Chapter: 7

Summary of Thesis and Suggestions for Future Work

7.1 Summary of the Present Work

In this chapter, we have summarized the important findings of the present Ph.D. thesis. The crystal structure, microstructure, composition and temperature dependent dielectric and phase transition behaviour of (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics solid solution have been investigated in detail. All the samples used in the present work were synthesized by conventional solid state ceramic method. Rietveld structural analysis of the powder x-ray powder diffraction data have been done to investigate the crystal structure, phase stability and phase coexistence as a function of composition and temperature in various samples across MPB. The Microstructures of the samples were characterized by scanning electron microscopy. Nature of the phase transitions has been investigated by temperature dependent dielectric and x-ray diffraction measurements. Our detailed investigations on (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics have resulted several new important findings, not reported earlier for this system. The important findings of the present thesis are summarized below:

7.1.1 Discovery of Ordered Tetragonal and Cubic Phases in the Morphotropic Phase Boundary Region of (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ Ceramics

Rietveld structural and Raman spectroscopic investigation of (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics in the composition range $0.45 \leq x \leq 1.0$ reveals the coexistence of the ordered cubic (*Fm*-3*m*) and ordered tetragonal (*I*4/*m*) structures for the composition range $0.60 \leq x \leq 0.70$ corresponding to the mrophotropic phase boundary. The compositions with $x \leq 0.55$ have ordered cubic structure in *Fm*-3*m* space group and the compositions with $x \geq 0.72$ have ordered tetragonal structure in *I*4/*m* space group which gradually transform to disordered tetragonal (*P*4*mm* space group) phase at higher PT concentrations. The (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ compositions around MPB exhibit two dielectric anomalies in the temperature dependence of permittivity above room temperature. The first anomaly exhibit relaxor nature of phase transition and second anomaly is due to dielectric relaxation of defects resulting from the multiple charge states of B-site cations. On the basis of our detailed structural and temperature dependent dielectric studies we have constructed a new phase diagram of (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics.

7.1.2 Structural Characterization and High Temperature Dielectric Studies on off-Stoichiometric 0.38BMW-0.62PT Ceramics

Crystal structure, microstructure, dielectric and phase transition behaviour of the off-stoichiometric 0.38$Bi(Mg_{3/4}W_{1/4})O_3$-0.62$PbTiO_3$ ceramics prepared by adding 1, 2, 3 and 5 mol% of excess PbO, Bi_2O_3, MgO, H_2WO_4 and TiO_2 have been investigated in detail. The Rietveld structure refinement of the off-stoichiometric 0.38$Bi(Mg_{3/4}W_{1/4})O_3$-0.62$PbTiO_3$ samples chemically modified with Bi_2O_3, MgO, H_2WO_4 and TiO_2 confirms the coexistence of cubic (*Fm*-3*m*) and tetragonal (*I*4/*m*) crystal structures similar to stoichiometric sample. The crystal structure of the samples with excess PbO off-stoichiometry exhibits coexisting cubic (*Pm*-3*m*) and tetragonal (*P*4*mm*) phases due to transformation of ordered structure in to disordered structure. All the off-stoichiometric samples exhibit two dielectric anomalies in the temperature dependence of permittivity similar to that for the stoichiometric samples. The grain size is significantly increased for the samples with excess PbO while the grain size is significantly decreased in the samples with excess TiO_2 in comparison to the grain size of the sintered stoichiometric sample.

7.1.3 Electric Field Induced Phase Transformations in (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ Ceramics

The crystal structure analysis of the electric field poled samples of (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics reveals that the coexisting ordered cubic and ordered tetragonal phases, for the compositions close to the MPB, transform into disordered ferroelectric tetragonal phase with *P*4*mm* space group. The lattice parameters and unit cell volume slightly decrease after electric field poling due to the transformation from the ordered to disordered structure. The electric field induced structural transformation is associated with large c-axis lattice strain of 0.51% in the MPB composition.

7.1.4 Grain Size Dependent Phase Transformation Studies on (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x $PbTiO_3$ Ceramics

Crystal structure and phase stability as a function of the grain size have been investigated for the (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics with x = 0.60, 0.61, 0.64 and 0.67. All the studied compositions exhibit coexistence of ordered tetragonal (*I*4*/m*) and ordered cubic (*Fm*-3*m*) structures for the samples prepared at 850 °C with smaller grain size. The crystal structure of the nano-crystalline 0.36$Bi(Mg_{3/4}W_{1/4})O_3$-0.64$PbTiO_3$ sample, obtained after high energy ball milling, transforms into disordered tetragonal phase with *P*4*mm* space group. The structure of the (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics with x = 0.60 and 0.61 transform into ordered cubic phase with space group *Fm*-3*m* by increasing the sample preparation temperature to 1000 °C due to increased grain size. In contrast, the composition with x = 0.67, which also exhibits the coexistence of ordered cubic (*Fm*-3*m*) and tetragonal (*I*4*/m*) phases for the sample calcined at 850°C, transform into ordered tetragonal (*I*4*/m*) phase by increasing the sample preparation temperature to 1000 °C.

7.2 Suggestions for Future Work

My Investigation on the (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramic have revealed many interesting and new aspects linked with the crystal structure and phase transition behaviour. There are several important issues that need to be settled in future investigations. Some important suggestions for the future work are given below:

1. Low temperature XRD studies should be carried out in future to investigate the structural phase transition at cryogenic temperature in (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics.

2. Temperature dependent Neutron/Synchrotron and Raman studies should be carried out for detailed investigation of the structural phase transitions in (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics.

3. Piezoelectric characterization of the off-stoichiometric samples should be done for device applications.

4. Low temperature dielectrics studies on stoichiometric and off-stoichiometric (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics should be carried out to investigate the low temperature dielectric behaviour and effect of off-stoichiometry on the nature of phase transitions.

5. Grain size dependent structural, dielectric, piezoelectric and phase transition behaviour of (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ ceramics should be investigated in the samples prepared by wet-chemical methods