Preface

Study of magnetoelectric multiferroics, in which, the ferromagnetic (FM) or antiferromagnetic (AFM) and ferroelectric (FE) or antiferroelectric (AFE) orders coexist and are mutually coupled, is on focus point in materials research [Ramesh et al. (2007), Eerenstein et al. (2006), Hill (2000)] The coexistence and coupling of the magnetic (M) and electric order parameters (P) in a single phase multiferroic materials leads to novel physical phenomena and offers possibilities for new multifunctional sensors, actuators, data storage devices and 4-state logic systems [Fiebig (2005), Scott (2007)]. Recently, several multiferroics manganites like $ReMnO_3$, $ReMn_2O_5$ etc. where Re is a rare earth element [Kimura et al. (2003)A, Hur et al. (2004), Johnson et al. (2012)] showing improper ferroelectricity have been found to exhibit strong magnetodielectric response at their magnetic transition temperature. The gigantic magnetoelectric and magnetocapacitance effect in $TbMnO_3$ has been reported due to the switching of the electric polarization induced by magnetic fields [Cheong and Mostovoy (2007)]. Amongst the multiferroics showing proper ferroelectricity, the room temperature multiferroic $BiFeO_3$ (BF) with ferroelectric transition temperature T_c ~ 1103 K and antiferromagnetic transition T_N ~ 643 K holds considerable promises. This material has rhombohedral structure with *R*3*c* space group and shows electric field induced spin flop. The magnetic structure of BF is G-type canted antiferromagnetic with a superimposed incommensurate modulated spiral spin structure of periodicity wavelength $\lambda \sim 620$ Å. Because of the spin spiral, the weak ferromagnetism due to spin canting is not observed and accordingly the linear magnetoelectric effect also averages to zero and only the quadratic magnetoelectric effect has been observed indeed. However, linear magnetoelectric effect has been reported to appear in BF by destroying spiral spin structure on application of intense magnetic field of

~ 20 kOe [Popov et al. (1993)]. The melting of the spiral spin structure leads to the appearance of the weak ferromagnetic moment of the order ~ 0.3emu/g at 10 K and ~ 0.15 emu/g at 300 K. A more convenient way of destroying the spin spiral structure of BF, to observe linear magnetoelectric coupling, is by chemical substitutions at Bi and Fe sites. For example, the linear magnetoelectric coupling in solid solution of BF with $BaTiO_3$ i.e. (1-x)$BiFeO_3$-x$BaTiO_3$ with x = 0.1 and 0.2 has already been reported [Singh et al. (2008)C & (2011)]. Thus there is considerable interest in studying the multiferroic behavior of $BiFeO_3$ solid solutions with other perovskites. The present thesis deals with a new solid solution of the two perovskites $BiFeO_3$ (BF) and $Sr(Fe_{0.5}Nb_{0.5})O_3$ (SFN) i.e. mixed (1-x)$BiFeO_3$-x$Sr(Fe_{0.5}Nb_{0.5})O_3$ (BF-xSFN) solid solution system. This thesis consists of the results of a comprehensive study on synthesis, room temperature crystal structure, dielectric and magnetic behaviour and associated phase transitions, M-H hysteresis and nature of the crystallographic phase transitions in the (1-x)BF-xSFN solid solution system, as a function of composition and temperature.

The main findings of the present thesis work are listed below:

1. Room temperature structure and high temperature structural and magnetic phase transition in $Sr(Fe_{0.5}Nb_{0.5})O_3$ 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 crystal 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 around ~ 630K from tetragonal (*I*4*/mcm*) to cubic (*Pm*$\bar{3}$*m*) structure. This phase transition is also confirmed by the heat flow experiment using differential scanning calorimetry. To confirm the nature of phase transition, we have studied the temperature dependent variation of integrated intensity (I_{SL}) of superlattice peak and the oxygen octahedral tilt angle (φ) in tetragonal structure. The temperature variations of these two parameters provide the evidence of the 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. This work is published in **J. Appl. Phys. 125,** 174102 (2019).

2. Investigation of the morphotropic phase boundaries in (1-x)$BiFeO_3$-x$Sr(Fe_{0.5}Nb_{0.5})O_3$ solid solution along with Magnetic [M-H and M(T)] and dielectric studies as a function of composition 'x'

Rietveld crystal structure refinement of the various compositions of (1-x)BF-xSFN has been done to investigate the crystallographic phase transitions as a function of composition. The room temperature crystal structure of (1-x)BF-xSFN in the composition range $0.1 \leq x \leq 0.15$ exhibit monoclinic structure with *Cc* space group rather than the pre-existing rhombohedral structure of BF with *R*3*c* space group. A morphotropic phase transition occurs in the composition range $0.15 < x < 0.33$ where, monoclinic phase coexists with a cubic phase. The monoclinic (*Cc*) to cubic (*Pm*-3*m*) phase transition is completed at $x_c \sim 0.33$. In the composition range $0.33 \leq x \leq 0.70$ cubic phase remains stable and then gradually transforms to the coexistence of two phases in the composition range $0.70 < x \leq 0.85$. The two coexisting phases are of tetragonal structure with *I*4*/mcm*

space group and cubic structure with *Pm*-3*m* space group. Above x = 0.85 and in the composition range $0.85 < x \leq 1$, the solid solution (1-x)BF-xSFN has tetragonal structure with *I*4/*mcm* space group. The variation of room temperature dielectric permittivity with the composition (x) shows two peaks in the MPB regions around the compositions at $x \approx 0.30$ and $x \approx 0.80$. The antiferromagnetic transition temperature (T_N) and spin re-orientation phase transition (SPT) temperature were found to decrease as the $Sr(Fe_{0.5}Nb_{0.5})O_3$ concentration increases in the solid solution. The composition dependent study of remnant magnetization (Mr), obtained from magnetization (M) versus magnetic field (H) plots (M-H hysteresis loop) for each composition, exhibits two peaks over the entire composition range. The first peak was observed at x = 0.15 (Mr ~ 0.0578 emu/g) and the second one at x = 0.80 (Mr ~ 0.23emu/g).

3. First order isostructural magnetic phase transition with a magnetodielectric anomaly in $0.9BiFeO_3$-$0.1Sr(Fe_{0.5}Nb_{0.5})O_3$: (XRD, dielectric [ε(T)] and magnetic [M(T), χ(ω, T)] studies)

Analysis of temperature dependent x-ray powder diffraction data of $0.9BiFeO_3$-$0.1Sr(Fe_{0.5}Nb_{0.5})O_3$ ceramic by Rietveld method shows three anomalies in the unit cell volume and lattice parameters, corresponding to the isostructural phase transitions below room temperature, as the crystal structure remains same at all the temperatures. The temperature of two anomalies are coincident to magnetic anomaly temperature appearing in the dc magnetization M(T) measurement. The first anomaly appears at 255K with robust nature and the second one appears as a broad hump around 145K. These two anomalies in M(T) are also supported by temperature variation of coercive field (H_c). Our experimental results on structural, dielectric and ac susceptibility χ(ω,T) studies rules out the possibility

of spin glass transition around 255K. It supports the existence of a first order isostructural magnetic transition that is accompanied with magnetoelastic coupling and 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. The third anomaly appearing around 40K in the temperature dependent variation of unit cell volume and lattice parameters was found to be very close to the temperature of the peak in the magnetic ac susceptibility measurement. This shows that the last anomaly has glassy nature with the magnetoelastic effect.

4. Investigation of new magnetoelastic and magnetic transitions accompanied with magnetoelectric coupling in $0.1BiFeO_3$-$0.9Sr(Fe_{0.5}Nb_{0.5})O_3$ multiferroic:

The multiferroic solid solution $0.1BiFeO_3$-$0.9Sr(Fe_{0.5}Nb_{0.5})O_3$ composition at the SFN end has been characterized for structure, phase transition, magnetoelectric and magnetoelastic coupling. In contrast to the composition at BF end [**0.9BF-0.1SFN]**, temperature dependent measurement of dc-magnetization M(T) on $0.1BiFeO_3$-$0.9Sr(Fe_{0.5}Nb_{0.5})O_3$ ceramic shows two magnetic transitions one around ~ 42K and the second at ~130K. The real part of dielectric permittivity exhibits step like change at the magnetic anomaly temperature (~130K) which indicates the presence of magnetoelectric coupling. The room temperature polarization (P)-electric field (E) hysteresis loop measurement shows week ferroelectric nature of sample while the magnetization (M) versus magnetic field (H) measurement suggest weakly ferromagnetic character. The Rietveld structural analysis of low temperature X-ray powder diffraction data does not reveal any crystallographic phase transition in terms of peak splitting or new reflections. However, temperature dependence of lattice parameters, tetragonality, unit cell volume,

$(Nb/Fe)O_6$ octahedral tilt angle (φ), Sr/Bi-O bond length and Fe/Nb-O-Fe/Nb bond angles reveal discontinuous changes at both the magnetic transitions observed in temperature dependence of magnetization. This confirms that both the magnetic anomalies (around ~ 42K and ~ 130K) exhibit magnetoelastic coupling accompanied with isostructural phase transitions.

This thesis is organized into seven chapters:

Chapter-1: The basic definitions, details of the fundamental concepts on the multiferroic materials along with brief literature review on $BiFeO_3$, $Sr(Fe_{0.5}Nb_{0.5})O_3$ and solid solutions based on $BiFeO_3$ are given in this chapter.

Chapter-2: The details of the sample preparation and characterization of phase purity and microstructure of $(1-x)BiFeO_3$-$xSr(Fe_{0.5}Nb_{0.5})O_3$ solid solution is given in this chapter.

Chapter-3: The room temperature crystal structure and high temperature structural phase transition along with the magnetic and dielectric behavior of $Sr(Fe_{0.5}Nb_{0.5})O_3$ is described in this chapter.

Chapter-4: The room temperature crystal structure of $(1-x)BiFeO_3$-$xSr(Fe_{0.5}Nb_{0.5})O_3$ solid solution investigated by Rietveld technique using high resolution x-ray diffraction data in the composition range $0.1 \leq x \leq 1.0$ is described in this chapter. This chapter also presents the study of room temperature dielectric and magnetic properties in entire composition range.

Chapter-5: The temperature dependent dc magnetization M(T), ac $\chi(\omega,T)$, M-H hysteresis loop, dielectric and structural analysis is performed to investigate magnetoelectric and magnetoelastic effects in $0.9BiFeO_3$-$0.1Sr(Fe_{0.5}Nb_{0.5})O_3$ ceramic. The results of these investigations are discussed in this chapter.

Chapter-6: This chapter presents the results of crystallographic, magnetoelastic and magnetic phase transition studies below room temperature in $0.1BiFeO_3$-$0.9Sr(Fe_{0.5}Nb_{0.5})O_3$ multiferroic ceramic. Magnetic phase transitions are shown to be accompanied with magnetoelectric coupling.

Chapter-7: This chapter summarizes the main findings of the research work carried out for the present Ph.D. thesis and lists few important suggestions for future investigations.