Chapter 7

Summary of Thesis and Suggestions for Future Work

7.1 Summary of the Present Work

In this chapter, we have summarized the important findings of the present thesis. The crystal structure, phase transition and physical properties of multiferroic (1-x)BF-xSFN solid solution have been investigated. The phase pure samples were synthesized by conventional solid state reaction method. The phase purity and crystal structures of various compositions were characterized by using x-ray powder diffraction in conjugation with Rietveld crystal structure refinement. Microstructure was characterized by scanning electron microscopy (SEM). Composition and temperature dependent structural, magnetic and dielectric properties were investigated by analysing x-ray diffraction, dc magnetization M(T), alternating current magnetic susceptibility ac $\chi(\omega,T)$, magnetic hysteresis loop (M-H) and dielectric permittivity $\varepsilon(\omega, T)$ data. Since this solid solution is investigated for the first time, we have discovered several new crystallographic, magnetic and dielectric phase transitions along with magnetoelastic and magnetodielectric couplings. Our detailed investigations on various compositions of this material have revealed several new important findings are summarized below:

1. Discovery of Room Temperature Crystal Structure and High Temperature Structural and New Magnetic Phase Transitions in Phase Pure $Sr(Fe_{0.5}Nb_{0.5})O_3$ Ceramic

The room temperature structure of perovskite $Sr(Fe_{0.5}Nb_{0.5})O_3$ (SFN) ceramic has been investigated by Rietveld structure refinement using high resolution X-ray diffraction data. The correct structure is determined to be tetragonal in the space group *I*4*/mcm* ruling out orthorhombic (*Pbnm*), tetragonal (*P*4*mm*) and monoclinic structures reported by earlier authors. The high temperature structural phase transition has been studied by Rietveld analysis of the high resolution XRD data in the temperature range of 300K to 850 K. A high temperature structural phase transition is observed from tetragonal (*I*4/*mcm*) to cubic ($Pm\bar{3}m$) phase around ~630K. This phase transition was also confirmed by the heat flow experiment using differential scanning calorimetry. To confirm the nature of phase transition, we have studied the variation of integrated intensity (I_{SL}) of superlattice peak and the oxygen octahedral tilt angle (φ) in tetragonal structure with temperature. The temperature variations of these two parameters provide the evidence of tricritical nature of the phase transition. A magnetic phase transition is discovered in temperature dependence of magnetization M(T) around ~ 708K, which coincides with the dielectric anomaly temperature in loss tangent.

2. Room Temperature Crystal Structure, Magnetic and Dielectric Behaviour of (1-x)$BiFeO_3$-*x*$Sr(Fe_{0.5}Nb_{0.5})O_3$ Solid Solution ($0.1 \le x \le 1.0$)

Comprehensive crystallographic and Rietveld structural analysis of x-ray diffraction data for the room temperature crystal structure of (1-x)BF-xSFN solid solution reveals that a new monoclinic structure with space group *Cc* is observed for the composition range $0.1 \le x \le 0.15$. The monoclinic structure transforms to cubic structure with increasing the concentration of SFN in the solid solution. Coexistence of monoclinic (*Cc*) and cubic (*Pm*-3*m*) structure is obtained for the composition range $0.15 < x < 0.33$. The monoclinic (*Cc*) to cubic (*Pm*-3*m*) phase transition gets completed at xc ~ 0.33. A single phase cubic structure with local disorder of A and B-site cations is observed for the intermediate composition range $0.33 \le x \le 0.70$ in (1-x)BF-xSFN solid solution. Another phase coexistence region is observed for the composition range $0.70 < x \le 0.85$ in which tetragonal structure with space group *I*4/*mcm* and cubic structure with space group *Pm*-3*m* are present. At SFN end, for the composition range $0.85 < x \le 1.00$, the structure of (1-x)BF-xSFN is single phase tetragonal with *I4/mcm* space group. Composition dependent variation of dielectric permittivity shows two peaks around the compositions x ≈ 0.30 and x ≈ 0.80 for (1-x)BF-xSFN ceramic. Investigation of magnetization (M)-applied magnetic field (H) hysteresis loops for the various composition of 1-x)BF-xSFN ceramic reveals induction of weak ferromagnetism in canted antiferromagnetic order of $BiFeO_3$ due to solid solution formation with SFN. The composition dependent variation of remnant magnetization for (1-x)BF-xSFN ceramic exhibit two peaks around x ≈ 0.15 and x ≈ 0.80.

3. Investigation of First Order Isostructural Magnetic Transition with a Magnetodielectric Coupling in $0.9BiFeO_3$-$0.1Sr(Fe_{0.5}Nb_{0.5})O_3$ Solid Solution

We have discovered that the substitution of 10% $Sr(Fe_{0.5}Nb_{0.5})O_3$ in $BiFeO_3$ lead to a structural transformation from pre-existing rhombohedral structure of $BiFeO_3$ in *R*3*c* space group to monoclinic structure in *Cc* space group. The Rietveld analysis of temperature dependent x-ray powder diffraction data at various temperatures reveals three anomalies in the temperature dependence of the unit cell volume and lattice parameters. All anomalies are found to be isostructural. Out of three anomalies, two are also observed to be coincident in dc magnetization M(T) measurement at 255K and 145K. Our experimental results on structural, dielectric and ac susceptibility $\chi(\omega,T)$ ruled out the possibility of spin glass transition at 255K and support the existence of a first order isostructural magnetic transition that is accompanied with magnetoelastic coupling. This is also accompanied with an intrinsic magnetodielectric relaxation step, with a negative linear magnetodielectric coupling. Further, the second anomaly in M (T) and structural results support the presence of weak magnetoelastic coupling at 145K where a spin reorientation transition takes place. The third anomaly appearing in unit cell volume and lattice parameters around 40K has glassy nature with the presence of magnetoelastic effect.

4. Investigation of New Magnetoelastic and Magnetic Transitions Accompanied with Magnetoelectric Coupling in $0.1BiFeO_3$-$0.9Sr(Fe_{0.5}Nb_{0.5})O_3$ Solid Solution Below Room Temperature

We have discovered two new magnetic transitions and magnetodielectric and magnetoelastic coupling in $0.1BiFeO_3$-$0.9Sr(Fe_{0.5}Nb_{0.5})O_3$ ceramic below room temperature. Temperature dependent variation of dc-magnetization M(T) reveals magnetic transitions at 42K and 130K. The magnetic transition at 130K is found to be weakly coupled to the polarization as the temperature dependent variation of dielectric permittivity also shows an anomaly at 130K confirming magnetoelectric coupling. Temperature dependent variation of unit cell volume, lattice parameters and tetragonality exhibits discontinuous changes at the two magnetic transition temperatures confirming magnetoelastic nature of the two transitions. The temperature dependence of FeO_6 octahedral tilt angle (φ), Sr/Bi-O bond length and Fe/Nb-O-Fe/Nb bond angle also show discontinuity at the two magnetic transition temperatures that further confirms the magnetoelastic coupling.

7.2 Suggestions for Future Work

Our investigations on (1-x)BF-xSFN solid solutions have revealed many interesting and new aspects linked with structural, magnetic and dielectric behavior of this new system. However, a number of things are needed to be settled in future investigations. Few important suggestions for future work are given below:

1. High resolution synchrotron diffraction measurements and pair distribution function (PDF) analysis should be carried out to investigate the local structure of the (1-x)BF-xSFN solid solution in the composition range $0.33 \leq x \leq 0.70$ with pseudocubic structure.

2. High resolution neutron diffraction measurement should be carried out to study the room temperature magnetic structure of (1-x)BF-xSFN solid solution.

3. High temperature neutron and synchrotron diffraction study should be carried to investigate the ferroic phase transitions for the $BiFeO_3$ end compositions.

4. Insulating samples should be synthesized for the dielectric and P-E loop measurements. Additives like MnO_2, Mn_2O_3 and $LiCO_3$ etc., should be tried to reduce the hopping conductivity and increase the insulating resistance through charge compensation effects.