Preface

Perovskite oxides with the general formula ABO_3 represent a fascinating class of materials that have captivated the interest of the scientific community for decades. The unique crystal configuration and structural adaptability of perovskites allow an array of physical phenomena, making it suitable for science and technology. Owing to structural tunability, the perovskite oxides exhibit fascinating properties *viz.*, ferromagnetism, ferroelectricity, ferroelasticity, ferrotoroidicity, etc. Among these, ferroelectricity has been widely studied for its range of applications. Ferroelectric materials possess a spontaneous electric polarization whose direction can be reversed on the application of suitable electric field, making them useful for non-volatile memories (ferroelectric RAMs), capacitors, sensors, actuators, and energy harvesting systems. Most of the prominent ferroelectric materials are Pb-based, which have detrimental effects on human health and the environment. Consequently, there is an ongoing search for Pb-free materials. In this search, alkali niobates ($LiNbO_3$, $NaNbO_3$, $KNbO_3$), alkaline earth metal titanates ($BaTiO_3$, $SrTiO_3$, $CaTiO_3$), and their solid solutions are potential alternatives. The high physical properties of Pb-free materials are achieved by exploiting polymorphic phase boundary (PPB), morphotropic phase boundary (MPB), relaxor ferroelectrics, etc., which can be obtained by compositional engineering. Moreover, enhanced physical properties in the vicinity of polymorphic/morphotropic phase boundary results from the co-existence of ferroelectric phases, demonstrating strong/weak temperature-dependence. Owing to excellent physical properties, which are also thermally stable, MPBs have been a subject of continuous research. The prominent Pb-free alkali niobate-based MPBs are $Li_{0.2}Na_{0.8}NbO_3$ (LNN20) and $K_{0.5}Na_{0.5}NbO_3$ (KNN50). Among these, KNN50 has been widely studied for more than five decades for its structure and physical properties. Different authors have reported different crystal structures (orthorhombic or monoclinic) for KNN50.

Firstly, we have reinvestigated the atomic ordering of $K_{0.5}Na_{0.5}NbO_3$ (KNN50) and its nearby compositions at various length scales using high-resolution X-ray diffraction and pair distribution function data. We have confirmed a monoclinic phase (Space Group: *Pm*) at long/short ranges differing from a report by Saha *et al*. published recently in Journal of Physics: Condensed Matter [Saha, M., Niranjan, M. K. & Asthana, S. Journal of Physics: Condensed Matter 36, 425703 (2024)]. Moreover, the ferroelectric dominance of short-range ordering (SRO) over long-range ordering (LRO) has been observed and quantified using the amplitude of the ferroelectric mode (Γ_4^-), thereby connecting the crystal structure with the ferroelectric property of a widely studied MPB (KNN50) and its nearby compositions *viz*., $K_{0.4}Na_{0.6}NbO_3$ (KNN40) and $K_{0.6}Na_{0.4}NbO_3$ (KNN60). Two uniquely identified monoclinic phases have been observed at short (M_{SRO}) and long ranges (M_{LRO}) for all the compositions. The amplitude of ferroelectric mode (Γ_4^-) corresponding to M_{SRO} is significantly higher ($\approx$ 150 % - 180 %) than M_{LRO}. A peak is observed in the amplitude of Γ_4^- and the intensity of prominent Raman peaks for KNN50, which is held responsible for high physical properties *viz*., dielectric permittivity, piezoelectric coefficient, remnant polarization, electromechanical coupling coefficient, and many more widely reported in literature.

Next, we have synthesized the solid solution of KNN50 with $Ba_{0.9}Sr_{0.1}TiO_3$ (BST10) *viz*., (1-*x*)KNN50-*x*BST10 (KBST*x*) and explored the long/short-range structure and dielectric property of KBST*x* for $0.00 \leq x \leq 0.20$. The combined analysis of composition-dependent X-ray diffraction and Raman scattering data demonstrates the emergence of long-range ferroelectric order (observed for $x < 0.20$) from short-range polar order (at

x = 0.20) as a function of composition (x). A two-phase coexistence (monoclinic and tetragonal) with a relatively high dielectric constant is observed for x = 0.05 (KBST5) in the ferroelectric region ($0.00 \leq x < 0.20$). Owing to the high dielectric constant and two-phase coexistence, the structure at long- and short-range for KBST5 ceramics has been explored using temperature-dependent synchrotron X-ray diffraction, Raman scattering, and pair distribution function data. The temperature-dependent Raman scattering data demonstrates a wide co-existence of two ferroelectric phases (monoclinic and tetragonal) at long ranges stable for 225 K $< T <$ 400 K, suggesting a morphotropic phase boundary-like behavior for KBST5. Moreover, the unit cell volume and the primary order parameter (*i.e.*, amplitude of ferroelectric phonon mode; Γ_4^-) corresponding to long and short ranges exhibit anomalies at T $\approx$ 400 K (corresponding to a transition from (Pm + $P4mm$) $\rightarrow$ $P4mm$ at long ranges) and $T_C \approx$ 550 K (corresponding to a transition from $P4mm \rightarrow Pm\bar{3}m$ at long ranges). Further, the room temperature dielectric constant of KBST5 is found to be greater than adjacent compositions *viz.*, KNN50 and KBST10 by 62% and 83%, respectively, confirming the morphotropic phase boundary at KBST5. Furthermore, the dielectric constant of KBST20 (x = 0.20) is maximum for $0.00 \leq x \leq 0.20$, and has been attributed to a transition from a ferroelectric to relaxor state as a function of composition (x).

Subsequently, due to the high dielectric constant and high disorder observed for KBST20, we have explored temperature-dependent structure and physical properties of KBST20 *viz.*, dielectric constant, and thermal expansion. KBST20 demonstrates a long-range cubic structure stable for a wide temperature range (9 K $\leq T \leq$ 500 K) with zero thermal expansion (ZTE) at low temperatures ($T \leq$ 100 K). The linear coefficient of thermal expansion (α_l) obtained from the temperature-dependent neutron diffraction data is $0.255 - 5.75 \times 10^{-6}$ K^{-1} (9 K-500 K), which is considered a low value for Pb-free materials′ possessing long-range cubic symmetry. The temperature-dependent dielectric data of KBST20 exhibit a strong relaxational behavior with high frequency dispersion ($\Delta T \approx 27$ K), suggesting the presence of polar nanoregions (PNRs). The ZTE has been attributed to enhanced intra/inter-polar-cluster interactions (with polar clusters (PNRs) exhibiting ferroelectrostriction). Moreover, temperature-dependent Raman scattering data reveal polar monoclinic distortion at short ranges in contrast to cubic symmetry at long ranges. Also, the intensity of Raman modes increases with the decrease in temperature, suggesting enhancement of the polar content of PNRs at low temperatures, consequently resulting in ferroelectrostriction, thereby zero thermal expansion.

Further, we have explored the other end of the solid solution *viz.*, $0.90 \leq x \leq 1.00$. Here, distinct atomic ordering (non-polar/polar) has been determined at long/intermediate/short ranges using temperature-dependent synchrotron X-ray diffraction (SXRD), Raman scattering, and pair distribution function (PDF) data. Two different polar phases with distinct symmetries have been identified at short/intermediate ranges for $x = 0.90$, where a monoclinic phase at short ranges gradually transforms into a rhombohedral phase at intermediate ranges. In contrast, a non-polar phase with an average cubic symmetry is found to be stable at long ranges for a wide temperature range (100 K $\leq T \leq$ 500 K). The polar behavior of short/intermediate-range ordering has been quantified using the amplitude of ferroelectric phonon mode (Γ_4^-). The amplitude of Γ_4^- phonon mode increases with decreasing temperature, suggesting an enhancement in ferroelectric polarization at short/intermediate ranges on lowering temperatures. Enhanced ferroelectric polarization at low temperatures is also reflected by an increase in the magnitude of Spontaneous Volume Ferroelectrostriction (SVFS). Consequently, Zero Thermal Expansion (ZTE) is observed in KBST90 at low temperatures.

Finally, we have investigated the intermediate region of KBSTx ceramics ($0.20 \leq x \leq 0.90$), demonstrating an average cubic structure. A unique morphotropic relaxor boundary (MRB) has been discovered for KBSTx, stable for $0.30 \leq x \leq 0.50$. Here, MRB compositions exhibit two distinct polar symmetries *viz.*, monoclinic and rhombohedral at short ranges, in an average cubic symmetry at long ranges. The two distinct symmetries (*viz.*, monoclnic and rhombohedral) co-exist for the highest temperatures ($T \leq 427$ K) in KBST40 (x = 0.40), which has been uncovered using temperature-dependent Raman scattering data. Moreover, negative/zero thermal expansion (NTE/ZTE) has been discovered in the MRB composition *viz.*, KBST40, and has been attributed to multiple local symmetries. The linear coefficient of thermal expansion (α_l) for KBST40 at long ranges is -5.22 to $+10.12 \times 10^{-6}$ K^{-1} (8 K - 495 K), which is rare among Pb-free materials possessing average cubic symmetry. This low value of CTE (α_1) originates from NTE/ZTE observed at short ranges (1.7 Å $\leq r \leq$ 10 Å), which was uncovered by analyzing pair distribution function data. Further, the weak temperature dependence of MRB, along with NTE/ZTE, offers a promising avenue for enhancing the functional adaptability of dielectric materials.

Overall, the thesis is focused on investigating the crystal structure of $K_{0.5}Na_{0.5}NbO_3$ (KNN50) and its solid solutions *viz.*, (1-x)$K_{0.5}Na_{0.5}NbO_3$-$x$$Ba_{0.9}Sr_{0.1}TiO_3$ (KBSTx) for $0.00 \leq x \leq 1.00$, and, demonstrating the role of atomic ordering at various length scales in tuning the physical properties of KBSTx ceramics.