SYNOPSIS

Advanced piezoelectric ceramics are widely used as piezoelectric sensors, transducers, actuators, etc. Among the commercially viable piezoelectric systems, lead zirconate titanate, $PbZr_{1-x}Ti_xO_3$ (PZT) has dominated the market due to its superior properties and cost effective reproducibility. PZT exhibits enhanced piezoelectric properties in the vicinity of morphotropic phase boundary (MPB). The mechanism(s) associated with the anomalous piezoelectric response in the MPB systems is still a subject of considerable debate. The two contending theories in this regard are based on (i) field induced polarization rotation in single domain crystal and (ii) formation of a high density of low energy domain walls. Diffraction experiments in-situ with electric field can, in principle, give direct information about domain reorientation, lattice strain and phase transformation (if any) in ferroelectric systems. However, the combined effect of preferred orientation and severe overlapping of Bragg peaks in diffraction pattern of MPB compositions makes structural analysis very challenging. As a consequence, domain reorientation studies have mostly been reported for compositions away from the critical MPB, i.e., in the single phase regime. So far it has not been established how the domain switching and phase transformation influence each other in the core MPB compositions of piezoelectric alloys. In the present dissertation, we have addressed this issue in an important lead based piezoelectric alloy system (x)$BiScO_3$- (1-x)$PbTiO_3$ (BSPT). In spite of their superior piezoelectric performance, lead based systems have major drawback because of its toxicity and environmental concerns. Several legislations have been passed all over the globe to encourage the development of lead free alternatives. Lead free piezoelectrics belong to three major categories - $BaTiO_3$ (BT) based, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT) based and $K_{0.5}Na_{0.5}NbO_3$ (KNN) based. Among them, NBT based systems have been most widely investigated due to their promising piezoelectric properties –mostly with regard to their large electrostrain response. In this thesis, we have attempted to understand the underlying mechanisms associated with the large piezoelectric response in the lead-based MPB piezoelectric $BiScO_3$-$PbTiO_3$ and also in one of NBT-based lead-free piezoelectric. In the process, we investigated the effect of grain size in influencing the global structure, piezoelectric properties and electrical conduction behaviour of the parent compound NBT. For the first time, in this thesis, we have used rare-earth photoluminescence as a tool to probe the nature of local symmetry in the non-ergodic relaxor ferroelectric state. The thesis comprise of several novel results and ideas which has been systematically detailed in four comprehensive chapters (Chapter 3 to Chapter 6).

The thesis comprise of seven chapters. **Chapter 1** summarizes some of the basic concepts related to the work presented in this thesis. The experimental techniques and characterizations are discussed in **Chapter 2**. **Chapter 3** deals with a comparative in-situ electric field dependent high energy synchrotron x-ray diffraction (XRD) study on a critical MPB (x=0.3725) and a close by non-MPB (x=0.40) compositions of $(x)BiScO_3$- $(1-x)PbTiO_3$.We show that the rhombohedral ferroelectric-ferroelastic domain reorientation fraction is considerably reduced in the MPB composition as compared to the non-MPB composition. The reduction in the rhombohedral domain reorientation is also accompanied by a corresponding anomalous reduction in the field-induced rhombohedral lattice strain in the MPB along the nonpolar direction. The MPB composition however shows electric-field-induced rhombohedral to tetragonal phase transformation, the fraction of which follows the same hysteretic trend as the lattice strain and domain reorientation fraction.

The non-MPB composition, on the other hand does not show field induced phase transformation. We use these results to propose that the field-induced structural transformation is most likely to be the dominant mechanism responsible for the larger macroscopic piezoelectric response in the critical MPB composition of this piezoelectric system. We also found a strong correlation between lattice strain and phase transformation with the field induced domain reorientation in the MPB composition. Although the magnitudes of the changes are very small, we could demonstrate that these phenomena and their coupling occur even in the subcoercive field regime.

Chapter 4 to **6** detail the results of the investigation carried out on pure and modified NBT. In **Chapter 4**, we have reported an extensive study of the effect of grain size on the global structure and piezoelectric response of pure NBT prepared via spark plasma sintering. The grain size was varied in the range 0.2 – 40 µm by changing the annealing temperature. We found that the reported global monoclinic (*Cc*) distortion of NBT collapses for grains size below ~2.5 microns even while it retains its non-ergodic relaxor state. This dramatic change in the global structure on such a large grain size confirms that the characteristic length scale responsible to alter the global structure in this system is mesoscopic in nature. We argue that the perceived difference in the global structure of NBT on size reduction is because of the change in nature of the assemblage of the mesoscopic structural heterogeneity (in-phase and out-of-phase octahedral tilts) inherently present in the system. Further, while we observed a dramatic decrease in the piezoelectric and ferroelectric properties of bulk ceramic with grains in the submicron range, we used an innovative powder poling technique to demonstrate unambiguously that the lack of piezoelectric response is not because of the submicron grains loosing ferroelectric character, but rather because of the inability of the grains to transform to a long ranged rhombohedral ferroelectric state on application of electric (poling) field due to clamping effect and/or increased incoherence of grain boundaries.

In **Chapter 5**, we have demonstrated that the highly efficient nature of the photoluminescence emission of rare earth ions, in conjunction with the sensitivity of the Stark manifolds to the local symmetry, can be utilized to examine the nature of the local structure in the non-ergodic relaxor ferroelectric state of $0.94Na_{0.5}Bi_{0.5}TiO_3$-$0.06BaTiO_3$. This composition exhibits a cubic like phase on the global structure and there is no unanimity in literature on its structural state on the local length scale. We used Eu and Er as two rare earths to examine the local symmetry in the unpoled and poled states of this system. A series of Eu and Er modified compositions were synthesized as per the nominal formula $0.94Na_{0.5}Bi_{0.5-x}(Eu/Er)_xTiO_3$–$0.06BaTiO_3$ and a systematic structural, microstructural, piezoelectric and dielectric measurements was carried out. Surprisingly, we found that the number of Stark manifolds in the PL spectra of cubic-like phase is more as compared to that in the field stabilized rhombohedral (R3c) phase. This proves that the local symmetry on the A-site of what appears to be globally more symmetric cubic phase is lower than that in the field stabilized rhombohedral (R3c) phase.

Chapter 6 details the results of an extensive investigation to understand the structural mechanism associated with the large electrostrain reported in the lead free system $(0.94-x)Na_{0.5}Bi_{0.5}TiO_3$-$0.06BaTiO_3$-$xK_{0.5}Na_{0.5}NbO_3$ ($0.0 \le x \le 0.025$). We show that in the unpoled state, while XRD data suggest cubic like structure, neutron powder diffraction data shows weak superlattice peaks. A systematic structural analysis led us to propose a long period structural modulation of the type $\sqrt{2}$ x $\sqrt{2}$ x 16, contradicting the earlier proposal of coexistence of rhombohedral (R3c) and tetragonal (P4bm) phases. We show that the large electrostrain is associated with field induced transformation of the long period modulated structure to rhombohedral (R3c) ferroelectric phase. We also demonstrated that if the field induced R3c phase is partly retained when the field is reduced to zero in the previous cycle, the electrostrain is substantially reduced in the next cycle. The reduced large electrostrain could however be reproduced after heating the specimen above depolarization temperature (~75 ^{o}C).

Chapter 7 summarizes the essential results of this thesis and also suggests prospects for further research.