Preface

Piezoelectricity is the Property of certain crystalline materials to develop electric charges by the application of external mechanical stress and strain on application of electric field [Jaffe et al. (1971)]. Nowadays, a large number of piezoelectric materials are used as sensors and actuator devices, which are used in aircraft, aerospace, automotive, medical imaging, ultrasonic and telecommunication devices [Jaffe et al. (1971), Turner et al. (1994), Shrout et al (2004)]. 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 (P) which can be switched into crystallographically equivalent directions by an external applied electric field (E). Therefore, it possesses 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 at the phase transition temperature [Schmid (1994)].

Among the stable ferroelectric ceramics investigated, $PbTiO_3$ possesses the largest saturation polarization ($\sim 81 \mu C/cm^2$) and very large tetragonality (c/a = 1.0635) [Jona and Shirane (1962)]. The Lead based morphotropic phase boundary [MPB] piezoceramics such as $PbZr_{1-x}TixO_3$ [PZT] [Schönau et al. (2007), Ranjan et al. (2005)], $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ [Li et al. (2008)], $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ [Singh and Pandey (2003)] etc. have been widely used in piezoelectric applications from several decades due to their high piezoelectric responses. Morphotropic phase boundary in ferroelectric perovskite solid solutions is defined as a nearly vertical phase boundary in the temperature-composition phase diagram separating stability regions of two crystallographic phases. Coexistence of the neighboring phases and maximization of piezoelectric responses are obtained for the MPB compositions [Goldschmidt (1929)]. PZT have been found most successful piezoceramics so far, due to its high electromechanical coupling coefficient $k_P \sim 0.55$, $d_{33}\sim600\mu C/N$ and high $T_C\sim400^oC$. Lead is highly toxic and leads to cancer and other health issues; therefore it is being banned worldwide in most of the applications. Lead is released into the environment during calcinations and sintering process of Pb-based piezoelectric ceramic materials [Rödel et al. (2009)]. 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 $(1-x)Bi(Mg_{3/4}W_{1/4})O_3-xPbTiO_3$ [Verma and Singh (2019)], $(1-x)Bi(Mg_{1/2}Zr_{1/2})O_3-xPbTiO_3$ [Pandey et al. (2014)], $(1-x)BiScO_3-xPbTiO_3$ [Eitel et al. (2001)], $(1-x)Bi(Mg_{1/2}Ti_{1/2})O_3-xPbTiO_3$ [Upadhyay and Singh (2015)], $(1-x)Bi(Ni_{1/2}Ti_{1/2})O_3-xPbTiO_3$ [Pandey and Singh (2014)], $Bi_{1/2}Na_{1/2}TiO_3$ and solid solutions based on them 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 piezoelectric. It is therefore imperative to investigate electric field induced structural changes also, in these materials, to get a better insight for development of new materials with superior electromechanical responses. The electric field induced structural transformations have very crucial role on the piezoelectric response and have been investigated in several Bi-based solid solutions recently. For the present Ph.D. thesis, a detailed structure, dielectric properties and phase transition studies has been done on $(1-x)Bi(Mg_{3/4}W_{1/4})O_3-xPbTiO_3$ samples of various compositions. The effect of changing grain size and electric field poling on the structure and properties has also been investigated in detail.

The main findings of the presented thesis work are listed below:

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-xPbTiO_3 piezoceramics

We have investigated in detail the structure of (1-x)Bi($Mg_{3/4}W_{1/4}$)O_3-xPbTiO_3 ceramic in the composition range $0.45 \leq x \leq 1.0$, using Rietveld refinement of powder x-ray diffraction data. Composition dependent phase transformation from cubic $x \leq 0.55$ (space group *Fm*-3*m*) to tetragonal $x \geq 0.75$ (space group *I*4*/m*) is observed via two phase region separated by the morphotropic phase boundary for intermediate compositions. The results of Rietveld analysis reveals that the cubic (space group *Fm*-3*m*) and tetragonal (space group *I*4*/m*) phases coexist in the morphotropic phase boundary region ($0.55 < x < 0.72$). The compositions dependent room temperature dielectric permittivity and temperature dependence of permittivity is investigated for various compositions across MPB. The temperature dependent variation of dielectric permittivity shows two anomalies above room temperature for the compositions inside MBP region. The first anomaly is found to be caused by ferroelectric to paraelectric phase transition or relaxor transitions while the second one is observed to be due to ordering of the defect structure. With the help of the results of structural and temperature dependent dielectric studies we have established a new phase diagram of (1-x)BMW-xPT ceramics.

2. Structural characterization and high temperature dielectric studies on off-stoichiometric 0.38BMW-0.62PT ceramics

To understand the effect of off-stoichiometry, we have chemically modified $0.38Bi(Mg_{3/4}W_{1/4})O_3$-$0.62PbTiO_3$ with 1, 2, 3 and 5 mol% excess of PbO, Bi_2O_3, MgO, H_2WO_4 and TiO_2. The Rietveld structural analysis of Powder XRD data of chemically modified 0.38BMW-0.62PT ceramic reveals the coexistence of cubic (space group *Fm*-3*m*) and tetragonal phases (space group *I*4*/m*) for all the off-stoichiometric samples. Variation of lattice parameters and unit cell volume is investigated systematically. The surface morphology studied by Scanning Electron Micrograph (SEM) analysis reveals that the grain size increases in the samples with Lead oxide (PbO) off-stoichiometry while it decreases with off-stoichiometry of the titanium dioxide (TiO_2) in comparison the that for the stoichiometric 0.38BMW-0.62PT ceramic. The microstructure is not affected by off-stoichiometry of Bi_2O_3, MgO and H_2WO_4 in 0.38BMW-0.62PT. The temperature dependent dielectric measurements carried out in the various frequency range (100Hz to 2MHz) reveals that the dielectric constant and dielectric anomaly temperatures are slightly modified in the off-stoichiometric samples 0.38BMW-0.62PT. However, the nature of phase transition is almost similar to that in the stoichiometric sample.

3. Field induced phase transition in MPB region of $(1-x)Bi(Mg_{3/4}W_{1/4})O_3$-$xPbTiO_3$ ceramics

We have investigated dc electric field poling induced structural phase transition in $(1-x)Bi(Mg_{3/4}W_{1/4})O_3$-$xPbTiO_3$ ceramic across the morphotropic phase boundary region with the compositions x = 0.61, 0.62, 0.63 and 0.67. The structural analysis of unpoled and poled samples of (1-x)BMW-xPT is done. The reorientation of domain along c-axis is observed for the tetragonal phase after electric field poling. The Rietveld analysis of XRD data of poled samples confirm that the coexisting cubic (*Fm*-3*m*) and tetragonal (*I*4/*m*) structures of the unpoled samples transform to disordered tetragonal phase with space group *P*4*mm* after electric field poling.

4. Grain size-dependent phase transformation studies on (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ piezoceramics

The samples of varying grain sizes of (1-x)$Bi(Mg_{3/4}W_{1/4})O_3$-x$PbTiO_3$ (BMW-xPT) ceramic were prepared by high energy ball milling method and heat treatment at various temperatures for the compositions with x = 0.60, 0.61, 0.64 and 0.67. Rietveld structural analysis all the four compositions confirms the coexistence of ordered tetragonal (I4/m) and ordered cubic (Fm-3m) 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.

The thesis is organized into **7** chapters.

Chapter 1: gives an introduction to fundamental concepts related to the piezoelectric materials and a brief review of the literature on MPB based solid solutions.

Chapter 2: describes the details of the sample preparation and characterizations for synthesizing Phase pure ordered perovskite of (1-x)BMW-xPT solid solutions.

Chapter 3: deals with the investigations of room temperature crystal structures of (1-x)BMW-xPT solid solutions using Rietveld analysis of x-ray diffraction data and locations of the morphotropic phase boundary region. Temperature depended dielectric and x-ray diffraction studies have been done to investigate the phase transition behaviour. Results of Raman spectroscopy and XPS studies is also presented..

Chapter 4: present the results of structural characterization and high temperature dielectric studies on off-stoichiometric 0.38BMW-0.62PT ceramics.

Chapter 5: describes the results of electric field induced phase transformation studies on (1-x)BMW-xPT solid solution across the MPB, poled at various electric field strength.

Chapter 6: presents the results of grain size dependent phase transformation studies on (1-x)BMW-xPT ceramic.

Chapter 7: summarizes the main findings of the present work and lists a few suggestions for future investigations.