of the 1T-TaS₂ surface. (E) STM topography ($V_b = -0.52$ V and $I_t = 0.1$ nA) of a region with structural imperfections. (F) Spatially resolved dI/dV spectra along a red dotted arrow in panel (E); magenta and black dashed lines represent the upper and lower Hubbard band (UHB and LHB) states, respectively. (G) Comparison of height profile (gray) and Mott gap (blue) extracted (from F) along the red dotted arrow in panel (E).

To investigate the momentum-space structure of electronic modulations in the CCDW phase near structural imperfections, we performed spatially resolved $dI/dV(\mathbf{r}, E)$ mapping over the region shown in Fig. 2(A). Selected LDOS maps at $+0.47$ eV, $+0.21$ eV, 0.0 eV, -0.16 eV, and -0.47 eV are presented in Figs. 2(C – G), with their corresponding FFTs in Figs. 2(H – L). The FFT of the topography [Fig. 2(A)], displayed in Fig. 2(B), exhibits three sets of Bragg peaks (marked in red, green and blue) aligned with the CCDW crystallographic directions. Their angular orientations and reciprocal-space magnitudes, referenced to the dashed-line axis in Fig. 2(B), served as benchmarks for analyzing the LDOS FFTs. Figs. 2(M – O and Q) demonstrate that, across all three directions, the LDOS Bragg peaks closely match the topographic peaks in both orientation and magnitude, indicating perfect locking between the electronic modulations and the CCDW lattice. The energy dependence of the FFT peak intensities [Fig. 2(P)] reveals a pronounced modulation and suppression near -0.26 eV and an almost complete disappearance around E_F (0 eV) and $+0.31$ eV. LDOS mapping within the Mott gap unambiguously shows periodic modulations matching the SOD periodicity, indicating the presence of states inside the gap. This observation is consistent with spatially resolved 1D spectroscopy in Fig. 1, where surface imperfections lead to a suppression, and in some cases a collapse, of the Mott gap.

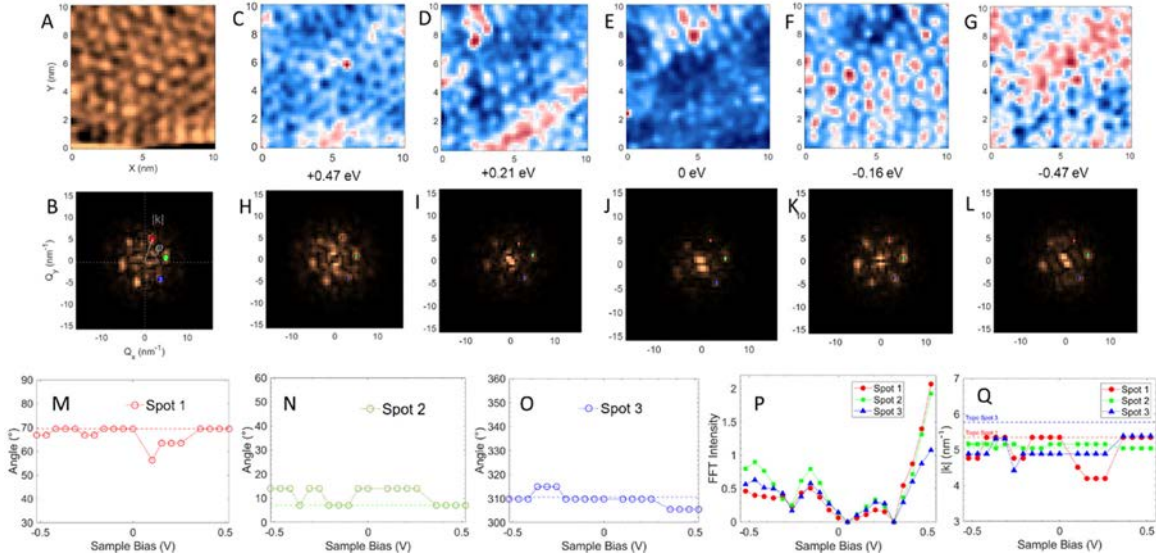


FIGURE 2. (A) STM topography ($V_b = -0.52$ V, $I_t = 0.31$ nA) of 1T-TaS₂ simultaneously taken during 2D maps. (B) FFT of panel (A), with three Bragg peaks of CDW marked 1-3 (red, green, and blue). (C)-(G) dI/dV maps ($V_b = -0.52$ V, $I_t = 0.31$ nA, and $V_{mod} = 8$ mV), and (H)-(L) their FFTs, energy cuts are marked between real and reciprocal space maps. (M)-(O) Angular and (P) intensity variation of the FFT spots as a function of sample bias. (Q) Magnitude of FFT spots plotted for topography and dI/dV maps as a function of sample bias.

CONCLUSION

Our STM/S measurements reveal that in the CCDW phase of 1T-TaS₂, electronic modulations remain spatially locked to the lattice even in the presence of defects. Structural imperfections locally suppress and, in some cases, collapse the Mott gap. Momentum-space mapping shows that electronic states inside the 2D Mott gap retain the Star-of-David periodicity, with energy-dependent intensity modulation reflecting their dispersion. These results highlight the robustness of lattice–electronic locking and the sensitivity of spectral weight to nanoscale disorder.

ACKNOWLEDGMENTS

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Thermoelectric coefficients in Graphene and Non-relativistic systems

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Abstract. The present investigation provides a comprehensive analysis of thermoelectric coefficients, including the Peltier and Thomson effects, within the context of the hydrodynamic behavior of charge carriers in the graphene system. Using the kinetic theory formalism with the Boltzmann transport equation under the relaxation-time approximation, we observe distinct higher-order thermoelectric coefficients in the graphene system at room temperature, compared to those in the non-relativistic metallic system. Under hydrodynamic conditions near the charge-neutrality point, deviations arise in the fluid-based expressions for the Peltier and Thomson effects in graphene, distinguishing them from their non-relativistic counterparts.

INTRODUCTION

In graphene, the strong interaction between the charged particles leads to a collective behavior, where carriers behave like a fluid [1]. Unlike metals, graphene exhibits two distinct transport regimes: the Dirac fluid ($\frac{\mu}{k_B T} \ll 1$) and Fermi liquid ($\frac{\mu}{k_B T} \gg 1$) [2,3] where μ is the Fermi energy or chemical potential, and $k_B T$ is thermal energy. Here k_B and T are the Boltzmann constant and the system's temperature, respectively. In the Dirac fluid domain, the electron-electron interaction (momentum-conserving) is dominated over the electron-impurity/disorder/defect interaction (momentum-relaxing), which is the desired condition for the existence of hydrodynamics [1,2]. Graphene shows a remarkable feature where μ can be tuned up to some meVs via doping techniques. In this context, μ of metals (non-relativistic) is almost constant, with values ranging from 2 to 10 eV. Here, we investigate how fluid-like flow affects the thermal transport of charge carriers in the graphene system compared to the metallic system. Thermoelectrics appear to be an invasive tool for probing the scattering mechanism underlying transport phenomena in the material system. Due to hydrodynamic effects, an enhanced thermal conductivity is expected, leading to violations of conventional physical relations, such as the Wiedemann-Franz law [2-4] and thermoelectric effects [5-8] near the Dirac or charge-neutrality point. Thermoelectrics basically comprises two processes: the Seebeck effect, or thermopower (S), and the Peltier effect (II). The Peltier effect is the generation of a temperature gradient when an electric current is driven through a system. Thomson effect (Th) arises due to the temperature dependence of thermopower. It measures the heating in the Dirac fluid domain and cooling in the Fermi liquid domain [8] in the graphene system. Thermoelectric properties have recently been explored experimentally [5,6] and theoretically [7] in graphene. A change in the sign of the thermoelectrics has been observed experimentally, near the charge neutrality point, when the charge carriers switch from electrons to holes [6]. The thermoelectric coefficients can be calculated using a semiclassical formulation for non-relativistic systems (metals) [9]. In contrast, it shows a distinct nature near the Dirac point at a significant temperature T , thereby breaking the Fermi-liquid paradigm [5]. Here in this article, we derive the Peltier and Thomson coefficients for graphene, where the charge carriers show fluidic behavior, and the non-relativistic metal system, where the electrons show the conventional electron flow governed by the Ohm's law.

FORMALISM

For dissipative hydrodynamics, the energy-momentum tensor $T^{\mu\nu}$ and number flow N^μ can be written as,

$$T^{\mu\nu} = g \int \frac{d^2 p}{h^2} p^\mu v^\nu f, \quad (1)$$

and

$$N^\mu = g \int \frac{d^2 p}{h^2} v^\mu f. \quad (2)$$

Here, $f = f_0 + \delta f$ is the non-equilibrium distribution function, caused by some external bias from the equilibrium.

Here, f_0 is the Fermi-Dirac distribution, i.e., $f_0 = \frac{1}{e^{\beta(\epsilon - \mu)} + 1}$ where $\beta = \frac{1}{k_B T}$. Here $\epsilon = p v_F$ is the dispersion relation

of the charge particles and $\vec{v}_F = 1.1 \times 10^6$ m/s is the Fermi velocity of the electron in the graphene. δf is the deviation from the equilibrium that provides dissipation within the system.

The current density from Eq. (2) can be written as,

$$\vec{j} = eg \int \frac{d^2 p}{h^2} \vec{v}_F \delta f, \quad (3)$$

where e is the electronic charge, g is the degeneracy factor, that includes spin and valley counterparts ($g=4$).

To find the value of δf we have used the Boltzmann transport equation for the fluid case as follows,

$$\frac{\partial f}{\partial t} + \vec{v}_F \cdot \frac{\partial f}{\partial x} + e \vec{E} \cdot \frac{\partial f}{\partial p} = -\frac{\delta f}{\tau_c}. \quad (4)$$

Where τ_c is the relaxation time that carries the information regarding the scattering processes

Solving for the values of δf and putting in Eq. (3), the current density can be written in the following format,

$$\vec{j} = \frac{eg}{2} \int \frac{d^2 p}{h^2} v_F^2 \tau_c \left[-e \vec{E} + \left(\frac{\epsilon - Q_i \tilde{h}}{T} \right) \vec{\nabla} T \right] \frac{\partial f^0}{\partial E}, \quad (5)$$

where $\vec{E}$ is the applied electric field, $Q_i = \pm 1$ for electron and hole, and $\tilde{h}$ is the enthalpy per particle, a crucial parameter for characterizing the deviation near the charge-neutrality point.

The macroscopic definition of electric and heat current density can be written in the following matrix form,

$$\begin{pmatrix} \vec{j}_e \\ \vec{j}_{th} \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} \vec{E} \\ \vec{\nabla} T \end{pmatrix} \quad (6)$$

The matrix elements can be written as, $a_{11} = I^{(0)}$, $a_{12} = -\frac{1}{eT} I^{(1)}$, $a_{21} = -\frac{1}{e} I^{(1)}$, and $a_{22} = \frac{1}{e^2 T} I^{(2)}$. Here,

$$I^{(\alpha)} = \int_{-\infty}^{\infty} d\epsilon \left(\frac{\partial f^0}{\partial \epsilon} \right) (\epsilon - \tilde{h})^\alpha \sigma. \quad (7)$$

Here σ is the electrical conductivity. By applying the Onsager condition $a_{21} = -a_{12} T = \Pi a_{11}$. The Peltier coefficient (Π) can be defined as follows [9],

$$\Pi = \frac{a_{21}}{a_{11}}. \quad (8)$$

Solving Eq. (8) with the values of a_{21} and a_{11} using Eq. (7), the Peltier coefficient for the graphene system can be calculated as follows,

$$\Pi_G = -\frac{k_B T}{e} \left[2 \frac{f_2(A) - f_2(A^{-1})}{f_1(A) + f_1(A^{-1})} - \tilde{h} \beta \right]. \quad (9)$$

Here $f_v(A)$ and $f_v(A^{-1})$ are the Fermi integral functions for electron and hole, respectively [3], where $v=1,2,3,\dots$ and $A = e^{\mu/k_B T}$, is the fugacity of the system. The Thomson coefficient can be calculated as follows,

$$Th_G = T \frac{d}{dT} \left(\frac{\Pi_G}{T} \right). \quad (10)$$

Equations (9) and (10) represent the fluid-based expressions for the graphene system.

In the non-relativistic scenario where $\epsilon = p^2/2m$, the Peltier coefficient can be calculated by following the semi-classical formalism, where τ_c is independent of the energy [9],

$$\Pi_{NR} = -\frac{\pi^2 k_B^2 T^2}{2 e \mu}. \quad (11)$$

The corresponding Thomson coefficients can be determined as follows [9],

$$Th_{NR} = -\frac{\pi^2 k_B^2 T}{2 e \mu}. \quad (12)$$

RESULTS AND CONCLUSIONS

In this section, we plot the higher-order thermoelectric coefficients derived from our theoretical framework. Our main aim is to show the different behavior of these coefficients in the fluidic and non-relativistic (metal) scenarios. In Fig 1. (A) we have depicted the variation of the Peltier coefficient with respect to the values of $\mu/k_B T$ based on the Eqs. (9) and (11). For the graphene-fluid case (red dashed curve), the Peltier coefficient deviates from that of the non-relativistic counterpart (blue solid curve). Here, we note that Peltier heating due to holes may exceed that due to electrons in Peltier cooling [6]. In Fig. 1 (B), we have depicted the nature of the Thomson effect in both graphene (red dashed curve) and the non-relativistic system (blue solid curve) given by Eqs. (10) and (12). It shows a deviated value from the non-relativistic counterpart. An enhancement is observed in both cases near the Dirac fluid domain, whereas in the Fermi-liquid domain, they converge.

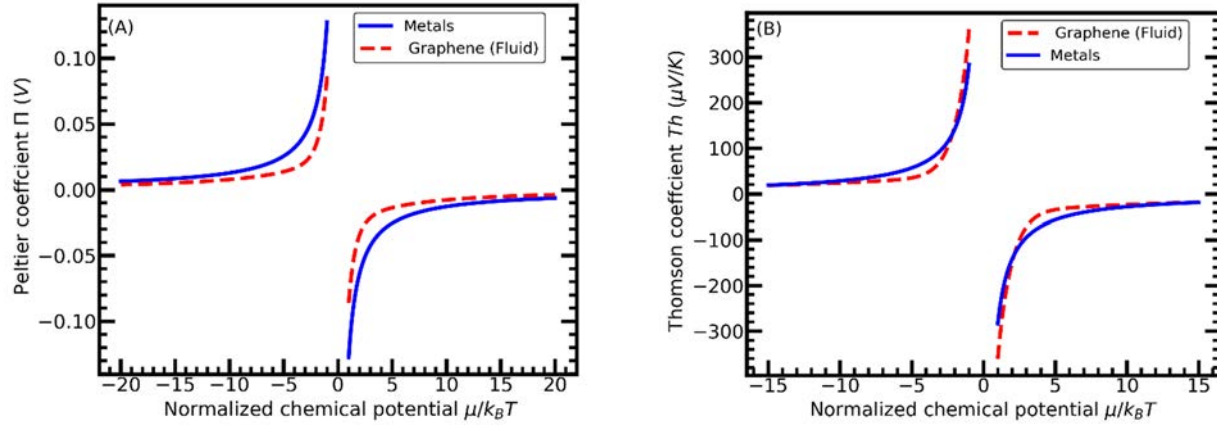


FIGURE 1. (A) Peltier coefficient and (B) Thomson coefficient vs $\mu/k_B T$ at $T = 300$ K.

For metals, as a non-relativistic electronic system, it is very hard to reach low values of $\mu/k_B T$. So, their Peltier and Thomson coefficient values almost constant within the range $\mu = 2 - 10$ eV. Here, for theoretical interest we have extended the non-fluid expressions of Peltier and Thomson coefficients of a non-relativistic electron system (metal) towards lower values of $\mu/k_B T$. We have found a difference between the non-fluid expression of the Peltier coefficient for the non-relativistic electron system in metals and the fluid expression of the Peltier coefficient for electrons in the graphene system. This difference is noticed in the entire domain of $\mu/k_B T$, although in the Fermi-liquid domain they tend to merge. For the Thomson coefficient, their difference is quite small but noticeable. In conclusion, the present work aims to highlight the differences between fluid and non-fluid aspects through these thermoelectric coefficients, which may help in understanding and distinguishing the electron hydrodynamic phenomenon in graphene from standard condensed-matter phenomena in other systems, such as metals.

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SCAPS Simulation of Lead-Free $\text{Cs}_2\text{AuBiCl}_6$ Double Perovskite-Based Solar Cell

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Abstract. This study investigates the response of $\text{Cs}_2\text{AuBiCl}_6/\text{CuSbS}_2$ -based solar cell structure using SCAPS simulation. The key performance parameters, i.e., short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE), have been evaluated using various experimental data reported in the literature. The influence of absorber layer parameters (thickness, energy band gap, electron affinity, and doping concentration) on solar cell performance has been assessed. The simulated performance parameters V_{oc} , J_{sc} , FF, & PCE are 1.14 V, 34.25 mA/cm², 89.05%, and 34.71%, respectively, for an optimized solar cell, suggesting its utility for efficient solar cells.

INTRODUCTION

Solar energy is the most significant and sustainable form of renewable energy. Recent progress in solar cell technology has led to the emergence of perovskite solar cells, which offer tremendous potential as cost-effective and high-efficiency alternatives to traditional silicon-based photovoltaics [1]. Pb based perovskites are studied extensively and have shown promising P-V performance; however, their toxicity limits their utility. The limited adoption of perovskite-based solar cells (PSCs) for large-scale commercial applications is primarily driven by concerns over the long-term stability of perovskite absorbers, which pose challenges in meeting stringent environmental regulations [2]. They are less stable than silicon and non-perovskite-based solar cells [3]. Consequently, there are continuous research efforts to explore stable perovskite materials with efficient P-V performance. The $\text{Cs}_2\text{AuBiCl}_6$ (CABC) halide-based double perovskite is more stable than copper, titanium, and tin-based perovskite because gold provides excellent stability [4]. Accordingly, the present study investigates the performance of the CABC-based solar cell structure using the SCAPS 1D simulator. Herein, Indium zinc oxide (IZO), Zinc selenide (ZnSe), Dicaesium gold (III) bismuth (III) hexachloride ($\text{Cs}_2\text{AuBiCl}_6$) double perovskite, and Copper (I) antimony (III) disulfide (CuSbS_2) is utilized as transport conductive oxide (TCO), electron transport layer (ETL), absorber and hole transport layer (HTL), respectively.

DEVICE STRUCTURE AND SIMULATION PARAMETERS

This solar cell features an IZO/ZnSe/ $\text{Cs}_2\text{AuBiCl}_6$ / CuSbS_2 structure, utilizing Au as both front and back contacts. The material parameters have been taken from various reported literature and also tuned to optimize the overall structure. The simulations were performed under AM1.5G light at 300 K with no series and shunt resistance. Figures 1(a) and 1(b) represent the solar cell structure and the stimulated band diagram illustrating the charge separation across the layers, respectively. The well-like structure formed at the interface of ZnSe and IZO (Figure 1(b)) is due to the formation of an ohmic contact [5].

RESULTS AND DISCUSSION

Initially, the performance of the proposed solar cell structure was analyzed using the material parameters listed in Table 1. Figure 1(c) presents the current density–voltage characteristics of the device, exhibiting a V_{oc} of 0.75 V, J_{sc} of 42.31 mA/cm², FF of 76.85%, and PCE of 24.44%. Figure 1(d) shows the wavelength-dependent quantum efficiency (QE), revealing high QE values in the visible region and a sharp decline near 1100 nm, corresponding to the absorber band gap. Furthermore, absorber thickness, band gap, defect density, and acceptor doping concentration significantly influence device performance and were therefore systematically investigated.

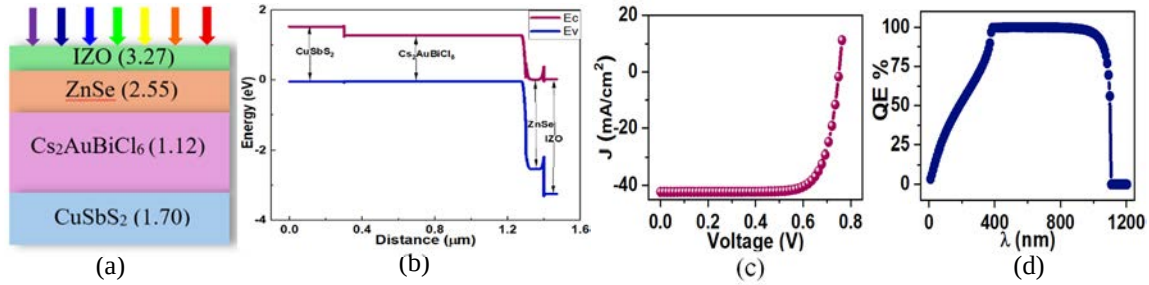


FIGURE 1. (a) Device structure; (b) Simulated band diagram of IZO/ZnSe/Cs₂AuBiCl₆/CuSbS₂ solar cell structure; (c) The J_{SC} vs Voltage curve; (d) Wavelength vs quantum efficiency curve.

TABLE 1. Simulation parameters of IZO, ZnSe, CABC, and CuSbS₂ layers.

Parameters	IZO [6]	ZnSe [7]	CABC [8]	CuSbS ₂ [9]
Thickness (nm)	70	100	1000	300
Band Gap (eV)	3.27	2.55	1.12	1.58
Electron Affinity (eV)	4.5	4.09	4.5	4.2
Dielectric Permittivity	9	9.4	3.56	14.6
C _B effective density of states (cm ⁻³)	2.2×10^{18}	1.7×10^{18}	1.7×10^{18}	2.0×10^{18}
V _B effective density of states (cm ⁻³)	1.8×10^{19}	0.8×10^{17}	0.8×10^{18}	1.0×10^{19}
Thermal velocity of electrons	1.0×10^7	1.2×10^7	2.66×10^7	1.0×10^7
Thermal velocity of holes	1.0×10^7	0.7×10^7	2.14×10^7	1.0×10^7
Electron Mobility (cm ² /Vs)	100	50	10	4.9
Hole Mobility (cm ² /Vs)	25	50	10	4.9
Shallow Donor Density (cm ⁻³)	1.0×10^{18}	1.0×10^{18}	1.0×10^{10}	0
Shallow Acceptor Density (cm ⁻³)	0	0	1.0×10^{10}	1.38×10^{18}
Defect N _T (cm ⁻³)	1.0×10^{14}	1.0×10^{14}	1.0×10^{14}	1×10^{14}

Impact of thickness and energy band gap

To examine the effect of absorber layer thickness on photovoltaic performance, the absorber thickness was varied from 100 nm to 1000 nm while keeping all other parameters constant. Figure 2(a) shows the variation of Voc and Jsc with thickness. An opposite trend is observed, where Voc decreases while Jsc increases with increasing absorber thickness. The decrease in Voc and enhancement in Jsc are attributed to increased carrier recombination in thicker absorber layers, leading to an increase in reverse saturation current [10]. Figure 2(b) presents the dependence of FF and PCE on absorber thickness. A gradual decrease in FF is observed with increasing thickness. However, PCE initially increases and reaches a maximum value of 24.81% at around 600 nm, followed by a slight decline at higher thicknesses. This improvement in PCE is mainly due to the dominant increase in Jsc compared to the reduction in Voc and FF. After optimizing the absorber thickness at 600 nm, the energy band gap was varied from 0.92 eV to 1.42 eV while maintaining other parameters constant. The band gap strongly affects photon absorption, as lower band gap materials absorb low-energy photons more effectively. Figure 2(c) shows that Voc increases while Jsc decreases with increasing band gap. This behavior is associated with reduced reverse saturation current and lower electron-hole pair generation. Figure 2(d) indicates a continuous increase in FF with band gap, while PCE reaches a maximum value of 29.42% at 1.32 eV due to the combined enhancement in Voc and FF.

Impact of defect and acceptor doping density

In addition to the absorber's thickness and band gap, the defect density is varied from 10^{13} to 10^{18} cm⁻³. Figure 2(e) and Figure 2(f) show that Voc and Jsc, as well as FF and PCE, decrease consistently with increasing defect density from 10^{13} to 10^{18} cm⁻³, which can be attributed to increased non-radiative recombination pathways that reduce the carrier lifetime and overall charge collection [11]. However, the maximum efficiency is obtained at 10^{13} cm⁻³, implying

that higher defect concentration can deteriorate the performance of the solar cell. Finally, the acceptor doping density is tuned from 10^{11} to 10^{20} cm^{-3} , keeping the 600 nm thickness, 1.32 eV energy gap and defect density of 10^{13} cm^{-3} . Figure 2(g) shows that V_{OC} remains unaffected upto 10^{16} cm^{-3} , and then increases, indicating reduced recombination and a corresponding decrease in reverse saturation current.

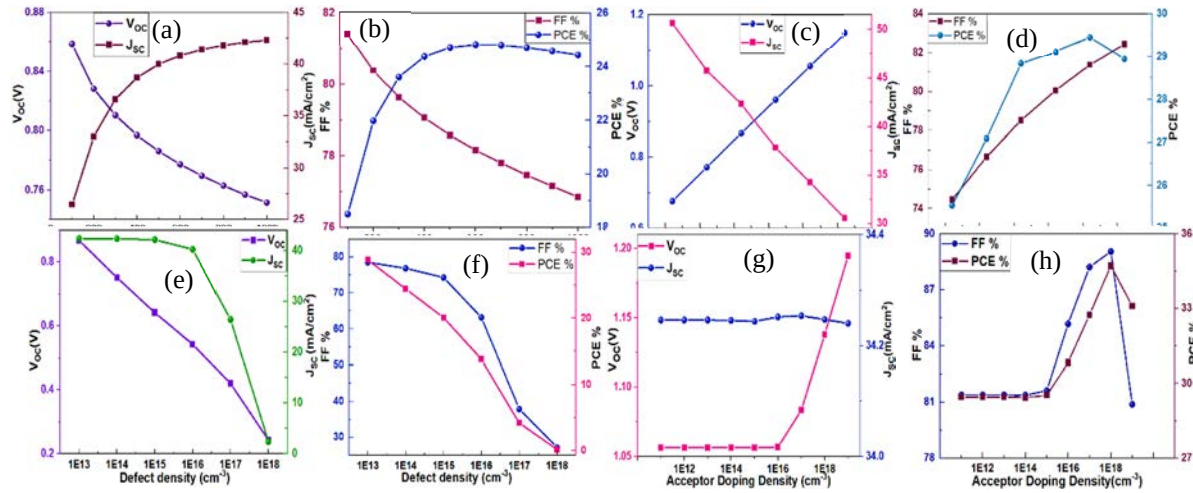


FIGURE 2. Variation of V_{OC} & J_{SC} (a, c), and FF & PCE (b, d) with absorber layer thickness (a–b), energy gap (c–d). Variation of V_{OC} & J_{SC} (e, f), and FF & PCE (g, h) with defect density (e–f), acceptor doping density (g–h).

However, the change in J_{SC} is negligible, while moderate carrier concentrations promote the generation of electron-hole pairs; higher concentrations hinder their formation. Both FF and PCE (Figure 2(h)) show an increasing trend from 10^{15} to 10^{18} cm^{-3} , which decreases at a carrier concentration of 10^{19} cm^{-3} .

CONCLUSION

IZO/ZnSe/Cs₂AuBiCl₆/CuSbS₂ structure is proposed to enhance photovoltaic performance through systematic optimization of the absorber layer. Incorporating CABC as an absorber, ZnSe as ETL, and CuSbS₂ as HTL leads to remarkable efficiency. The optimized absorber parameters: thickness of 600 nm, band gap of 1.32 eV, defect density of 10^{13} cm^{-3} , and doping concentration of 10^{18} cm^{-3} , yield improved device performance with V_{OC} of 1.14 V, J_{SC} of 34.25 mA/cm^2 , FF of 89.05%, and PCE of 34.71%.

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DFT Investigation on the Structural, Electronic and Optical Properties of SmVO₄ Orthovanadates

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Abstract. We present a first-principles study of zircon-type SmVO₄, combining structural, electronic, and optical properties within a unified framework. The optimized lattice parameters, $a=b=7.289$ Å, $c=6.385$ Å, are in good agreement with experimental values, confirming structural stability. A direct band gap of 2.89 eV is obtained, with O-2p and V-3d states predominantly forming the valence and conduction bands. The static dielectric function constant $\epsilon_1(0) = 4.62$ and the $\epsilon_2(\omega)$ peak at 5.3eV indicate strong O-2p $\rightarrow$ V-3d optical transitions. The low-loss electron energy-loss spectra reveal plasmonic and interband excitations that correlate well with the corresponding joint density of state features. This work establishes direct correlations among the structural, electronic, and optical properties of SmVO₄, providing a benchmark framework for rare-earth orthovanadates and their potential in optoelectronic applications.

INTRODUCTION

Zircon-type rare-earth orthovanadates, RVO₄ (R = rare-earth), crystallize in the $I4_1/amd$ space group with a corner-sharing network of VO₄ tetrahedra and RO₈ polyhedra, making them attractive for optoelectronic applications [1]. Structural studies of SmVO₄ (SmV) reveal V–O bond length of ≈ 1.74 Å and Sm–O split into four shorter (~ 2.39 Å) and four longer (~ 2.50 Å) interactions, characteristic of a zircon framework. Hydrothermally synthesized SmV nanocrystals exhibit lattice parameters of $a = b = 7.265$ Å and $c = 6.389$ Å. Optical absorption measurements indicate a wide band gap of ~ 3.7 – 3.8 eV. Also, high-pressure Raman studies reveal that the zircon phase remains stable up to ~ 5.8 GPa, before undergoing successive structural transitions, highlighting its sensitivity to external stimuli[2]. Despite extensive experimental investigation, a unified study combining structural, electronic, and optical characteristics within a unified framework for SmV. Addressing this gap, our study combines exhaustive DFT– based simulations with spectroscopic modelling to establish quantitative correlations between crystal structure, electronic excitations, and optical response. This methodology not only benchmarks SmV for optoelectronic applications but also sets a precedent for rational design of other rare–earth orthovanadate systems.

COMPUTATIONAL DETAILS

All calculations were performed within the framework of density functional theory (DFT) using the Quantum ESPRESSO package[3]. The electron exchange–correlation effects were treated using the Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) in conjunction with the projector augmented-wave (PAW) method. During structural optimization, the Broyden-Fletcher-Goldfarb-Shanno (BFGS) method was used, and Monkhorst-Pack scheme with a k-point grid set of $5 \times 5 \times 5$ and $12 \times 12 \times 12$ (dense for non-self-consistent field calculation) and the cutoff energy is set to 700 eV for the plane wave expansion[4]. Optical properties were calculated within the Independent Particle Approximation (IPA), which describes single-particle electronic excitations. For these calculations, a self-consistent field (SCF) ground-state calculation was first performed using norm-conserving pseudopotentials, followed by NSCF calculations to obtain the electronic states required for evaluating the absorption spectrum and related optical properties.

RESULTS AND DISCUSSIONS

Structural and Electronic Properties

FIGURE 1(a) shows the tetragonal zircon-type crystal structure of SmV (space group- $I4_1/amd$), characteristic of rare-earth orthovanadates. In this structure, Sm^{3+} ions are coordinated by eight oxygen atoms, forming SmO_8 dodecahedra, while V^{5+} ions occupy VO_4 tetrahedra. These polyhedra are interconnected through corner-sharing, forming a robust three-dimensional framework along the crystallographic axes. **FIGURE 1(b)** illustrates the local coordination environment of Sm and V ions. These structural units govern the electronic, vibrational, and optical properties of zircon-type orthovanadates. While explicit theoretical predictions of oxygen rotational distortions around these centres in SmV are not detailed in the existing literature, such local lattice distortions are known to significantly influence electronic structure, phonon behavior, and dielectric response in related zircon-type orthovanadate compounds. Structural convergence tests were performed by varying the plane-wave cutoff energy and k-point grid sets shown in **FIGURE 1(c, d)**. The total kinetic energy stabilized beyond 70 Ry with variations < 0.003 eV/formula unit[5]. Therefore, these parameters were adopted for all subsequent calculations, ensuring a balance between accuracy and computational efficiency, consistent with previous DFT studies of orthovanadate compounds.

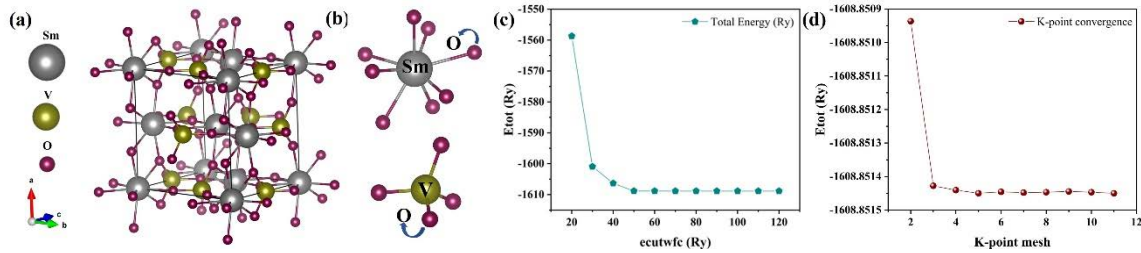


FIGURE 1(a, b) Crystal structure and local coordination environment of Sm and V ions of SmVO_4 . (Sm: Silver, V: Golden, and O: Purple). (c, d) Plane-wave cutoff energy and k-point convergence plots.

FIGURE 2(a) shows the electronic band structure of SmV calculated within DFT using GGA exchange–correlation functional. The energies are referenced to the Fermi level, $E_{\text{EF}} = 0$ eV, along the high-symmetry k-path Γ –X–M– Γ –Z–P–N– Γ –M–X in the Brillouin zone. Both the valence band maximum and conduction band minimum occur at the Γ point, indicating a direct band gap of ~ 2.89 eV, and confirming the semiconducting nature of SmV. The valence band near the Fermi level is mainly composed of O–2p states hybridized with V–d states, while the conduction band is dominated by V–3d states. As expected, the calculated band gap is smaller than the experimental optical band gap (~ 3.73 – 3.81 eV). **FIGURE 2(b)** presents the total and orbital-projected density of states (DOS) contribution from Sm–5d, V–4d, and O–2p states are referenced to $E_{\text{EF}} = 0$ eV. The valence band region (-6 eV to E_{EF}) is dominated by O–2p states with hybridization, indicating strong V–O covalency. This is consistent with the band structure results.

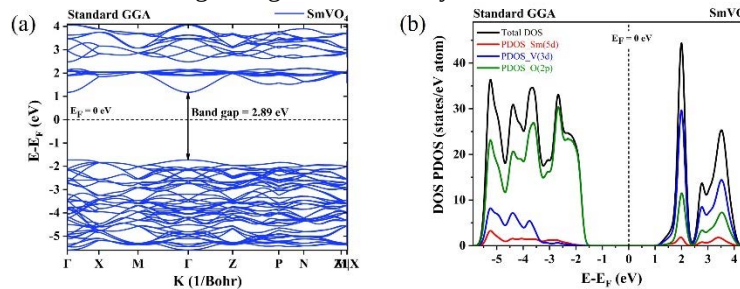


FIGURE 2(a) Electronic band structure, (b) total and projected density of states of SmVO_4 .

Optical Properties

Furthermore, we calculated the real (ϵ_1), and imaginary (ϵ_2) parts of the dielectric function, Joint DOS and low-loss electronic energy loss (EEL) spectra of SmV. The complex dielectric function, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, provides deep insight into the optical and electronic response. The static $\epsilon_1(0) \approx 4.92$, indicates moderate electronic polarizability at zero photon energy. The $\epsilon_1(\omega)$ spectrum shown in **FIGURE 3(a, b)** remains nearly constant in the low-energy regime, exhibits pronounced oscillation above ~ 3.25 eV due to interband electronic transitions. A

maximum value of ~ 6.75 observed near 5 eV, signifies strong photon–electron coupling while the subsequent decrease and sign change around 8 eV suggest the onset of plasmonic behavior, beyond which the material exhibits metallic-like optical behavior[6]. The $\epsilon_2(\omega)$ spectrum shows an absorption onset near the optical bandgap and prominent peaks around 5–8 eV, arising mainly from transitions between O–2p derived valence states and V–3d derived conduction band states. The strong correlation between $\epsilon_2(\omega)$ and $\epsilon_1(\omega)$ features satisfies the expected Kramers–Kronig relationship and confirms the strong ultraviolet optical response. **FIGURE 3(c)** shows the calculated low-loss EEL spectrum of SmV, which provides information on the energy-dependent loss function $Im(-1/\epsilon(\omega))$ directly linked to dielectric response and optical transitions. The dominant peak near ~ 15 eV is attributed to a collective plasmon excitation of the valence electrons, whereas weaker low-energy features originate from interband transitions. Additional structures at higher energies reflect contributions from higher-energy electronic excitations. These results indicate that both single-particle transitions and collective electronic effects contribute to the energy-loss behavior. **FIGURE 3(d)** presents the calculated Joint DOS, which describes the number of allowed electronic transitions at a given excitation energy. Pronounced Joint DOS maxima occur near ~ 6 eV and ~ 20 eV and correlate with corresponding features in the EEL spectrum[7]. This agreement indicates that the observed optical excitations are strongly influenced by the underlying electronic band structure. The correlation between Joint DOS and EEL spectra provides insight into the microscopic origin of the optical and energy-loss features in SmV.

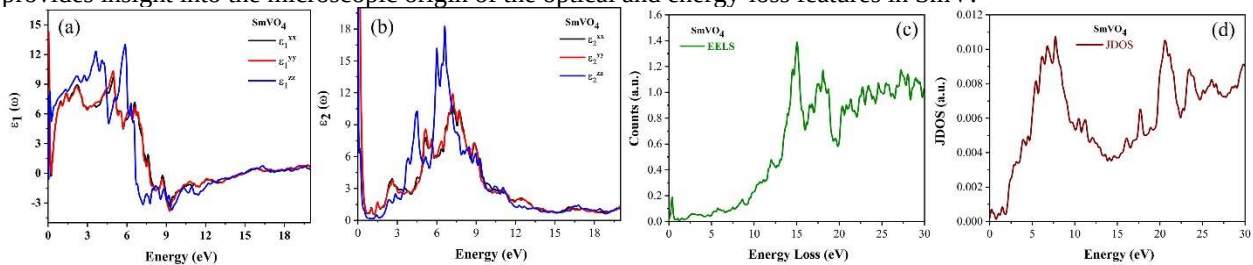


FIGURE 3. Optical properties of SmVO₄: Imaginary dielectric function (a), real dielectric function (b), Joint DOS (c), and low-loss EEL spectra (d).

CONCLUSION

First-principles DFT calculations were performed to investigate structural, electronic, and optical properties of SmVO₄. The optimized zircon-type tetragonal structure agrees well with reported experimental data. A direct band gap of 2.85 eV confirms the semiconducting nature. The bands and DOS analysis show that the valence band is dominated by O–2p contributions in the valence band and V–3d states in the conduction band. The static dielectric constant, $\epsilon_1(\omega) = 4.62$, indicates moderate electronic polarizability, whereas $\epsilon_2(\omega)$ peak at 5.3 eV arises from O–2p $\rightarrow$ V–3d transitions. The correlation between EEL spectrum and Joint DOS features further confirms the dominance of interband electronic transitions. These findings highlight the potential of SmVO₄ for optoelectronic applications.

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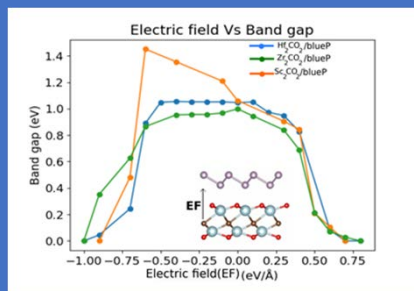
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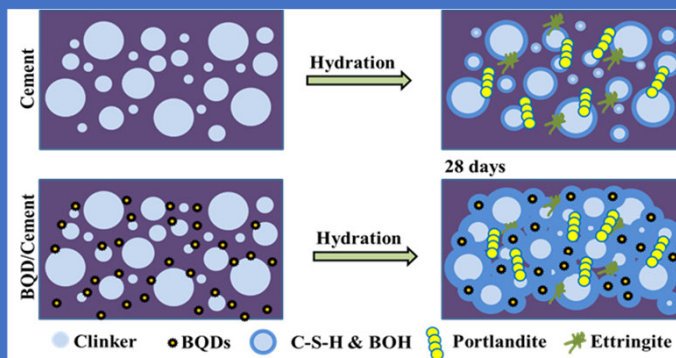
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