अगली पीढ़ी के संदीप्त पदार्थ

Next Generation Luminescent Materials

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Lanthanide ions doped in nanoparticles/ nanomaterials of different inorganic hosts are considered to be next generation luminescent materials and have potential applications in the area of sustainable lighting, bio-labelling and up-conversion luminescence based technologies [1]. Synthesizing such nano-materials in different sizes and shapes and understanding their photo-physical properties constitutes one of the frontline research activities for the past few years in our group. Representative systems investigated are described briefly in this manuscript.

Luminescent properties of inorganic nano-phosphates

$CePO^4$, $CePO^4$:Tb and $CePO^4$:Dy nano-rods with monoclinic structure were prepared at a low temperature of 140°C in ethylene glycol medium. These nanorods are found to be dispersible in solvents like methanol and water. High Resolution Transmission Electron Microscope (HRTEM) and Selected Area Electron Diffraction (SAED) images reveal that the nano-rods are highly crystalline with very high degree of homogeneity. These nano-rods are crystallo-graphically aligned to each other. Strong Tb^{3+} and Dy^{3+} emission has been observed on direct excitation of the $Ce3^+$ levels in the $CePO_4$ host, due to energy transfer from the host to Tb^{3+}/Dy^{3+} ions. These nano-rods were dispersed in sol-gel films and such materials exhibited improved photo-physical properties.

Bi^{3+} is considered to be an ideal substitute for lanthanide ions due to its comparable ionic radii and coordination characteristics. Keeping this in mind hexagonal and monoclinic forms of $BiPO_4$ nanomaterials were prepared based on the reaction of Bi^{3+} and PO_4^{3-} ions in ethylene glycol medium at 100 and 185°C respectively. From the differential thermal analysis (DTA) studies it is confirmed that the difference in the nucleation mechanism rather than the phase transition is responsible for the monoclinic phase formation at low temperatures. Monoclinic $BiPO_4$ is quite stable and forms random solid solutions with lanthanide phosphates having both monoclinic (monazite) and tetragonal (xenotime) structures as confirmed by XRD, FTIR and ^{31}P solid state nuclear magnetic resonance studies. On excitation corresponding to the $^1S_0 \rightarrow {}^3P_1$ transition of Bi^{3+} in $BiPO_4$:Ln nanomaterials, energy transfer from host to lanthanide ions takes place. Upon doping Eu^{3+} ions, monoclinic form of $BiPO_4$, bright luminescence is observed (Fig.1). The studies are quite relevant as there is a growing interest all over the world in replacing lanthanide based hosts used for different applications with easily available, cost effective main group elements such as Sb, Bi etc., or such hosts.

Luminescent properties of oxide based hosts

Nano-crystalline $ZnGa_2O_4$ doped with varying concentrations of lanthanide and Ge^{4+} ions were prepared and

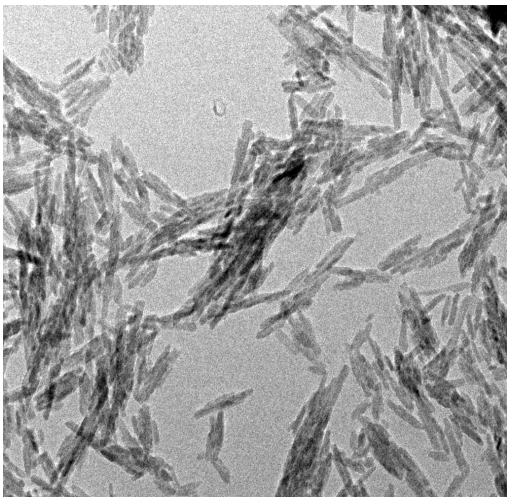

Fig.1: $CePO_4$: Dy nano-rods.

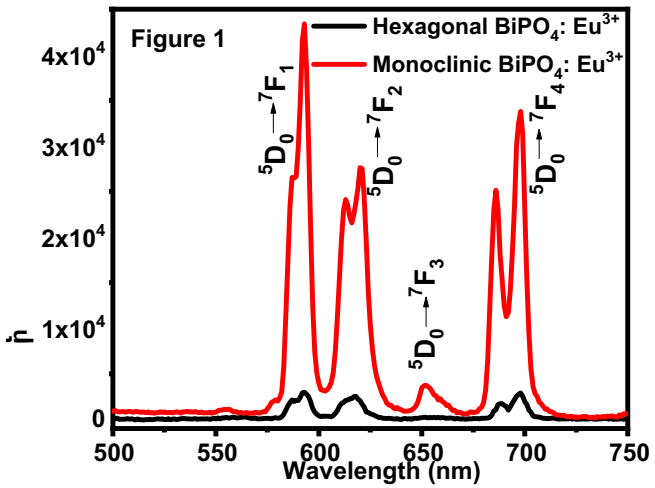

Fig.2: Upon doping Eu^{3+} ions, monoclinic form of $BiPO_4$ exhibits bright luminescence.

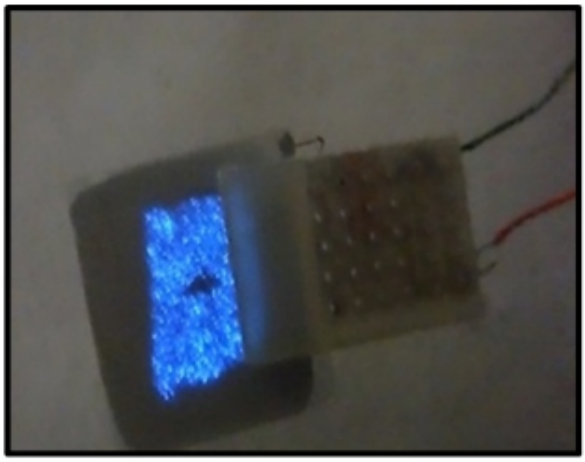

Fig.3: Electro-luminescence from $ZnGa_2O_4$:1%Ge.

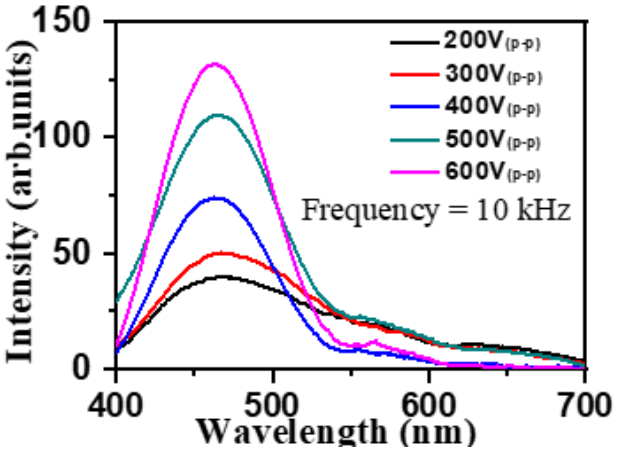

Fig.4: Electro-luminescence spectra.

their photo- and electroluminescence properties were investigated in detail before and after annealing at 900°C. X-ray diffraction (XRD) studies confirmed that Ge^{4+} doping even to a level of 0.5 at.% at the expense of Ga^{3+} in $ZnGa_2O_4$, leads to incorporation of significant extent Ga^{3+} ions (~29%) at Zn^{2+} site (tetrahedral site) in $ZnGa_2O_4$ lattice thereby increasing relative extent of distorted gallium-oxygen (GaO_x) structural units. XRD, UV-Visible optical reflectance and lifetime measurements confirmed that a maximum of 0.65 at.% Ge^{4+} is doped in nanocrystalline $ZnGa_2O_4$. Bright blue electro-luminescence has been observed from Ge^{4+} doped $ZnGa_2O_4$ nanoparticles upon application of AC voltages (shown above). Lack of oxygen vacancies in Ge^{4+} doped annealed samples facilitate selective excitation of regular GaO_6 and GaO_x structural units, upon application of AC voltages, leading to around 50% reduction in line width of electroluminescence peak from doped sample compared to undoped one. Variation in electroluminescence properties between doped and undoped samples is due to the difference in nature of defects generated in the lattice.

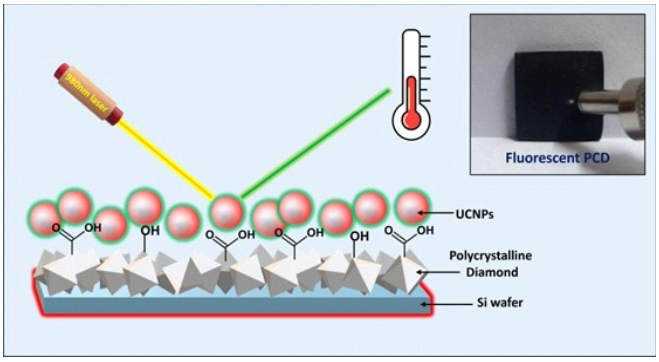

Fig.5: PCD films functionalized with $NaYF_4$:Er,Yb upconversion nanoparticles.

Luminescence properties of upconversion nanoparticles functionalised on lab grown diamond (LGD) films for non-contact temperature measurements

Preparation and characterization of lab grown diamond (LGD) films with luminescent nanoparticles on the surface, is the subject matter of this study. Polycrystalline diamond (PCD) films functionalized with NaYF4:Er,Yb upconversion nanoparticles (UCNPs) were developed and their temperature sensitivity of luminescence characteristics has been evaluated. UCNPs functionalized on surface treated PCD films (UCNPs – TPCD) exhibited superior temperature sensitivity (Sr = 1.08% at 300 K) compared to as prepared UCNPs and UCNPs coated on as grown PCD films (UCNPs – PCD). Surface oxidation of PCD films upon treatment and uniform distribution of UCNPs on PCD films were confirmed by upconversion luminescence, X-ray Photoelectron, IR and Raman spectroscopic techniques along with Scanning Electron Microscopic (SEM) and Atomic Force Microscopic (AFM) techniques. Increase in temperature of diamond lattice due to 980 nm laser irradiation leads to increase in population of 2H11/2 level of Er3+ and associated increase in the fluorescence intensity ratio and improved temperature sensitivity of UCNPs functionalized on treated diamond surface. Treatment of diamond surface led to surface oxidation and uniform functionalization of the nanoparticles on PCD film