Role of atomic ordering in tuning physical properties of $K_{0.5}Na_{0.5}NbO_3$-based smart materials

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Chapter 8

Summary and future work suggestions

8.1 Summary

Perovskite materials with ABO_3 framework are known to exhibit ferroelectricity, which is useful for a wide range of applications in sensors, actuators, energy storage, and memory devices. Various Pb-based perovskites have demonstrated excellent ferroelectric properties, but their toxic nature has led to the development of Pb-free alternatives. $K_{0.5}Na_{0.5}NbO_3$ (KNN50) is one of the most widely studied Pb-free alternatives exhibiting morphotropic phase boundary (MPB), demonstrating physical properties comparable to Pb-based ceramics. Moreover, there has been ambiguity regarding its long-range crystal structure, where authors have reported orthorhombic or monoclinic symmetry. In order to resolve this ambiguity, high-resolution X-ray diffraction and pair distribution function data were analyzed to investigate the atomic ordering of KNN50 and its nearby compositions at various length scales (*i.e.*, long/short ranges). A monoclinic phase (*Pm*) was concluded at short ranges (M_{SRO}) and long ranges (M_{LRO}) from our analysis, which differs from an orthorhombic structure reported recently at long ranges in Journal of Physics: Condensed Matter [167]. Moreover, the ferroelectric displacements at short ranges and long ranges in KNNx (x = 0.40, 0.50, and 0.60) ceramics have been quantified using the frozen phonon

mode approach. Further, it was found that the ferroelectric displacements at short ranges dominate the ferroelectric displacements of long ranges. Subsequently, an anomaly is observed in the monoclinic angle (β) at both long and short ranges for x = 0.50, which is explicitly seen in the separation parameter δd [118]. The monoclinic distortion is larger for M_{SRO} than M_{LRO}, resulting in clear structural differences. Thus, owing to differences observed in the monoclinic distortion parameters (*viz.*, β and δd), two unique monoclinic phases (M_{SRO} and M_{LRO}) were observed, with the short-range monoclinic phase exhibiting ferroelectric dominance over the long-range monoclinic phase. Furthermore, it was observed that the amplitudes of polar/ferroelectric phonon mode (a factor quantifying the ferroelectric polarization) were significantly higher at short ranges ($\approx$ 150 % to 180 %) than long ranges and peaks at x = 0.50. Overall, a qualitative blend of ferroelectric properties corresponding to short and long ranges has been thoroughly investigated and quantified using frozen phonon mode approach in order to explain the high physical properties of widely reported Pb-free MPB composition *viz.*, KNN50.

Subsequently, owing to MPB and high dielectric response of KNN50 and $Ba_{0.9}Sr_{0.1}TiO_3$ (BST10) at ambient conditions respectively, we have synthesized a Pb-free solid solution of KNN50 with BST10 *viz.*, (1-x)KNN50-xBST10 (KBSTx) for $0.00 \leq x \leq 0.20$. We have investigated the long/short range structures, quantified polar displacements using phonon mode crystallography, and explored the dielectric properties of KBSTx as a function of composition (x) and temperature (T). The study includes various novel findings, which are mentioned below:

- ***Emergence of a long-range ferroelectric order from a short-range polar order in KBSTx:*** The X-ray diffraction data reveals a monoclinic (Space Group: *Pm*), tetragonal (Space Group: *P*4*mm*), and cubic (Space Group: $Pm\bar{3}m$) phase at long ranges for x = 0.00 (KNN50), x = 0.15 (KBST15) and x = 0.20 (KBST20), respectively. Moreover, the composition-dependent Raman scattering data reveals

a monoclinic symmetry at short/long ranges for all the compositions (x). Thus, a combined analysis of X-ray diffraction and Raman scattering data demonstrates the emergence of a monoclinic phase at long ranges for $x < 0.20$ from a monoclinic phase at short ranges for $x = 0.20$.

- ***MPB-like behavior at $x = 0.05$ (KBST5):*** The morphotropic phase boundary-like behavior is confirmed for KBST5 ceramics based on the following inferences:

  1. The co-existence of two ferroelectric phases *viz.*, monoclinic and tetragonal (stable for 225 K < T < 400 K) is demonstrated by temperature-dependent Raman scattering data.

  2. The room temperature dielectric constant is found to be maximum for KBST5 in the ferroelectric region ($x < 0.20$). Moreover, the dielectric constant (at 100 kHz) of KBST5 is more than its adjacent compositions, *viz.,* KNN50 and KBST10, by 62 % and 83 %, respectively. Further, the amplitude of the ferroelectric phonon mode (Γ_4^-) maximizes at KBST5 in the ferroelectric region ($x < 0.20$).

- ***Order-disorder type transition in KBST5:*** An order-disorder type transition has been observed for the MPB composition *viz.*, KBST5, demonstrating a disordered state at ambient conditions. The combined analysis of temperature-dependent synchrotron X-ray diffraction (SXRD) and Raman scattering data demonstrates a series of structural phase transitions *viz.,* $Pm \xrightarrow{\approx 225K} (Pm{+}P4mm) \xrightarrow{\approx 400K} P4mm \xrightarrow{\approx 550K} Pm\bar{3}m$. On the other hand, a monoclinic phase (Space Group: Pm) remains stable at short ranges throughout the studied temperature range (300 K $\leq T \leq$ 1000 K). Moreover, temperature-dependent SXRD and PDF data analysis demonstrate two anomalies in the unit cell volume and the amplitude of the ferroelectric phonon mode (Γ_4^-) at T $\approx$ 400 K and T $\approx$ 550 K. The first anomaly corresponds to the transition from

(Pm+$P4mm$) $\xrightarrow{\approx 400K}$ $P4mm$, while the second corresponds to the Curie temperature ($P4mm$ $\xrightarrow{\approx 550K}$ $Pm\bar{3}m$).

Furthermore, a transition from a ferroelectric to relaxor state has been observed for x = 0.20 (KBST20), resulting in high dielectric constant.

Owing to the relaxor behavior of KBST20, we have explored the temperature-dependent crystal structure of KBST20 and its physical properties *viz.*, thermal expansion and dielectric constant. The temperature-dependent dielectric data of KBST20 exhibits a single diffuse peak with strong frequency dispersion ($\Delta T \approx 27$ K), suggesting the presence of polar nanoregions (PNRs). Moreover, a centrosymmetric cubic phase at long ranges and a non-centrosymmetric monoclinic phase at short ranges is confirmed using temperature-dependent neutron diffraction and Raman scattering data, respectively. Subsequently, zero thermal expansion (ZTE) has been observed at low temperatures (*i.e.*, $T \leq 100$ K). The linear coefficient of thermal expansion calculated from temperature-dependent volume data ranges between ***0.255-5.75 $\times 10^{-6}$ K^{-1} (9 K-500 K)***. ***Such a small CTE is rare in Pb-free materials possessing cubic structure at long ranges***. Here, zero thermal expansion has been attributed to the enhanced intra/inter-polar-cluster interactions, which results in ferroelectrostriction, and, is clearly evident by the combined analysis of temperature-dependent Raman scattering and P-E loops.

Further, we have synthesized the compositions of the other end ($0.90 \leq x \leq 1.00$), and explored atomic ordering and dielectric properties using temperature-dependent synchrotron X-ray diffraction (SXRD), Raman scattering, and pair distribution function (PDF) data. A cubic phase with $Pm\bar{3}m$ space group was found to be stable for x = 0.90 (KBST90) and x = 0.95 (KBST95) ceramics, and a tetragonal phase with $P4mm$ space group was found to be stable for x = 1.00 (BST10) ceramics. The novel findings of this study include:

- ***Distinct atomic ordering at long/intermediate/short ranges in KBST90 ceramics:*** A non-polar ***cubic phase*** (Space Group: $Pm\bar{3}m$) was confirmed at long ranges

using temperature-dependent SXRD data, whereas two distinct polar orderings *viz.*, ***rhombohedral*** (Space Group: $R3m$) and ***monoclinic*** (Space Group: Pm) were found to be stable at intermediate and short ranges by temperature-dependent Raman scattering and PDF data.

- ***Thermally stable structures:*** The long/intermediate/short-range structures remain stable for a wide temperature range (100 K $\leq T \leq$ 500 K). The ferroelectric distortions at intermediate/short ranges increase with the decrease in temperature, which is confirmed by the increase in the amplitude of ferroelectric phonon mode (Γ_4^-). Moreover, increase in ferroelectric ordering at intermediate/short ranges is held responsible for volume gain (ferroelectrostriction) at low temperatures. This consequently results in ZTE at low temperatures.

- ***Low coefficient of thermal expansion (CTE):*** The linear coefficient of thermal expansion (CTE) observed for KBST90 ceramics ranges between ***(0.623-10.109) × 10^{-6} K^{-1} (100 K-500 K)***, thereby confirming ZTE in the material at low temperatures.

Furthermore, we have investigated the intermediate compositions *i.e.*, $0.20 \leq x \leq 0.90$ (KBSTx) using X-ray diffraction and temperature-dependent Raman scattering data. The X-ray diffraction data demonstrate an average cubic structure stable for KBSTx ceramics for $0.20 \leq x \leq 0.90$. Moreover, a unique morphotropic relaxor boundary (MRB) has been discovered in KBSTx ceramics stable for $0.30 \leq x \leq 0.50$ using Raman scattering data. The novel findings of this study include:

- ***Discovery of an MRB:*** An MRB has been discovered in KBSTx ceramics stable for $0.30 \leq x \leq 0.50$. The MRB compositions exhibit multiple (two) local symmetries, *viz.*, polar monoclinic and polar rhombohedral, at short ranges in an average cubic symmetry stable for a wide temperature range. It is important to note that the monoclinic symmetry has been identified for the very first time at short ranges in an

MRB, which is different from other MRBs, where tetragonal symmetry was reported (in place of monoclinic symmetry) at short ranges [15, 61]. Moreover, the MRB composition *viz.*, $x = 0.40$ (KBST40) exhibits a two-phase co-existence at short ranges (in a cubic phase at long ranges), stable for a wide temperature range below 427 K.

- ***Impact of MRB in fine-tuning CTE, thereby NTE/ZTE:*** For the very first time, Negative/Zero thermal expansion has been discovered in an MRB composition *viz.*, KBST40. A remarkable value of the coefficient of thermal expansion (CTE) (α_l) *i.e.*, $\boldsymbol{-5.22 \text{ to } +10.12 \times 10^{-6} \text{ K}^{-1} \text{ (8 K – 495 K)}}$ has been observed for KBST40 at long ranges. Moreover, a comparison of the linear CTE (α_l) of KBST40 (exhibiting multiple local symmetries) with end compositions possessing average cubic structure, *viz.*, KBST20 and KBST90 (exhibiting single local symmetry), clearly reveal that KBST40 exhibits a minimum value of CTE for $T \leq 200$ K. The minima at KBST40 has been attributed to the cumulative effect of local monoclinic and local rhombohedral ordering, thereby resulting in NTE/ZTE.

- ***Microscopic origin of very low CTE in MRB:*** The remarkably low CTE of KBST40 at long ranges derives its origin from enhanced local ferroelectric order at low temperatures. The enhancement in ferroelectric order at low temperatures is demonstrated by the increase in the amplitudes of the ferroelectric phonon modes (Γ_4^-) associated with multiple local symmetries. Thus, a very low CTE at short ranges acts as a source of NTE/ZTE observed at long ranges.

8.2 Future work suggestions

In the future, various studies have been planned, which are as follows:

- ***Field-dependent ferroelectric/structural phase transitions:*** It is well known that relaxor ferroelectrics exhibit a unique structural configuration with different atomic orderings at long and short ranges. For relaxor ferroelectric compositions *viz.*, KBST20 and KBST90, the polar nanoregions, become static on cooling below the freezing temperature (T_{VF}). Moreover, an ordered phase (transformation of short-range order into long-range order) can be achieved on the application of a suitable electric field. Therefore, we plan to carry out temperature-dependent X-ray/neutron diffraction studies under a suitable electric field to study the relaxor to ferroelectric phase transition.

- ***Atomic level evidence of characteristic temperatures in relaxor ferroelectrics:*** Relaxor ferroelectrics demonstrate characteristic temperatures *viz.*, Burns temperature (T_B), intermediate temperature (T^*), temperature corresponding to dielectric maxima (T_m), and freezing temperature (T_{VF}). These temperatures dictate the structural changes (at long/short ranges) in the material. Atomic level evidences of characteristic temperatures will be explored using Raman scattering and pair distribution function data.

- ***Transmission Electron Microscopy (TEM) studies:*** Various compositions of KBSTx ceramics ($0.20 \leq x \leq 0.90$) exhibit distinct atomic orderings at various length scales. TEM studies will be carried out for various KBSTx compositions to confirm the presence of multiple local symmetries at short ranges.