Neutron Scattering Studies of Eco-friendly Functional Materials

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Niobate based materials are environment friendly and appropriate for wide piezoelectric applications due to their piezo-response that is comparable to Pb(Zr Ti)O. Beyond the technological application, NaNbO has been a rich model system for understanding of mechanisms of structural phase transitions when subject to changes in thermodynamical conditions like: temperature, pressure, and/or composition, particle size and external stimuli like electric/magnetic field etc. In the present work, we report systematic investigation of structural phase transitions with variations in temperature, external pressure and chemical pressure (via compositional modification) using the neutron scattering technique.

Keywords: structural phase transition, neutron scattering, ferro/antiferroelectric

Introduction
Materials exhibiting piezoelectric properties have been widely used in sensors and actuators. Most of the compounds used in these applications have lead as one of the constituents. Due to toxic nature of lead and environmental regulations, there is a need to replace lead. A considerable amount of research activity is directly aimed to explore lead –free piezoelectric materials. In this regards, alkaline niobate based solid solutions have shown considerable promise because they show ultrahigh piezo-response. Beyond the technological application, NaNbO has been a rich model system for understanding of the mechanism of structural phase transitions. The present work combines state-of-the-art methodologies to understand the nature of phase transitions and identify the correlation between structure and phonon dynamics.

We have employed systematic neutron diffraction measurements as a function of temperature (T=12 K to 1050 K) and pressure to investigate the temperature/pressure induced structures and understand the sequence of structural phase transitions of NaNbO. Neutron diffraction offers certain unique advantages over x-ray diffraction especially in the accurate determination of positions of oxygen ions, which are crucial for resolving the controversies reported in the literature. The diffraction pattern of a polycrystalline sample shows a large numbers of peaks in intensity as a function of the angle of diffraction. Each peak may arise from one or more Bragg reflections from the crystallites. Any Bragg reflection is indexed by three integers (h,k,l), known as Miller indices, which tell us about the specific plane in the crystal which gives the Bragg reflection. After a phase transition new Bragg reflections may appear. In some cases, especially a second order phase transition, these new reflections may be due to change in the structure arising from freezing of some phonon vibrations.

The phonon modes that may condense or freeze are called soft phonons. A soft phonon is one whose frequency may tend to zero as we approach the phase transition. Softening of a phonon is also referred as phonon instability. Different phase transitions may be related to different soft phonons. The wave vector of the soft phonon is important in deciding the new frozen crystal structure. The wave vector may correspond to certain special points in the Fourier space (or reciprocal space). A primitive unit cell in the reciprocal space is called Brillouin Zone. As we discuss below, certain points like M (½ ½ 0), R (½ ½ ½), T (½, ½,¼) etc are of particular interest in case of NaNbO.

Based on our detailed temperature dependent neutron diffraction studies, the phase diagram of sodium niobate is presented that resolves existing ambiguities in the literature about the different structures. We have also shown for the first time direct experimental evidence of presence of antiferroelectric and ferroelectric instabilities at low temperature. We have investigated phase transitions induced by chemical substitution in Li Na NbO system. We found that a variety of phases stabilized ranging from non-polar antiferrodistortive to ferroelectric and antiferroelectric in nature. The stability of various crystallographic phases could be understood in terms of phonon instabilities. In this context, the combination of inelastic neutron scattering and first-principles calculations forms an adequate framework to obtain accurately phonon frequencies. Both the experimental and computational techniques are helpful to understand the role of structural distortions and their correlation to phonon instabilities, leading to phase transitions in this material.

Temperature Induced Phase Transition
Neutron diffraction patterns of materials exhibiting perovskite structure contain two types of reflections: (1) the main perovskite reflections and the (2) super-lattice reflections due to the tilting of oxygen octahedra. Both types of reflections can be indexed with respect to a doubled perovskite unit cell. The super-lattice reflections assume Miller indices represented by one or more odd integers, while the main Bragg reflections are represented by all even
integered indices. Super-lattice reflections with all-odd integered indices, i.e., "ooo" type and two-odd and one-even integered indices (in Glazer’s notation) result from anti-phase and in-phase tilting of the adjacent oxygen octahedra due to structural phase transitions driven by softening and freezing of the zone boundary phonons at R (q = ½, ½, ½) and M (q = ½, ½, 0) points of the cubic Brillouin zone, respectively.

Figure 1 (a) depicts a portion of the powder neutron diffraction patterns of NaNbO₃ at some selected temperatures in the range from 12–975 K. At the highest temperature (T = 975 K), all the Bragg reflections present in powder diffraction patterns could be indexed as main cubic perovskite reflections. The reflection labeled as F in the diffraction pattern of cubic phase is from the furnace material. Below 950 and 900 K, two additional reflections called as "superlattice reflections" (S) marked with (S1) appear. Further, below 810 K, an additional set of superlattice reflections (S2) appear and some of them diminish followed by enhancement of the intensity of super lattice reflection (S3), which disappears below 680 K. Below 680 K, some of super lattice reflections vanish and new super lattice reflection (S4) appear. Superlattice reflections, in different temperature regime, are also present at higher angles with prominent intensities. The intensity of these super lattice reflections gradually decreases on lowering the temperature while some of the peaks show drastic changes in the diffraction data. Splitting in the peak around d= 2.25 Å (index as (111) in pseudo-cubic cell) appears into two peaks with the intensity ratio of 3:1, which is an unambiguous signature of rhombohedral distortions and reveals the stabilization of the ferroelectric (R3c) phase at 25 K. Thus, disappearance and reappearance of superlattice reflections in the powder neutron diffraction provide unambiguous evidence for structural phase transitions in sodium niobate with temperature [4-5].

To examine the phase stability region, we have carried out detailed Rietveld analysis of temperature dependent powder neutron diffraction data. Our studies present unambiguous evidence for the presence of the ferroelectric R3c phase of NaNbO₃ coexisting with an antiferroelectric phase (Pbcm) over a wide range of temperatures below 300 K (Fig. 1 (b &c). Theoretical lattice dynamics calculations of NaNbO₃ show that the potential energy barriers from the paraelectric Pm3m to antiferroelectric Pbcm and ferroelectric R3c phases are quite similar. New superlattice reflections appear at 680 K (R phase) and 770 K (S phase) [Fig. 1 (d)] that could be indexed using an intermediate long-period modulated orthorhombic structure whose lattice parameter along <001> direction is 3 and 6 times that of the CaTiO₃-like Pbnm structure respectively. The critical exponent (β) for the second order tetragonal to cubic phase transition about 950 K, corresponds to a value β ≈ ½, as obtained from the temperature variation of order parameters (tilt angle and intensity of superlattice reflections) around 2.25 Å.
reflections). It is argued that this exponent is due to a second order phase transition close to a tri-critical point. Based on our detailed temperature dependent neutron diffraction studies, the phase diagram of sodium niobate is presented that resolves existing ambiguities in the literature.

**Pressure Induced Phase Transition**

The hydrostatic pressure influence on ferroelectric (FE) and antiferrodistortive phase transitions has received considerable attention for materials exhibiting perovskite structure. The stability of the FE phase (driven by zone center instability at q=0) is reduced under pressure due to modification of the short-range interatomic and long range Coulomb interactions. On the other hand, the stability region of the antiferrodistortive phase (driven by the zone boundary instabilities at q≠0) expands with increasing pressure. Thus, it is interesting to investigate the effect of pressure on sodium niobate which has both competing (zone centre and boundary) instabilities simultaneously. Neutron diffraction patterns at room temperature were collected up to 11 GPa in pressure increasing cycle. To investigate the phase transitions, detailed Rietveld analysis of pressure dependent powder neutron diffraction data was carried out. NaNbO₃ has an antiferroelectric phase (Pbcm) at ambient condition. The paraelectric phase is found to stabilize above 8 GPa and its crystal structure has been determined in orthorhombic symmetry with space group Pbnm (Figure 2 left panel). Application of pressure changes the structural parameters such as the Nb–O bond length, Nb–O–Nb bond angles, and the distortion of the NbO₆ octahedra. Figure 2 (a) shows that the averaged Nb–O bond length shrinks almost continuously whereas a small jump of the Nb–O–Nb bond angle can be clearly seen at 8 GPa. It is evident from the figure that with increasing pressure, Nb–O–Nb bond angle first increases upto 2 GPa and then monotonically decreases upto 8 GPa. On the other hand Nb–O1–Nb bond angle sharply decreases upto 2 GPa and then it decreases monotonically with increasing pressure (Fig. 2(b)). It is found that the tilt angle increases with increasing pressure with sharp enhancement above the phase transition pressure (~ 8 GPa). It could be noticed that the distortion in Pbnm phase is larger in comparison to that in Pbcm phase. We have not found evidence for a structural phase transition around 2 GPa as previously suggested in the literature based on Raman scattering experiments. However, significant changes in the Nb–O–Nb bond angles are found around this pressure. The response of the lattice parameters to pressure is strongly anisotropic with a largest contraction along <001>. The structural phase transition around 8 GPa is followed by an anomalous increase in the orthorhombic strain and tilt angle associated with the R point. Ab-initio calculation of the enthalpy in the various phases of NaNbO₃ is able to predict the phase transition pressure well [6].

**Chemical and Particle Size Induced Phase Transition**

The properties of materials can be tailored by chemical substitution. This technique has been found to be of special technological significance for preparing new devices. To investigate chemical substitution induced structural phase transitions, we have selected the solid solution LiₐNa₉NbOₓ with x=0.06 and 0.12 [8-10].

We have also investigated the structural phase transitions in Liₐ₉Na₉₋ₓNbO₃ (LNN12) in detail using the high temperature neutron diffraction techniques and determined in detail the phase diagram of this important material. We observed interesting changes with the appearance or disappearance of the super-lattice reflections in the powder diffraction patterns [figure 3 (a)]. This clearly reveals that LNN12 undergoes hitherto unreported structural phase transitions as a function of temperature. We infer that anomalies in dielectric measurements as reported in the literature correspond to successive phase transitions from orthorhombic O2 (Pmc2₁) to O1 (Cmcm) to tetragonal (P 4/bmb) to cubic (Pm3m), respectively. Subsequently, we suggest that the application of chemical pressure as a result of Li substitution in NaNbO₃ matrix favors the freezing of zone centre phonons over the zone boundary phonons that are observed in pure NaNbO₃.
We provide direct experimental evidence of a ferroelectric to paraelectric phase transition in \((\text{Li}_{0.06} \text{Na}_{0.94}) \text{NbO}_3\) with reduction of particle size using a combination of x-ray and neutron powder diffraction techniques at room temperature. Detailed Rietveld analyses of the x-ray data shows variation of the particle size from micrometer to nanometer for sintered, calcined, and ball milled powders. The ferroelectric orthorhombic phase of micron sized powder (1.2 µm) is found to transform to paraelectric phase by reducing the particle size to 11 nm. The crystal structure of the paraelectric phase has been identified with tetragonal symmetry \((P4/mmc)\) and is found to be a post perovskite phase. The low temperature neutron diffraction studies on the powders with different particle sizes reveal that the orthorhombic to rhombohedral phase transition gets suppressed with reducing particle size (Figure 3 right panel).

**Phonon Dynamics and Phase Transition**

Virtually all perovskites exhibit the high-symmetry cubic structure at high temperatures. The superlattice reflections observed in diffraction patterns originate from the condensation of zone-centre and zone-boundary soft phonon modes. Thus, the stability of various crystallographic phases could be understood in terms of phonon instabilities.

In order to detect these phonon instabilities using first principle technique, we have calculated the phonon dispersions from the zone centre \((\Gamma)\) to the zone boundary points \(R\) and \(M\) (Figure 4). We found that the polar instability strength at the \(\Gamma\) point is stronger than the antiferrodistortive instabilities at the \(R\) and \(M\) points, and the instability extends over a wider region of the Brillouin zone. As explain above, the \(R\) and \(M\) point soft phonons involve the anti-phase and in-phase tilting of adjacent oxygen octahedra respectively. Further, the strength of the \(M\) and the \(R\) point instabilities are quite similar. Interestingly, the branches along the \(-R\) and \(-M\) directions, show dramatic changes when reaching the \(R\) and \(M\) points. When moving away from \(M\) to \(R\), two unstable modes are detected. One of them is rather flat and the other one shows rapid stiffening and becomes stable. Moreover, one of the stable modes becomes unstable at \(T\left(\frac{1}{2}, \frac{1}{2}, 0\right)\) point.

Above 950 K, \(\text{NaNbO}_3\) occurs in the cubic phase. On decreasing the temperature, it transforms to a tetragonal phase \((P4/mmb)\). The structural transformation is from the cubic to tetragonal structure, where the unit cell is doubled in the plane perpendicular to the rotation axes of the \(M\) mode. By further lowering the temperature, condensation of the \(R\)-point phonon leads to the orthorhombic \(Cmcm\) \((T_2)\ phase. Unstable phonon-branches along the \(M-R\) line contribute to the occurrence successive phase transitions. These phonons play an important role in stabilizing the different phases \((P, S\) and \(R)\) in \(\text{NaNbO}_3\). We have proposed \([7]\) that the additional
superlattice reflections are due to the condensation of the zone boundary phonons at $T (q = \frac{1}{2}, \frac{1}{2}, g)$. The orthorhombic structures of the S, R and P phases result from the condensation of the phonon modes $(q = \frac{1}{2}, \frac{1}{2}, g)$; with $g = 1/12$, 1/6 and 1/4. These orthorhombic phases originate from the modulation of the high symmetry cubic phase, associated with the phonon modes at $q = (\frac{1}{2}, \frac{1}{2}, g)$. Further, the freezing of the R-point phonon mode and a zone-centre phonon stabilizes the low-temperature ferroelectric rhombohedral phase. Based on our calculation we are able to assign the characteristic Raman modes in the antiferroelectric phase, which are due to the folding of the T ($=95 \text{ cm}^{-1}$) and $(=129 \text{ cm}^{-1})$ points of the cubic Brillouin zone, to the $A_{1g}$ symmetry.

Conclusion

Powder Neutron scattering technique has been used to study variety of phase transitions under various thermodynamical conditions like temperature, chemical substitution and pressure in NaNbO$_3$. These transitions are characterized by the appearance and disappearance of superlattice reflections in the powder diffraction patterns. The superlattice reflections originate from the condensation of zone-centre and zone-boundary phonon modes. The stability of various crystallographic phases could be understood in terms of phonon instabilities.

References


