

Synopsis

The multiferroic perovskite solid solution $x\text{BiFeO}_3-(1-x)\text{PbTiO}_3$ (BF-PT) exhibits very unique features such as giant tetragonality ($c/a \sim 1.19$), coexistence of ferroelectric and magnetic order (in certain composition range) and a high Curie point. The system has an added advantage of being semiconducting in nature with an optical band gap of ~ 2 eV which makes it interesting from the viewpoint of photocatalyst and photovoltaic applications. The end members BiFeO_3 and PbTiO_3 show rhombohedral ($R3c$) and tetragonal ($P4mm$) structures, respectively. The system is reported to exhibit morphotropic phase boundary (MPB) separating the rhombohedral and tetragonal phases near $x \sim 0.73$. Despite considerable research, the morphotropic phase boundary (MPB) region characterized by the coexistence of tetragonal and rhombohedral phases, is still an unresolved issue. In this work we have examined (i) the factors that leads to the uncertainty in the MPB region of this system, (ii) the pressure induced structural transformation behavior of the tetragonal compositions, (iii) photocatalytic performance of the different phases, and finally (iv) an extensive study on the ferroelectric, piezoelectric and high-field electrostrain behavior of La-modified BF-PT. The thesis has seven chapters. Chapter 1 presents the fundamental concepts and definitions which are relevant to understand the results presented in the thesis. It also contains a summary of the literature pertaining to BiFeO_3 and its various derivatives. Chapter 2 explains the details of the experimental methodology and analysis used in this work. The main results of the thesis are presented in the next four chapters (3-6).

Chapter 3 deals with the erratic phase formation behavior in a wide range of compositions in $(1-x)\text{BiFeO}_3-(x)\text{PbTiO}_3$ (BF-PT) system in a certain composition range, often referred to as the MPB region. Under similar sintering conditions, sometimes the pellets would spontaneously disintegrate to powder (completely/partially) after cooling and sometimes not. Structural analysis revealed that the disintegrated powder was invariably tetragonal ($P4mm$) phase and the pellet which survives exhibit coexistence of $P4mm$ and $R3c$ phases. Detailed microstructural investigation revealed that this different in the phase formation behavior is intimately related to the size of the grains. For the composition $x=0.29$, a composition within the reported MPB region of this system, the spontaneously disintegrated powder grains exhibit size of ~ 10 microns. When the size of the grains was reduced to $\sim 0.5 \mu\text{m}$ by mechanical grinding, the same powder specimen shows a rhombohedral ($R3c$) phase after annealing at ~ 700 oC (annealing was done to get rid of the residual stress induced effect during the grinding process, if any).

Neutron diffraction experiment revealed that the size induced rhombohedral phase is also antiferromagnetic in nature. This suggests a strong coupling of the antiferromagnetic phase with the rhombohedral ($R3c$) structure. Based on the structural results, we argue that the driving force for this size driven coupled inter-ferroelectric-magnetic transformation is the large depolarizing and the stress fields due to large polarization and domain walls energy (which are intimately related to the giant tetragonality).

Chapter 4 is an extension of the findings reported in Chapter 3. Keeping in view the fact that BiFeO_3 and its derivatives are semiconducting ferroelectric with a band gap of ~ 2 eV, we investigated the behavior of the different phases (tetragonal and rhombohedral) regarding their photocatalytic properties. As discussed in Chapter 3, reducing the size of the grains to below 0.5 micron switches the ground state from tetragonal to rhombohedral. But then this was possible only after the ground specimen was annealed above the Curie point, i.e. after taking the system

to the paraelectric state. When the annealing was not done, the as-ground 0.5 micron grains still retained the tetragonal phase. The pinned tetragonal domain walls which are already present in the large grains act as barriers for the bulk tetragonal regions to transform to rhombohedral when the size is reduced physically at room temperature. By taking the system to the paraelectric phase, the tetragonal domain walls are “dissolved”. In the absence of the tetragonal domain wall as barriers, the system lands in the rhombohedral ($R3c$) ground state during cooling. The trapped tetragonal phase at room temperature in the 0.5 microns grains are therefore metastable in nature. We therefore had the opportunity to examine the catalytic performance of the same powder in its stable rhombohedral phase (obtained after annealing) and metastable tetragonal phase (before annealing).

For the sake of reference, we also made compositions with stable tetragonal phase (with grains having the same specific area as the metastable tetragonal phase). The photocatalysis experiments were carried out using these powders as catalysts to degrade typical organic contaminants. We found that when the metastable phase was used as the catalyst, the rate of dye degradation increased by nearly five times as compared to its stable phase counterparts. Our results suggest that the metastable ferroelectric phase either increase the availability of the photogenerated charge carriers to participate in the redox reaction associated with dye degradation or increase the adsorption rate of the dyes on the surface of the particles.

Chapter 5 gives the details of the investigation pertaining to pressure induced structural transformations in the tetragonal phase of $(x)\text{BiFeO}_3-(1-x)\text{PbTiO}_3$. High pressure experiments were carried out using complementary Raman and x-ray diffraction techniques to capture the structural changes on both the local and global length scales. We found two different types of pressure induced phase transformations in two different composition ranges. We established a correlation of the transition pressure with the tetragonality of the parent phase at the ambient pressure and temperature conditions. While the compositions ($x < 0.4$) with relatively low tetragonality show a transition from tetragonal $P4mm$ to a non-polar rhombohedral $R3c$ phase, the compositions in the range $0.4 < x < 0.71$ with a relatively high tetragonality undergo a transformation first to polar rhombohedral ($R3c$) phase before transforming to the non-polar $R3c$ phase. The transition pressure at which the composition loses its tetragonal structure decreases with the increasing BF content. Our study confirmed that the MPB at room temperature can be stabilized even by pressure in tetragonal systems with large tetragonality.

Chapter 6 reports the discovery of an extraordinary large electrostrain ($\sim 1.3\%$) in polycrystalline specimens of La modified BF-PT, more specifically in the system with chemical formula $0.55(\text{Bi}_{0.7}\text{La}_{0.3})\text{FeO}_3-0.45\text{PbTiO}_3$. This is the largest electrostrain value reported so far in a polycrystalline ceramic specimen.

We carried out a detailed investigation to understand the mechanism associated with this ultrahigh electrostrain response using Raman, XRD, neutron powder diffraction, and electron microscopy with specimen subjected to poling field. We found that the composition $y = 0.30$ exhibiting the ultrahigh electrostrain exhibit a cubic-like structure in the unpoled state. On poling it transforms to a majority tetragonal phase. Neutron diffraction revealed very weak superlattice reflections, characteristic of antiphase tilted octahedra in both the unpoled and poled specimen. Detailed analysis using group theoretical ideas and Rietveld analysis of the neutron diffraction data, revealed that the true structure of this system is monoclinic (space group Cc) although the pseudocubic lattice parameters are tetragonal-like. Raman and electron microscopic studies

revealed that what appears as a cubic-like to tetragonal-like transformation on application of the poling field is primarily a manifestation of increase in the coherence length of the tetragonal-like domains. This composition behaves as a relaxor ferroelectric and the HAADF-STEM analysis revealed that the cubic—like phase is associated with the presence of considerable positional disorder, the degree of which is noticeably reduced after poling. An extensive XRD study in-situ with electric field was also carried out to understand the domain switching behavior with field. This study proved that the ultrahigh electrostrain of the critical composition ($y = 0.30$) is primarily associated with (i) the large reverse switching of the tetragonal-like non-180° ferroelectric-ferroelastic domain walls and (ii) the large tetragonality ($c/a \sim 1.23$) of the tetragonal-like phase. The important results of the thesis and the scope for further studies are summarized in Chapter 7.