Preface

Piezoelectricity is the ability of certain crystalline materials to develop an electric charge proportional to externally applied mechanical stress and vice-versa[1]. Nowadays, a large number of piezoelectric sensors and actuator devices are used in automotive, aerospace, aircraft, medical imaging, telecommunication and ultrasonic devices[2-3]. Most of the piezoelectric ceramics are derived from ferroelectric ceramics by poling at high dc electric field to introduce anisotropy and piezoelectricity. The ferroelectric materials exhibit spontaneous polarization which can be switched into crystallographically equivalent directions with an applied electric field (E). Therefore, it possess a P-E hysteresis loop. The hysteresis loop disappears above the Curie temperature (T_C). It has domain structure, and high dielectric permittivity rising to a peak at the Curie temperature. The falling-off of its dielectric permittivity above the Curie temperature follows a Curie-Weiss law. The ferroelectric transition from a high symmetry paraelectric state to lower symmetry ferroelectric state is characterized by the appearance of spontaneous polarization (P) at the phase transition temperature[4].

Among the stable ferroelectric ceramics investigated up to now $PbTiO_3$ possesses the largest saturation polarization (~81μC/cm^2) and very large tetragonality (c/a=1.0635)[1,5]. The Lead based morphotropic phase boundary [MPB] piezoceramics such as $PbZr_{1-x}Ti_xO_3$ [PZT][6-7], $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$[8-9], $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$[8], etc. have been widely used in piezoelectric applications from several decades due to their high responses. Morphotropic phase boundary in ferroelectric perovskite

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solid solutions is defined as a nearly vertical phase boundary in the temperature-composition phase diagram separating stability regions of two crystallographic phases[1,10]. Coexistence of the neighbouring phases and maximization of piezoelectric responses are obtained for the MPB compositions[1,10]. PZT have been found most successful piezoceramics so far due to its high electromechanical coupling coefficient k_P~0.55, d_{33}~600μC/N and high T_C~400°C. Lead is highly toxic and leads to cancer and other health issues, therefore it is being banned worldwide in most of the applications[11]. Lead is released into the environment during calcination and sintering process of Pb-based piezoelectric ceramic materials[11]. In view of this, currently extensive research is being done to develop lead free or reduced lead materials with large piezoelectric response and high T_C. Recently several bismuth based piezoelectric solid solutions such as $(1-x)Bi(Mg_{1/2}Zr_{1/2})O_3-xPbTiO_3$[12], $(1-x)BiScO_3-xPbTiO_3$[13], $(1-x)Bi(Mg_{1/2}Ti_{1/2})O_3-xPbTiO_3$[14], $(1-x)Bi(Ni_{1/2}Ti_{1/2})O_3-xPbTiO_3$[15], $Bi_{1/2}Na_{1/2}TiO_3$ and solid solutions based on it[16,17] have been investigated exhibiting good piezoelectric response and high T_C with reduced lead content. Detailed structure-property correlations in these new solid solutions are yet to be done. Since piezoelectricity cannot be observed in ceramic samples unless they are poled, the ferroelectric ceramics are subjected to poling at high electric field to convert them into piezoelectric1. It is therefore imperative to investigate electric field induced structural changes in these materials to get a better insight for development of new materials with superior electromechanical responses. The electric field induced structural

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transformations have very crucial role on the piezoelectric response and have been investigated in several Bi-based solid solutions recently[18-21].

With the objective of developing a new high temperature piezoelectric ceramics, in the present thesis, we have investigated the structure-property correlations in (1-x)$Bi(Mg_{1/2}B'_{1/2})O_3$-x$PbTiO_3$ [B'=Ti, Zr] solid solutions using Rietveld structural analysis of the XRD data. We have also investigated the electric field induced phase transitions in these materials. Being a new material, the structure property correlations have not been investigated in detail for these solid solutions. Our detailed investigations on these materials have resulted in several new important findings, which were not reported earlier.

The important new results reported in this thesis are listed below:

(I) Structure of MPB region in (1-x)$Bi(Mg_{1/2}B'_{1/2})O_3$-x$PbTiO_3$ [B'=Ti,Zr]:

We carried out the detailed structural analysis of (1-x)$Bi(Mg_{1/2}Ti_{1/2})O_3$-x$PbTiO_3$ [BMT-PT] solid solutions in the vicinity of MPB. The stability region of various crystallographic phases at room temperature for (1-x)$Bi(Mg_{1/2}Ti_{1/2})O_3$-x$PbTiO_3$ is determined precisely in the composition range x=0.28-0.45. Structural transformation from monoclinic structure (space group Pm) ($x<0.33$) to tetragonal ($x>0.40$) phase is observed via phase coexistence region demarcating the morphotropic phase boundary (MPB). The morphotropic phase boundary region consists of coexisting tetragonal and monoclinic structures with space group P4mm and Pm, respectively, stable in composition range $0.33\leq x\leq 0.40$ as confirmed by Rietveld analysis. The results of Rietveld analysis completely rule out the coexistence of rhombohedral and tetragonal phases in the morphotropic phase boundary region reported by earlier workers.

We also show that the crystal structure of the MPB composition strongly depends upon grain size. The sample 0.65$Bi(Mg_{1/2}Ti_{1/2})O_3$-0.35$PbTiO_3$ sintered at various temperatures reveal that phase fraction of the coexisting phases in the morphotropic phase boundary region varies with grain size. The structural parameters of the two coexisting phases also changes slightly with changing grain size.

The structure of the morphotropic phase and the phase coexistence region have been investigated in (1-x)Bi($Mg_{1/2}Zr_{1/2}$)O_3-xPbTiO_3 piezoceramics also using Rietveld analysis of the powder x-ray diffraction data. The structure is cubic with space group Pm3m for the compositions with $x<0.57$ and tetragonal with space group P4mm for the compositions with $x>0.59$. For the compositions with $0.56<x<0.60$, both the tetragonal and cubic phases coexist, which suggests a very narrow morphotropic phase boundary region of compositional width $\Delta x \sim 0.03$. Rietveld refinement of the structure using x-ray diffraction data confirms the coexistence of the tetragonal and cubic phases in the MPB region and rules out the coexistence of tetragonal and rhombohedral structures reported by earlier workers.

(II) Electric Field Induced Phase Transformation in (1-x)Bi($Mg_{1/2}B'_{1/2}$)O_3-xPbTiO_3 [B'=Ti, Zr] Solid Solution:

We have investigated new electric field induced structural phase transformation in (1-x)Bi($Mg_{1/2}B'_{1/2}$)O_3-xPbTiO_3 [B'=Ti, Zr] piezoceramics investigated across the morphotropic phase boundary. Rietveld structural refinement of electrically poled (1-x)Bi($Mg_{1/2}Ti_{1/2}$)O_3-xPbTiO_3 piezoceramics, across morphotropic phase boundary reveals significant modification in crystal structure for the compositions with x=0.28, 0.35, 0.38 and 0.40. The pseudocubic monoclinic phase outside the phase coexistence region undergoes isostructural phase transformation to long range monoclinic phase with significantly larger lattice parameters than that in the unpoled state. Tetragonal compositions x=0.38 and 0.40 show domain extension and domain reorientation along c-axis after poling. The compositions having coexisting tetragonal and monoclinic phases in the unpoled state exhibit modification in relative proportion of the two phases in addition to domain reorientation and extension. After poling pseudocubic compositions exhibit highest polarization due to transformation into long range monoclinic structure.

Polarization-electric field hysteresis loop measurement on the cubic composition with x=0.56 of BMZ-PT piezoceramics shows a well-saturated hysteresis loop similar to that reported in $Pb(Mg_{1/3}Nb_{2/3})O_3$ relaxor below the freezing temperature. Our dielectric studies on the composition with x=0.56, in the temperature range 300-763K, reveals a relaxor ferroelectric transition at ~530K with Vogel-Fulcher freezing temperature 482K. The structural analysis of electrically poled samples of polycrystalline, $(1-x)Bi(Mg_{1/2}Zr_{1/2})O_3-xPbTiO_3$ piezoceramics across morphotropic phase boundary reveal significant domain reorientation and electric field induced cubic to tetragonal phase transition. The c-axis domain elongation is observed for tetragonal compositions after poling. The morphotropic phase boundary composition, having coexisting tetragonal and cubic phases in the unpoled state, exhibits alteration in relative proportion of the two phases in addition to domain extension and reorientation along c-axis. For the morphotropic phase boundary composition the tetragonality (c/a) is enhanced with significantly large c-axis strain ~0.92% after poling.

(III) Low temperature phase stability of $(1-x)Bi(Mg_{1/2}B'_{1/2})O_3-xPbTiO_3$ Solid Solution:

Temperature dependence of the dielectric permittivity below the room temperature has been investigated for tetragonal, pseudocubic/monoclinic and MPB compositions of BMT-PT and BMZ-PT piezoceramics. We did not observe phase transition in the temperature dependence of dielectric permittivity in BMT-PT and BMZ-PT piezoceramics below room temperature. The low temperature x-ray diffraction pattern of BMT-PT piezocerzmics also confirms that there is no structural phase transition. Therefore the BMT-PT piezocerzmics is very stable system below room temperature.

The thesis is organized into VI chapters.

Chapter I gives an introduction to fundamental concepts related to the piezoelectric and ferroelectric materials and a brief review of the literature on MPB based solid solutions.

Chapter II describes the details of the sample preparation for synthesizing Phase pure perovskite (1-x)Bi($Mg_{1/2}B^{/}_{1/2}$)O_3-xPbTiO_3 [$B^{/}$=Ti, Zr] solid solutions.

Chapter III deals with the investigations of room temperature crystal structures of BMT-PT and BMZ-PT solid solutions using Rietveld analysis of the laboratory x-ray diffraction data and locations of the morphotropic phase boundary region. Results of grain size dependent phase stability of BMT-PT is also presented.

Chapter IV describes the electric field induced phase transformation in BMT-PT and BMZ-PT solid solution across the MPB, poled at different electric field strength. Results of polarization-electric field hysteresis measurement are also given in this chapter.

Chapter V presents the low temperature dielectric studies on several composition of BMT-PT and BMZ-PT solid solutions across MPB. The structural analysis of XRD data for BMT-PT with the composition x=0.32, and 0.35 below room temperature is also given.

Chapter VI summarizes the major findings of the present work and lists a few suggestions for future investigations.