Impact of long- and short-range atomic ordering on the functional properties of Sodium Niobate based ceramics

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HARSH KUMAR

Under the supervision of
Dr. Saurabh Tripathi

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY
VARANASI - 221 005

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Chapter 7

Summary and future work suggestions

7.1 Summary

Lead-based functional materials have been widely used for their exceptionally high physical properties. However, the adverse effects of lead on human health stimulated renewed interest in lead-free functional materials. The physical responses of perovskite-based materials can be significantly enhanced via strategic doping (compositional modifications). Two commonly considered key approaches are: (i) inducing relaxor ferroelectric behaviour through the introduction of random field/strain, and (ii) tuning phase transitions to establish Polymorphic or Morphotropic phase boundaries. Here, the Morphotropic/Polymorphic phase boundary corresponds to long-range crystal structure, whereas relaxor ferroelectrics originate from distinct symmetries at long and short ranges (Polar nano regions). It is important to note that the two approaches can be achieved by manipulating long- and/or short-range ordering by compositional engineering, thereby serving as the motivation for the present thesis.

In search of novel lead-free multifunctional materials, we have developed the solid solution of antiferroelectric $NaNbO_3$ and ferroelectric $(Ba_{0.9}Ca_{0.1})TiO_3$, i.e., $(1\text{-}x)$ NN-xBCT for $0.00 \leq x \leq 1.00$ using the conventional solid state reaction method. Further, we have explored structural and electrical properties using powder X-ray diffraction, Raman spectroscopy, and temperature-dependent dielectric studies. The stability regions of various crystallographic/ferroic phases (determined by X-ray diffraction data) as a function of composition ($0 \leq x \leq 0.25$) are as follows:

- For x = 0 $\rightarrow Pbcm\ (AFE)$
- For x = 0.01 $\rightarrow Pbcm\ (AFE) + Pmc2_1\ (FE)$
- For $0.02 \leq x \leq 0.06 \rightarrow Pmc2_1\ (FE)$
- For $0.08 \leq x \leq 0.10 \rightarrow Pmc2_1\ (FE) + Amm2\ (FE)$
- For $0.12 \leq x \leq 0.15 \rightarrow Amm2\ (FE)$
- For x = 0.20 $\rightarrow P4bm\ (FE)$
- For x = 0.25 $\rightarrow Relaxorferroelectric$

Further, we have observed enhanced ferroelectric and dielectric properties at x = 0.10 due to the coexistence of two ferroelectric phases (*Pmc2₁* and *Amm2*) confirmed by combined analysis of X-ray diffraction and temperature-dependent dielectric data. At this composition, the remanent polarization (P_r) experiences a threefold increase compared to off-boundary composition (i.e., $x = 0.06$).

The compositions with $0.25 \leq x \leq 0.90$ demonstrate relaxor-like characteristics, which is clearly evident from temperature-dependent dielectric analysis. Moreover, the stability regions of crystal structures for higher BCT content (i.e., $x > 0.25$) evolve as follows:

- For $0.30 \leq x \leq 0.40 \rightarrow$ Pm$\bar{3}$m (C_{NN})
- For $0.50 \leq x \leq 0.90 \rightarrow$ Pm$\bar{3}$m (C_{NN}) + Pm$\bar{3}$m (C_{BT})
- For $x = 0.90 \rightarrow$ Pm$\bar{3}$m (C_{BT})

- For $x = 1.00 \rightarrow$ P4mm(FE)

Here, the two cubic phases, namely C_{NN} and C_{BT}, correspond to $NaNbO_3$ (smaller unit cell volume) and $BaTiO_3$ (larger unit cell volume), respectively. The two-phase region observed in the system for $0.50 \leq x \leq 0.80$ demonstrates a highly diffuse and strongly frequency-dependent dielectric behaviour, which constitutes an important ingredient for technological applications. Interestingly, we have observed a slim hysteresis loop in the aforementioned two-phase region. This contrapositive effect (i.e., the presence of a hysteresis loop in a centrosymmetric structure) contradicts the structural constraints of the two long-range centrosymmetric structures, both possessing the $Pm\bar{3}m$ space group. The above-mentioned contradictory results have been explained using the ordering at long ranges (X-ray diffraction) and the ordering at short ranges (Raman spectroscopy), coupled with the physics of dielectrics. The coexistence of two ferroelectric phases at room temperature (for $x = 0.10$) and a slim hysteresis loop with highly diffuse dielectric behaviour (for $0.50 \leq x \leq 0.80$) makes this system suitable for applications in ferroelectric memory and energy storage devices.

Subsequently, we have performed a temperature-dependent multiscale structural analysis on a technologically important composition, 0.9 $NaNbO_3$–0.1 $Ba_{0.9}Ca_{0.1}TiO_3$, i.e., NN-10BCT, via integrated analysis of temperature-dependent synchrotron powder X-ray diffraction, Raman spectroscopy, and Pair Distribution Function (PDF) data. The above-mentioned composition was chosen for its enhanced dielectric and ferroelectric response. The dielectric analysis as a function of temperature $\varepsilon'(T)$ suggests several first-order phase transitions. A prominent anomaly in dielectric permittivity ε' (T) with two-phase coexistence is observed in the vicinity of room temperature. Temperature-dependent Synchrotron X-ray diffraction (SXRD) analysis confirmed the presence of a Polymorphic Phase Boundary (PPB), with two coexisting ferroelectric phases (namely, *Amm2* and $Pmc2_1$) in the vicinity of room temperature. The phase coexistence persists for a wide temperature range (with a width $\Delta T \approx 80$ K). The origin of the enhanced dielectric and ferroelectric response in NN-10BCT has been explored in this work and attributed to PPB. Moreover, another PPB (with two coexisting ferroelectric phases, orthorhombic [SG: $Pmc2_1$] and rhombohedral [SG: $R3c$]) has been discovered at low temperatures, demonstrating wider phase coexistence ($\Delta T \approx 190$ K during heating and $\Delta T \approx 120$ K during cooling), in comparison to the PPB observed at ambient conditions. Thus, this composition can show potential applications also at cryogenic temperatures. Subtle changes in the Raman bands have been observed around the phase transition temperatures obtained from SXRD and dielectric analysis. Therefore, the Raman conclusions strongly support the results obtained from SXRD and dielectric analysis. Furthermore, Pair Distribution Function (PDF) analysis reveals the presence of lower symmetries at short ranges ($r < 20$ Å) in comparison to higher symmetries at long ranges (inferred from SXRD analysis). However, for higher spatial regions ($r > 20$ Å), the structural symmetry deduced from the PDF analysis aligns with that inferred from the long-range SXRD analysis. This smart material can serve as a potential candidate for tuning dielectric/piezoelectric/ferroelectric properties with excellent thermal stability at ambient conditions and cryogenic temperatures.

Further, we have performed a temperature-dependent multiscale structural investigations on the relaxor material, 0.75 $NaNbO_3$– 0.25 $(Ba_{0.9}Ca_{0.1})TiO_3$, i.e., NN-25BCT, via an integrated analysis of temperature-dependent synchrotron powder X-ray diffraction, Raman spectroscopy, and Pair Distribution Function (PDF) data, complemented by dielectric analysis. The dielectric analysis as a function of temperature ($\varepsilon'(T)$) suggests relaxor-like behaviour for NN-25BCT, with a Vogel-Fulcher freezing temperature $T_{VF} \approx 270$ K. Temperature-dependent Synchrotron X-ray diffraction (SXRD) data analysis clearly reveals a polar antiferrodistortive tetragonal phase (SG: $P4bm$; tilt system in modified Glazer's notation: $a^0_0a^0_0c^+_+$) transition at low temperatures (below T_{VF}) from a non-polar antiferrodistortive tetragonal phase (SG: $P4/mbm$; tilt system in modified

Glazer's notation: $a_0^0 a_0^0 c_0^+$). Temperature-dependent Raman analysis provides evidence for the characteristic temperatures (T_{VF} and T_B) by the evolution of the FWHM of the ferroelectric mode present around 250 cm^{-1}. Moreover, Pair Distribution Function (PDF) analysis reveals the presence of a polar antiferrodistortive tetragonal phase with *P4bm* space group at short ranges throughout the studied temperature range ($110 \leq T \leq 500$ K), verifying the results concluded from Raman analysis. Further to address the long-standing debate of the competitive/cooperative nature of octahedral rotations and ferroelectricity, we provided experimental evidence on the influence of in-phase octahedral tilting on ferroelectricity in perovskites using an ingenious approach of mode crystallography for the very first time. Our analysis addresses the controversy by exploring the temperature-dependent evolution of the two primary order parameters, namely Γ_4^- (responsible for ferroelectricity) and M_3^+ (responsible for in-phase octahedral tilting). The findings explicitly reveal that enhancement of the M_3^+ mode amplitude (quantifying in-phase octahedral tilt) suppresses the amplitude of the Γ_4^- mode (quantifying ferroelectric content), demonstrating a competitive interplay between these two order parameters. However, once the in-phase octahedral tilt reaches its saturation, the amplitude of the ferroelectric mode (Γ_4^-) starts increasing on decreasing temperature. Our experimental work clearly reveals that in-phase octahedral tilting suppresses ferroelectricity in perovskite-based systems. The relaxor-to-ferroelectric phase transition in the vicinity of room temperature may exhibit a large entropy change and a significant polarization change, making this material promising for electrocaloric devices, pyroelectric detectors, and multilayered ceramic capacitors.

Finally, we investigated the relaxor ferroelectric behaviour of the composition 0.40 $NaNbO_3$–0.60 $(Ba_{0.9}Ca_{0.1})TiO_3$ (NN-60BCT). Temperature-dependent synchrotron X-ray diffraction (SXRD) measurements revealed the coexistence of two long-range cubic phases(space group: *Pm*$\bar{3}$*m*) within the studied temperature range $100 \leq T \leq 500$K. The unit cell volume obtained from Le Bail refinements displays a significant deviation from the Debye–Grüneisen behaviour below the Burns temperature (identified from dielectric analysis). This anomalous thermal expansion behaviour was attributed to the nucleation and growth of polar nano-regions (PNRs) below T_B, typical of relaxor ferroelectrics. To quantify this anomalous thermal expansion, the concept of *spontaneous volume ferroelectrostriction* (ω_s) was employed, which gives a value of $\omega_s \approx 0.4\%$ at 100 K. In order to probe local polar order within the non-polar matrix, temperature-dependent Raman spectroscopy was employed, suggesting the presence of local polar distortions. Additionally, atomic pair distribution function (PDF) analysis was conducted to resolve the symmetry at the short ranges. The refinement of temperature-dependent PDF data reveals the presence of two distinct types of short-range polar orders, *viz.,* rhombohedral (space group: *R3m*) and tetragonal (space group: *P4bm*) corresponding to $BaTiO_3$and NN-25BCT, respectively. The results presented in this chapter underscore the role of local polar distortions in governing the anomalous thermal expansion of lead-free relaxor systems. The findings pave the way for deeper exploration of the ferroelectrovolume effect and related thermal expansion in perovskite oxides.

7.2 Future work suggestions

The present thesis provides valuable insights regarding the structural origin of observed dielectric/ferroelectric properties in a perovskite-based solid solution, i.e., $NaNbO_3$– x $(Ba_{0.9}Ca_{0.1})TiO_3$ (NN-xBCT). However, several avenues remain open for further exploration, which could significantly advance our understanding of these complex systems:

- **Thin film studies:** While this work is focused on bulk ceramics, translating these findings to thin-film geometries would be crucial for practical device applications. Investigating size effects, substrate-induced strain, and interface-driven phase stabilization in thin films can provide new opportunities for tuning physical properties.

- **Electric field-dependent structural analysis:** It would be interesting to study the effect of the electric field on compositions such as NN-25BCT & NN-60BCT, demonstrating short-range polar ordering in the non-polar matrix. This could reveal field-dependent phase transitions and the transition of short-range polar ordering into a long-range ferroelectric state.

- **First-principles and atomistic simulations:** The experimental findings can be complemented using first-principles calculations (e.g., DFT) or molecular dynamics simulations to understand local off-centering, lattice dynamics, and thermodynamic stability of competing phases.

- **Electron diffraction:** Advanced electron microscopic techniques, such as Transmission electron microscopy (TEM) combined with convergent beam electron diffraction (CBED), can help us to visualize domain structures.

Pursuing these directions will deepen our fundamental understanding of structure–property relationships in functional materials and pave the way for developing advanced materials for next-generation sensors, actuators, and energy harvesting applications.