

Study of magnetoelectric multiferroics, in which the antiferromagnetic (AFM) or ferromagnetic (FM) and antiferroelectric (AFE) or ferroelectric (FE) orders coexist and are mutually coupled, is a hot topic in materials science [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 material 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 or ReMn_2O_5 where Re is a rare earth element [Kimura et al. (2003), Hur N. et al. (2004), Johnson et al. (2012)] showing improper ferroelectricity have been found to exhibit strong magnetolectric 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 $T_C \sim 1103$ K and antiferromagnetic $T_N \sim 643$ K holds considerable promises. This material shows electric field induced spin flop [Lebeugle et al. (2008)]. The magnetic structure of BF is G-type canted antiferromagnet with a superimposed incommensurate modulated spiral spin structure of 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 indeed only the quadratic magnetoelectric effect has been observed. However, linear magnetoelectric effect

has been reported in BF by destroying spiral spin structure on application of intense magnetic fields 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 ~ 0.3 emu/g at 10 K and ~ 0.15 emu/g at 300 K. A more convenient way of destroying the spin spiral of BF to observe linear magnetoelectric coupling is by chemical substitutions. For example, the linear magnetoelectric coupling in solid solution of BF with BaTiO₃ i.e. (1-x)BiFeO₃-xBaTiO₃ with $x = 0.1$ and 0.2 has already been reported [Singh et al. (2008) & (2011)]. This is therefore considerable interest in studying the multiferroic behavior of BiFeO₃ solid solutions with other perovskites.

The present thesis deals with the solid solutions of the two multiferroic perovskites BiFeO₃ (BF) with Pb(Fe_{1/2}Nb_{1/2})O₃ (PFN) i.e. mixed (1-x) BiFeO₃-x Pb(Fe_{1/2}Nb_{1/2})O₃ (BF-xPFN) solid solution system. It consists a comprehensive study of synthesis, crystal (nuclear) structure, magnetic structure, magnetic transitions, M-H hysteresis and nature of the ferroelectric to paraelectric phase transitions in the BF-xPFN solid solution system as a function of composition and temperature.

The main findings of this work are listed below:

- 1.** The controversies related with the room temperature crystal structures of the BF-xPFN solid solution system and the structural phase boundaries have been resolved using the laboratory source x-ray diffraction data and also high energy synchrotron x-ray diffraction data. The room temperature crystal structure of BF-xPFN in the composition range $0.1 \leq x \leq 0.32$ is identical with BiFeO₃. A

morphotropic phase transitions occurs in the composition range $0.32 < x < 0.40$ where rhombohedral and cubic phases coexist. The rhombohedral (R3c) to cubic ($\text{Pm}\bar{3}\text{m}$) phase transition is occurred at $x_C \sim 0.40$. The cubic like phase in the composition range $0.40 \leq x \leq 0.90$, transforms to Cm phase for $x > 0.90$. The x-ray diffraction patterns recorded for the composition range $0.90 < x \leq 0.96$ are refined by monoclinic phase with Cm space group.

2. The local structure refinement using synchrotron x-ray diffraction data shows that $\text{Bi}^{3+}/\text{Pb}^{2+}$ and O^{2-} ions are not there ideal cubic position but they are locally displaced along $\langle \text{xxz} \rangle$ and $\langle \text{yy}0 \rangle$ for the compositions $0.40 \leq x < 0.80$ (locally Cc space group) and along $\langle \text{xxx} \rangle$ and $\langle \text{yy}0 \rangle$ for $0.80 \leq x \leq 0.90$ (locally R3m space group) respectively. This demonstrates evidence for two MPBs for the BF-xPFN solid solution. The R3c to locally Cc phase transition occurs at the first MPB at $x \approx 0.40$ while the locally Cc to R3m phase transition occurs at the second MPB at $x = 0.80$.

3. Composition dependent dielectric plot at room temperature reveals two dielectric anomalies at $x \approx 0.40$ and $x \approx 0.80$, corresponding to the two morphotropic phase boundaries (MPB) consistent with structural studies. The small hump in dielectric constant at $x \approx 0.90$ composition is due to the local rhombohedral (R3m space group) to global monoclinic (Cm space group) phase transition.

4. Rietveld analysis of the x-ray and neutron powder diffraction data reveals that BF-0.2PFN is isostructural with the well known multiferroic BiFeO_3 . It is shown

that room temperature ferroelectric phase of BF-0.2PFN in the R3c space group transforms to paraelectric/paraelastic cubic ($Pm\bar{3}m$) phase directly without any intermediate “ β ” phase reported in the literature for pure BiFeO₃. This transition is of first order type as confirmed by the coexistence of R3c and $Pm\bar{3}m$ phases over a 100 K range and discontinuous change in the unit cell volume. It is argued that the R3c to $Pm\bar{3}m$ phase transition is of trigger type involving simultaneous condensation of Γ_4^- and R_4^+ modes.

5. A weak ferromagnetism observed in the M-H hysteresis response of BF-xPFN solid solution system at room temperature for $x < 0.60$ suggests that spatially modulated spiral spin structure of BiFeO₃ might be completely or partially broken by PFN substitution. The Rietveld analysis of the neutron powder diffraction data using irreducible representational theory shows that the magnetic structure of the BF-xPFN solid solution is G-type at the room temperature for $x \leq 0.87$. Temperature dependent dc magnetization measurements at 2 kOe reveal that antiferromagnetic transition temperature of BF-xPFN solid solution decreases with increasing the concentration of the non-magnetic Nb⁵⁺ ion at the Fe³⁺ sublattice. The T_N versus x plot indicates that the BF-xPFN solid solution is paramagnetic for $x \geq 0.87$ at room temperature.

6. The temperature dependent M-H loop measurements confirm that weak ferromagnetic nature of M-H response completely disappeared above the antiferromagnetic transition temperature and paramagnetic behaviour was observed. The magnetic transition temperature was confirmed by dc magnetisation

and DSC measurements. The huge dielectric response at magnetic transition temperature reveals strong magnetoelectric coupling in BF-0.2PFN. X-ray diffraction studies reveal a very remarkable change in the rhombohedral distortion angle and unit cell volume below the magnetic transition due to the magnetoelastic effects. The atomic positions, obtained from Rietveld refinements neutron powder diffraction data, shift significantly below the magnetic transition temperature due to the first-order isostructural phase transition (IPT). The new atomic positions below T_N correspond to one of the irreducible representations of the R3c space group corresponding to the zone centre ($k = 0$). The first order isostructural phase transition (IPT) accompanying the magnetic ordering below $T_N \sim 566$ K, leads to a significant discontinuous change in the ionic polarization ($\Delta P_z \sim 1.63 \mu\text{C}/\text{cm}^2$) and octahedral tilt angle ($\sim 0.3^\circ$) at T_N . The ionic polarization, obtained from refined positional coordinates of the nuclear structure and Born effective charges is shown to scale linearly with sublattice magnetization, confirming the presence of linear magnetoelectric coupling in BF-0.2PFN at the atomic level. The critical exponent obtained by least square fitting of the refined ordered magnetic moment is $1/3$, which is comparable to the values obtained for pure BiFeO_3 .

7. A phase diagram of BF-xPFN solid solution is established using the results of temperature dependent dielectric, magnetization and structural (x-ray and neutron) studies on various compositions of BF-xPFN solid solutions.

This thesis is divided into IX chapters:

Chapter I: The details of the fundamental concepts on the multiferroic materials along with brief literature review on BiFeO_3 and its solid solution with $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ are given in this chapter.

Chapter II: The details of the sample preparation of BiFeO_3 - $x\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ solid solution are given in this chapter.

Chapter III: The room temperature crystal structure of the BiFeO_3 - $x\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ solid solution is investigated by Rietveld technique using laboratory source x-ray diffraction data in the composition range $0.1 \leq x \leq 1.0$.

Chapter IV: Temperature dependent dielectric measurement is presented to determine ferroelectric T_C for different composition of BF- x PFN solid solutions. The local structure refinement is carried out using high resolution synchrotron x-ray powder diffraction data in the whole cubic phase region $0.40 \leq x \leq 0.90$ to identify the actual local crystal symmetry to correlate it with the dielectric and P-E loops measurements. Composition dependent dielectric plot is also given to locate the MPBs.

Chapter V: The nature of the ferroelectric to paraelectric phase transitions in BF-0.2PFN solid solution is discussed using the laboratory source x-ray powder diffraction data. Evidence of “Trigger” type of phase transition is also given.

Chapter VI: The controversy related with existence of R3m phase as intermediate ‘ β ’ phase for ferroelectric to paraelectric phase transition in BF-

0.2PFN solid solution is resolved using high resolution neutron powder diffraction data.

Chapter VII: In this chapter, composition and temperature dependent dc magnetization studies are given. The magnetic structure at room temperature is determined by Rietveld refinement using high resolution neutron powder diffraction data.

Chapter VIII: In this chapter, results of temperature dependent magnetic hysteresis measurements presented as proof of results of weak ferromagnetism in BF-0.2PFN solid solution. The evidence of strong magnetoelectric coupling is evidenced by a huge dielectric anomaly at T_N . The evidence of the isostructural phase transitions (IPT) along with the atomic level evidence of the linear magnetoelectric coupling are also presented using temperature dependent neutron powder diffraction data.

Chapter IX: A phase diagram of BF-xPFN solid solution constructed by me is given in this chapter. The main findings of the present work are also summarized with a list of suggestions for future work.

During the course of this thesis work, the following papers have been published by me:

1. Jay Prakash Patel, Anatoliy Senyshyn, Hartmut Fuess and Dhananjai Pandey, "Evidence for weak ferromagnetism, isostructural phase transition, and linear magnetoelectric coupling in the multiferroic in the multiferroic $\text{Bi}_{0.8}\text{Pb}_{0.2}\text{Fe}_{0.9}\text{Nb}_{0.1}\text{O}_3$ solid solution" *Phys. Rev. B* **88, 104108(2013).**

2. Jay Prakash Patel, Anar Singh and Dhananjai Pandey, “Nature of ferroelectric to paraelectric phase transition in multiferroic $0.8\text{BiFeO}_3\text{-}0.2\text{Pb}(\text{Fe}_{0.5}\text{N}_{0.5})\text{O}_3$ ceramics”, **J. Appl. Phys.** **107**, 104115 (2010).

3. Anar Singh, **Jay Prakash Patel** and Dhananjai Pandey, “High temperature ferroic phase transitions and evidence of paraelectric cubic phase in the multiferroic $0.8\text{BiFeO}_3\text{-}0.2\text{BaTiO}_3$ ” **Appl. Phys. Letters** **95**, 142909 (2009).