Chapter: 6

Summary of thesis and Suggestions for Future Work

Chapter-6

6.1 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 piezoceramics solid solutions BMT-PT and BMZ-PT have been investigated. All the samples were synthesized by conventional solid state ceramic route. The room temperature x-ray powder diffraction measurements have been used to check the phase purity and crystal structures of the synthesized samples. The Rietveld crystal structure refinement technique has been used for the refinement of the crystal structure and phase transition in the prepared samples resulting from composition and temperature dependent phase transitions. The Microstructures of the samples were characterized by scanning electron microscopy. P-E measurements were carried out to investigate structure property correlations. Nature of phase transitions was investigated by temperature dependent dielectric and x-ray diffraction measurements.

Being new materials, the structure-property correlations have not been investigated in detail for these solid solutions. Our detailed investigations on these materials have resulted several new important findings, not reported earlier. The important findings of the present thesis are summarised below:

(1) Discovery of a new monoclinic phase and structure of MPB region in BMT-PT:

We carried out detailed structural analysis of several compositions of (1-x)$Bi(Mg_{1/2}Ti_{1/2})O_3$-x$PbTiO_3$ in the vicinity of MPB. The stability region of various crystallographic phases at room temperature for BMT-PT were determined precisely in the composition range x=0.28 to 0.45. Structural transformation from monoclinic structure (space group Pm) ($x<0.33$) to tetragonal ($x>0.40$) phase is observed with changing composition. 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 rules out the coexistence of rhombohedral and tetragonal phases in the morphotropic phase boundary region reported by earlier authors.

We have also shown 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 reveals 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. These results are published in **J. Appl. Phys. [Upadhyay et al. (2015)]**.

(2) Structure and location of MPB region in BMZ-PT:

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 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. These results are published in **Acta Mater. [Pandey et al. (2014)].**

(3) Electric field induced phase transition in BMT-PT:

Structural investigation on electric field 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. Tetragonal compositions show domain extension and domain reorientation along c-axis after poling in x=0.38 and 0.40. 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. 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. After poling pseudocubic compositions exhibit highest polarization due to transformation into long range monoclinic structure. Polarization (P) - electric field (E) hysteresis loop measurement on the cubic composition with x=0.28 gives a well-saturated hysteresis loop due to electric field induced phase transition. These results are published in **Scripta Mater. [Upadhyay et al. (2016)].**

(4) Electric field induced phase transition in BMZ-PT:

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 ~0.93% after poling.

(5) Low temperature phase stability in BMT-PT and BMZ-PT:

Temperature dependence of dielectric permittivity below room temperature has been investigated for tetragonal, pseudocubic/monoclinic and MPB compositions of BMT-PT and BMZ-PT piezoceramics. We did not observe any evidence of the phase transition below room temperature, in temperature dependence of dielectric permittivity. We observed significant dielectric relaxation at low temperatures which obey Arrhenius type behaviour. The low temperature x-ray diffraction patterns of BMT-PT piezocerzmics also confirm that there is no structural phase transition below room temperature.

6.2 Suggestions for Future Work

My Investigation on the BMT-PT and BMZ-PT system have revealed many interesting and new aspects linked with structure and phase transition behaviour of these new materials. There are several things need to be settled in future investigations. Few important suggestions for the future work are given below:

1. First principles density functional calculations should be carried out to understand the nature of phase transition as a function of composition and temperatures in these materials for the structure-property correlations.

2. High resolution neutron and synchrotron powder diffraction measurements should be carried out to study the structural phase transition at high and low temperatures in BMT-PT and BMZ-PT solid solutions. It will help to locate the exact position of various phase boundaries, order of phase transition and draw the temperature-composition phase diagram.

3. The dielectric constant and loss tangent of BMT-PT was found to be very high at low frequencies. P-E hysteresis also shows the lossy nature for BMT rich compositions. Suitable dopants may be explored in future to minimize these losses.

4. Atomic pair distribution function (PDF) analysis should be carried out to investigate the local structure of BMT-PT and BMZ-PT ceramics for all the composition.

5. Temperature dependent P-E hysteresis loop measurement should be carried out.

6. Grain size dependent phase stability in BMZ-PT piezoceramics should be carried out.