Preface

Ever since the discovery of PZT, the morphotropic phase boundary (MPB) solid solutions have been investigated extensively to explore their attractive physical properties and interesting phase transition[1-2]. The MPB is a nearly vertical phase boundary in the temperature composition phase diagram of ferroelectric perovskite solid solutions, separating stability region of two crystallographic phases. The physical responses are maximized around the phase boundary and phase coexistence or lowering of crystallographic symmetry is observed. The important MPB ceramics can be grouped into three broad categories: (i) Pb-based MPB systems (ii) Pb-free MPB systems and (iii) multiferroic MPB systems. However, after growing concern regarding the toxicity of Pb-based systems, there has been resurgence in the development of new MPB systems having reduced lead concentrations or totally lead-free[3-4]. Over the last few years, multiferroic materials with reduced lead content have attracted great interest due to their potential for applications in novel devices. Multiferroics are those materials in which two or more ferroic properties such as ferromagnetism (FM), ferroelectricity (FE) and ferroelasticity are present and coupled. The ability to couple the electric polarization and magnetization (known as magnetoelectric coupling) can provide the additional degree of freedom in device design. Multiferroic materials can revolutionize the application areas like as data storage, sensors, actuators, transducers, resonators and filters. The coupling between electric and magnetic response

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could permit to write the data electrically and read magnetically[5-8]. However, the magnetoelectric materials with satisfactory multiferroic response are still lacking and difficult to synthesize in the laboratory due to contradictory requirement of electronic configuration for ferroelectricity and magnetism[8]. Usually, ferroelectricity in perovskites requires the empty d-orbitals at B-site cation which soften the orbital overlapping between B-site cations and O anions in the ABO_3 perovskite[9]. Magnetism requires unpaired electrons in the d-orbitals of the ions at the B-site[10].

The first magnetoelectric multiferroic discovered was nickel iodine boracite ($Ni_3B_7O_{13}I$)[8,11]. The first multiferroic solid solution synthesized in the laboratory was $(1-x)Pb(Fe_{2/3}W_{1/3})O_3-xPb(Mg_{1/2}W_{1/2})O_3$ by replacement of some of the d^0 B-site cations in ferroelectric perovskite oxides (ABO_3) by magnetic d^n cations[12-13]. Evidence of magnetoelectric properties has been found in several other single phase materials like as $GaFeO_3$, $Y_3Fe_5O_{12}$, $TbMn_2O_5$, $HoMnO_3$, $BiFeO_3$, $BiCrO_3$, $YMnO_3$, $BiMnO_3$, $TbMnO_3$ etc. Most of them exhibit very weak magnetoelectric response which is observed at much below room temperature so that they cannot be used at room temperature[5]. To overcome this limitations of single phase multiferroics, composites are prepared where indirect coupling between magnetic and ferroelectric response is achieved via strain[5,14]. Multiferroic composites are prepared by taking suitable combination of magnetic and ferroelectric materials. Following this principle, various ME composites have been investigated by taking ferroelect-

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ric phases such as $BaTiO_3$, $Pb(Zr,Ti)O_3$, $BaPbTiO_3$, $Bi_4Ti_3O_{12}$ and magnetic phases as Ni, Co, Mg, (Ni, Zn), (Ni,Co,Mn) ferrites. Magnetoelectric coefficients obtained in the composites are significantly larger than single phase multiferroic magnetoelectric and appears at room temperature[15-20]. With the objective of developing a new multiferroic system, in the present thesis, we have investigated the structure property correlations in a newly discovered multiferroic solid solution $(1-x)Bi(Ni_{1/2}Ti_{1/2})O_3-xPbTiO_3$ and its composite with Ni-Zn ferrite. Being a new material, the structure property correlations have not been investigated in detail for this solid solution. We have investigated several new important aspects of this solid solution not reported earlier.

The important findings from this work are listed below:

(i) Structure of MPB region in $(1-x)Bi(Ni_{1/2}Ti_{1/2})O_3-xPbTiO_3$:

We carried out the detailed structural analysis of the BNT-PT across MPB. The stability region of various crystallographic phases at room temperature for $(1-x)Bi(Ni_{1/2}Ti_{1/2})O_3-xPbTiO_3$ is determined precisely in the composition range x=0.35-0.55. Structural transformation from pseudocubic (x<0.41) to tetragonal (x>0.49) phase is observed via phase coexistence region demarcating the morphotropic phase boundary (MPB). We find for the first time that the morphotropic phase boundary region of BNT-xPT consists of coexisting tetragonal and monoclinic structures with space group P4mm and Pm, respectively, stable in composition range $0.41 \leq x \leq 0.49$. The results of Rietveld structural analysis completely rule out the coexistence of rhombohedral and tetragonal phases reported by earlier workers.

(ii) Electric Field Induced Phase Transition in $(1-x)Bi(Ni_{1/2}Ti_{1/2})O_3-xPbTiO_3$ Solid Solution:

We have discovered for the first time an electric field induced phase transition by us in $(1-x)Bi(Ni_{1/2}Ti_{1/2})O_3-xPbTiO_3$ for the compositions with x=0.35, 0.43 and 0.50. The cubic structure of $0.65Bi(Ni_{1/2}Ti_{1/2})O_3-$

$0.35PbTiO_3$ transforms to monoclinic structure with space group Pm for the poling field $\geq 5kV/cm$. Significant value of planar electromechanical coupling coefficient (k_P) is observed after poling due to electric field induced cubic to monoclinic phase transition. Large c-axis microscopic lattice strain (1.6 %) is achieved at 30kV/cm poling field due to this structural phase transition. Domain reorientation along c-direction is observed after poling in x=0.43 and 0.50 (MPB and tetragonal) compositions.

(iii) Dielectric relaxation and new transitions:

We have investigated for the first time new anomaly in the temperature dependence of dielectric response below room temperature. Dielectric relaxation above and below the room temperature has been investigated for tetragonal, pseudocubic and MPB compositions of BNT-xPT ceramics. Two types of distinct behaviour are seen for the dielectric relaxation above and below the room temperature. Strong dielectric relaxation peak is observed above room temperature in the pseudocubic compositions with low PT concentration which weakens in the MPB region and disappears for the tetragonal compositions with high PT concentration similar to several relaxor based MPB ceramics. However all the compositions show strong dielectric peak below room temperature which systematically show composition dependent shifts also.

(iv) Multiferroic behaviour at room temperature in particulate Composite of $0.51Bi(Ni_{1/2}Ti_{1/2})O_3-0.49PbTiO_3$ with spinel $Ni_{0.6}Zn_{0.4}Fe_2O_4$:

We have investigated very high multiferroic response at room temperature in particulate $(1-y)0.51Bi(Ni_{1/2}Ti_{1/2})O_3-0.49PbTiO_3/yNi_{0.6}Zn_{0.4}Fe_2O_4$ (BNT-PT/NZFO) particulate composite. BNT-PT/NZFO particulate composite have been fabricated taking selected composition of ferroelectric $0.51Bi(Ni_{1/2}Ti_{1/2})O_3-0.49PbTiO_3$ and magnetic $Ni_{0.6}Zn_{0.4}Fe_2O_4$ phases. The ferroelectric phase $0.51Bi(Ni_{1/2}Ti_{1/2})O_3-$

0.49PbTiO$_3$ has tetragonal perovskite structure with space group P4mm. The magnetic phase Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ has spinel cubic structure with space group Fd$\bar{3}$m. Rietveld structural analysis for the each components of composite reveals that the tetragonality (c/a) of the ferroelectric phase 0.51Bi(Ni$_{1/2}$Ti$_{1/2}$)O$_3$-0.49PbTiO$_3$ continuously increases. Lattice parameter of the magnetic phase Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ also increases suggesting that part of Fe^{3+} ions are diffusing at the B-site of 0.51Bi(Ni$_{1/2}$Ti$_{1/2}$)O$_3$-0.49PbTiO$_3$ and Ti^{4+} in Ni$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ after the composite formation. The appearance of P-E hysteresis loops at room temperatures reveals that the system depicts the ferroelectric nature even after the composite formation. Very high magnetoelectric (ME) coefficient reveals the multiferroic nature of BNT-PT/NZFO composite.

These important results are presented in the seven chapters of the thesis as summarized below:

Chapter:I gives a brief introduction to the subject and fundamental concepts related to the multiferroic materials. A brief review of the existing literature on solid solution of Bi(Ni$_{1/2}$Ti$_{1/2}$)O$_3$ (BNT) with other perovskites is also given in this chapter.

Chapter:II describes the details of the sample preparation for synthesizing phase pure perovskite solid solution (1-x)Bi(Ni$_{1/2}$Ti$_{1/2}$)O$_3$-xPbTiO$_3$ (BNT-xPT) in the composition range 0.35≤x≤0.55 ceramics.

Chapter:III deals with the investigations of room temperature crystal structures of BNT-xPT solid solutions using Rietveld analysis of the laboratory x-ray diffraction data and locations of structural phase boundaries.

Chapter:IV describes the electric field induced phase transition in BNT-xPT solid solution poled at different electric field strength.

Chapter:V presents the temperature dependent dielectric studies for BNT-xPT solid solutions with $0.35 \leq x \leq 0.55$. Results of low temperature x-ray diffraction studies are also given in this chapter to correlate with dielectric anomalies.

Chapter:VI describes the synthesis of BNT-0.49PT/yNZFO composites, their structural analysis using Rietveld refinement and composition dependent P-E and ME characterization.

Chapter:VII summarizes the main findings of the present work and lists a few suggestions for future investigations.