Preface

Perovskites represent a family of compounds whose structures are based on the mineral Calcium Titanate ($CaTiO_3$) and are described by the general formula ABX_3. These materials have been discovered in the mid of twentieth century and are being continuously investigated for their properties such as dielectric, piezoelectric, ferroelectric, etc. Over time, their functional scope has broadened to encompass magnetic ordering, multiferroicity, thermal and optical properties, and many more. Among these, ferroelectric materials are known for their multifunctional properties and are widely utilized in various applications, *viz.,* sensors, actuators, memory devices, etc. Currently, most of the functional materials employed in practical applications are lead-based. The harmful effects of lead on human health and the environment have been recognized for a long time and have led to the development of numerous lead-free functional materials over the last few decades. Moreover, the European Union regulations of 2002 restrict the use of lead and other harmful elements, thereby promoting the discovery of lead-free functional materials. Alkali Niobates, Alkaline-earth Titanates, and their solid solutions have demonstrated strong potential as alternatives to lead-based materials. Generally, the physical properties of perovskite-based functional materials can be tuned/optimized via two effective approaches: (i) By tuning phase transitions to establish Polymorphic or Morphotropic phase boundaries, (ii) By inducing relaxor ferroelectric behaviour through the introduction of local strain/field. It is important to note that the Morphotrophic/Polymorphic phase boundary can be tuned primarily via modification in long-range structure. On the other hand, the relaxor nature can be induced by creating disorder via doping atoms with different ionic radii and/or oxidation states. Moreover, the above-mentioned ways play a vital role in tuning physical properties and serve as the primary motivation for the present thesis work.

In search of novel lead-free functional materials, we investigated the solid solution of antiferroelectric $NaNbO_3$ (NN) with ferroelectric $Ba_{0.9}Ca_{0.1}TiO_3$ (BCT), i.e. (1-x) NN - x BCT for $0 \leq x \leq 1.0$ using various characterization techniques *viz.,* powder X-ray diffraction (XRD), dielectric, and Raman spectroscopy. The composition-dependent long-range structural phase transitions were explored using X-ray diffraction and were complemented by short-range structural investigations using Raman spectroscopy. The incorporation of BCT disrupts the delicate antiferroelectric ordering (space group: *Pbcm*) of NN and stabilises various ferroelectric phases. The antiferroelectric phase of NN transforms into a ferroelectric phase (space group: $Pmc2_1$) for $x \geq 0.02$. On further increasing BCT content (i.e., $x > 0.06$), the ferroelectric phase (space group: $Pmc2_1$) of NN - x BCT undergoes a transformation into another ferroelectric phase (space group: *Amm2*) via a two-phase coexistence region ($0.08 \leq x \leq 0.10$). With a continued increase in BCT content, the *Amm2* phase subsequently transforms into the *P4bm* phase for $x > 0.15$, and finally stabilizes into a relaxor for $x = 0.25$. Interestingly, we found that the simultaneous presence of two ferroelectric phases *viz., $Pmc2_1$* and *Amm2* (for $x = 0.10$) enhance the remanent polarization three times in comparison to one of the off-boundary compositions ($x = 0.06$). Moreover, on further increasing BCT content, the system stabilizes into a two-phase region with two long-range cubic structures (characterised by $Pm\bar{3}m$ space group) for $0.50 \leq x \leq 0.80$. In spite of having a two-phase long-range centrosymmetric structure, we have observed a slim Polarization vs. Electric field (P-E) hysteresis loop for $0.50 \leq x \leq 0.80$. This contrapositive behaviour (i.e., hysteresis loop in a centrosymmetric structure) has been attributed to the correlations among local polar distortions of rhombohedral type ascertained by Raman spectroscopy. The coexistence of two ferroelectric phases at room temperature (for $x = 0.10$) and a slim hysteresis loop (for $0.50 \leq x \leq 0.80$) makes this system useful for applications in ferroelectric memory and energy storage devices.

Further, owing to its high ferroelectric response and coexistence of two ferroelectric phases, we have performed multiscale structural analysis of 0.9 $NaNbO_3$ - 0.1 $Ba_{0.9}Ca_{0.1}TiO_3$ (NN-10BCT) in order to explore the presence of Morphotropic or Polymorphic phase boundary. We have investigated the evolution of atomic ordering at long, medium, and short ranges using temperature-dependent Synchrotron X-ray diffraction (SXRD), Raman scattering, and Pair distribution function (PDF) in the guidance of dielectric data. Temperature-dependent Synchrotron X-ray diffraction data combined with dielectric analysis suggests two unique Polymorphic Phase boundaries (PPB) with two coexisting ferroelectric phases stable for wide temperature ranges. These PPBs are stable in different regions *viz.,* (i) cryogenic temperatures with coexisting $R3c$ & $Pmc2_1$ phases (ii) vicinity of room temperatures with coexisting $Pmc2_1$ & $Amm2$ phases. In contrast to long-range crystal structures inferred from SXRD, the structure at short ranges bears a lower symmetry (determined using PDF) for these PPBs. The presence of different long- and short-range symmetries (which accommodate tilt-oriented ferroelectric phases) in the unique polymorphic phase boundaries makes them thermally stable and useful for technological applications.

Subsequently, to explore the compositions with relaxor behaviour, we have investigated the temperature dependence of atomic ordering at multiple length scales in the lead-free sodium niobate-based relaxor, i.e., 0.75 $NaNbO_3$- 0.25 $Ba_{0.9}Ca_{0.1}TiO_3$ (NN-25BCT) using Synchrotron X-ray diffraction, Raman spectroscopy, and Pair distribution function data. High-resolution Synchrotron X-ray diffraction (SXRD) measurements reveal a relaxor to ferroelectric phase transition in NN-25BCT below the Vogel-Fulcher freezing temperature ($T_{VF} \approx 270$ K). In addition, SXRD analysis in conjunction with mode crystallography demonstrates the competitive nature of in-phase octahedral tilting with long-range ferroelectric order. On the other hand, Raman spectroscopic analysis provides evidence of polar ordering for $T > T_{VF}$ (with tetragonal symmetry) persisting up to the Burns temperature (T_B). Furthermore, Pair distribution function (PDF) analysis reveals the presence of a polar antiferrodistortive tetragonal phase with *P4bm* space group at short ranges throughout the studied temperatures (i.e., $110 \leq T \leq 500$ K), irrespective of non-polar long-range ordering above T_{VF}. Therefore, combined analysis provides direct evidence for the presence of short-range polar ordering (in a long-range non-polar matrix) and its gradual transformation into long-range polar ordering on lowering temperature. As a result of a transition from relaxor to a ferroelectric phase in the vicinity of room temperature, NN-25BCT can be exploited for applications in pyroelectric detectors, electrocaloric devices, and multi-layered ceramic capacitors.

Finally, we extended our investigations to higher BCT content, i.e., 0.40 $NaNbO_3$–0.60 $Ba_{0.9}Ca_{0.1}TiO_3$ (NN-60BCT). Synchrotron X-ray diffraction analysis revealed the presence of two cubic phases with $Pm\bar{3}m$ symmetry stable for the wide temperature range i.e., $100 \leq T \leq 500$ K. Notably, the unit cell volumes of both cubic phases deviate from their expected thermal expansion behaviour below the Burns temperature (T_B) (which is determined by temperature-dependent dielectric data). This anomalous thermal expansion has been attributed to the enhancement in interaction originating from the nucleation and growth of polar nano-regions (PNRs), thereby resulting in ferroelectrostriction. Further, Raman spectroscopy was used to probe local structural distortions, revealing the presence of polar nano-regions in a non-polar matrix stable up to T_B. Furthermore, an enhancement of the polar phased regions is evident from the increase in intensity (on decreasing temperature) of the ferroelectric Raman mode present around ≈ 305 cm^{-1}. Moreover, pair distribution function (PDF) analysis was used to identify the symmetry of the polar nano regions. PDF analysis suggests the coexistence of two distinct polar ordering (with rhombohedral and

tetragonal symmetries) at short ranges, originating from short-range ordering present in BT and NN-25BCT, respectively.

In summary, this thesis focuses on manipulating short- and long-range structural ordering in functional materials through chemical modification. The atomic ordering at multiple length scales has been systematically explored using advanced techniques, *viz.,* temperature-dependent Synchrotron X-ray diffraction, Raman spectroscopy, Pair distribution function analysis, and dielectric measurements. This methodology has enabled us to uncover the correlation between structure and physical properties (dielectric/ ferroelectric) in a lead-free sodium niobate based solid solution. We have discovered several important compositions that demonstrate potential for technological applications.