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Structural and electrical properties of cation and anion doped $BiScO_3$-$PbTiO_3$ ceramics

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ABSTRACT

Different amounts of MgF_2 were substituted in (1-x)$BiScO_3$-x$PbTiO_3$ (BS-PT) at x = 0.64. Magnesium as an acceptor was supposed to be incorporated at B-site and fluorine at anionic sites. Morphotrophic phase boundary (MPB) was found at 0.5% MgF_2 doping where tetragonal and monoclinic phases coexisted in almost equal proportion. Tolerance factor as well as cationic displacements played important role in enhancing T_c. MgF_2 doping enhanced Curie temperature (T_c) and electromechanical coupling factor (k_p) up to 490 °C and 0.66, respectively. Grain size and porosity increased with doping amount due to fluorine. The dielectric loss was suppressed with MgF_2 addition at room temperature.

1. Introduction

Lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) is a traditional piezoelectric material, which is widely used in electroceramic industry due to its superior electromechanical properties [1]. $Pb(Zr_{1-x}Ti_x)O_3$ is a solid solution of $PbZrO_3$ and $PbTiO_3$. $PbZrO_3$ has rhombohedral crystal structure whereas $PbTiO_3$ has tetragonal symmetry. These two phases form a boundary known as morphotrophic phase boundary (MPB) and generally rhombohedral and tetragonal phases coexist at MPB. But presence of monoclinic phase is also reported in PZT at MPB composition with synchrotron X-ray diffraction studies [2]. Monoclinic phase facilitates polarization rotation between tetragonal and rhomboheral phases [3–5]. Simultaneous presence of these phases provides multiple directions for piezoelectric activity, which significantly improves piezoelectric properties [3]. Therefore, enhanced ferroelectric properties are observed in MPB region. Different intrinsic (lower symmetry monoclinic phase and/or nanodomains) and extrinsic (domain wall mobility and/or phase boundaries) factors have been proposed to interpret the high dielectric and piezoelectric activity in these compositions [6–8].

At high temperature all the ferroelectric phases are ultimately transformed into cubic structure, which is paraelectric in nature and all the piezoelectric properties are lost. The Curie temperature (T_c) where ferroelectric to paraelectric phase transition occurs, is utmost important in device applications. In most applications piezoelectric materials are used well below half the T_c due to degradation of piezoelectric properties by the loss of polarization as a consequence of high operating temperature [9]. PZT has T_c around 386 °C and cannot be used above 200 °C whereas some applications in aerospace, geothermal, and automobile industry require piezoelectric devices to operate at 300 °C or even higher temperature [10]. Therefore, over the past two decades considerable efforts have been devoted to develop new materials, which not only possess better piezoelectric properties but also a high T_c [11,12]. Eitel et al. [13] have proposed that T_c can be increased by selecting a low tolerance factor end member with $PbTiO_3$ solid solution. However, it is generally observed that high T_c is achieved at the expense of piezoelectric properties. $BiFeO_3$-$PbTiO_3$ has T_c as high as 650 °C [14] but its piezoelectric properties are not worthy for device applications. $BiScO_3$-$PbTiO_3$ (BS-PT) system has emerged as a strong candidate not only for conventional applications but also for high temperature applications as it has demonstrated high T_c as well as good electrochemical performance [8,15,16]. Different reasons such as low tolerance factor of $BiScO_3$ [13], non-linear coupling of cations [17]; covalence of Bi-O bond [18] and hybridization of Pb/Bi 6p and O 2p orbitals [19] are reported in literature to explain the enhanced piezoelectric properties of BS-PT system. It is well established that BS-PT has MPB around $x = 0.64$ [3,13,16]. At this composition tetragonal and monoclinic phases are present in almost similar

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ratio and this delicate equilibrium can be exploited with external force such as electric field to further improve elecromechanical properties [3].

Higher Curie temperature and enhanced electrical properties can be achieved to some extent with doping of different elements at suitable sites in the piezoelectric materials. Therefore, different doping strategies of donor and acceptor elements such as Li, La, and Nd at A-site and Mn, Lu, Y, Yb, Er, Ga, Nb, Fe, Sb and Zr at B-site have been utilized to further enhance piezoelectric properties of BS-PT [9–12,19–26]. However, little attention has been paid towards anionic substitution. Previous attempts of anionic substitution of O with F have successfully improved electromechanical properties and reduced losses in PZT [1,27–29]. In present work, we have prepared $0.36BiScO_3$-$0.64PbTiO_3$ with different doping amounts of MgF_2 and studied their effects on structure, microstructure and electric properties.

2. Experimental procedure

Conventional mixed oxide ceramic processing route was used to synthesize MgF_2 substituted $0.36BiScO_3$-$0.64PbTiO_3$. Starting materials were high purity oxides (>99%). Stoichiometric amounts of starting powders were mixed in a ball-mill for 5 h using high purity zirconia balls and alcohol in a polyethylene jar. Slurry was dried at 120–130 °C and calcined in open crucibles at 750 °C for 2 h to achieve optimum perovskite phase. At this stage different amounts of MgF_2 were introduced into the BS-PT perovskite powder. MgF_2 doped samples were prepared for preferential substitution of Mg^{2+} for Ti^{4+}/Sc^{3+} site and F^- for O^{2-} site and their general stoichiometric formulation can be expressed as $Bi_{0.36}Pb_{0.64}[(Sc_{0.36}Ti_{0.64})_{1-x}Mg_x]O_{3-x}F_{2x}$. Similar mixing and heating cycles were repeated for all compositions and final powder was pressed into 1–2 mm thick pellets of 12 mm diameter. 5 wt% of polyvinyl alcohol (PVA) was added before making pellets to improve the green strength of compacts. Pellets were compacted at the load of 160 MPa with uniaxial pressing. Following a binder burnout at 500 °C, pellets were sintered at 1100 °C for 2 h in a sealed crucible with BS-PT powder of similar composition to minimize PbO volatilization. X-ray diffraction (XRD) data was measured with Rigaku (D/max 2400) diffractometer using Cu Kα radiation. Theoretical densities were measured with lattice parameters obtained by XRD data. The relative densities were then calculated based on the densities measured by Archimedes method. Rietveld refinement of XRD data was performed with FullProf software package [30]. The background was refined with 5th order polynomial and pseudo-Vigot peak shape function was adopted in the whole pattern fitting.

Before making electrical measurements, pellets were electroded with silver paste and fired at 825 °C for 15 min. These pellets were poled in a silicon oil bath at 150 °C with applied field of 3000 V/mm for 20 min. Microstructures of freshly fractured surface were examined by scanning electron microscope (SEM) JEOL (JSM-6360LV). Dielectric properties were obtained by measuring the capacitance and loss factor using an LCR meter (HP model 4284). High temperature dielectric measurements were made using a computer controlled furnace temperature up to 600 °C. The piezoelectric coefficient d_{33} was recorded from one-day aged samples using a Berlincourt d_{33} m (IAAS ZJ-2, Beijing, China) and k_p was measured using an impedance analyzer (Model HP4194).

3. Results and discussion

XRD patterns of $0.36BiScO_3$-$0.64PbTiO_3$ with different MgF_2 concentrations sintered at 1100 °C for 2 h are shown in Fig. 1. All the peaks belong to perovskite structure and no evidence of impurity phase was found in within detection limit of the diffractometer.

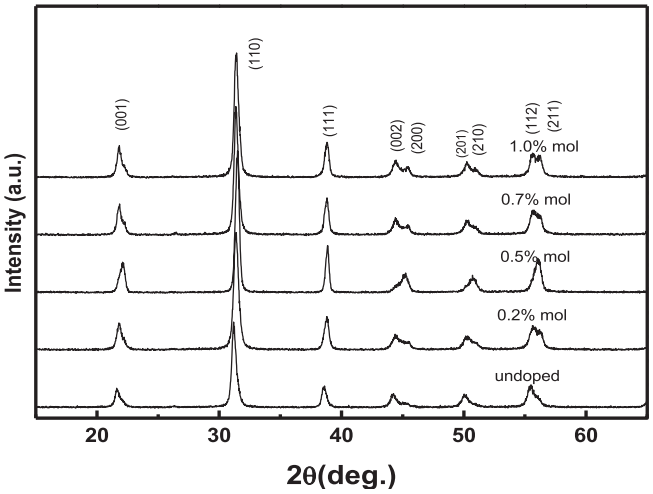

Fig. 1. Room temperature X-ray diffraction patterns of Magnesium Fluoride doped BS-PT.

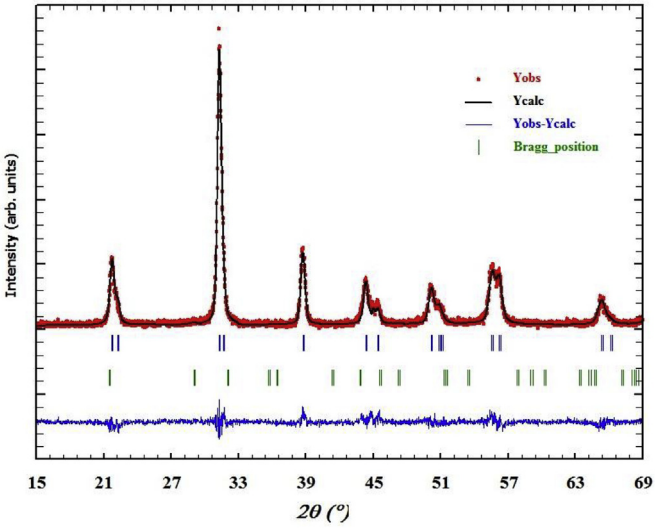

Fig. 2. Rietveld refined powder X-ray diffraction pattern of 1% MgF_2 doped BS-PT.

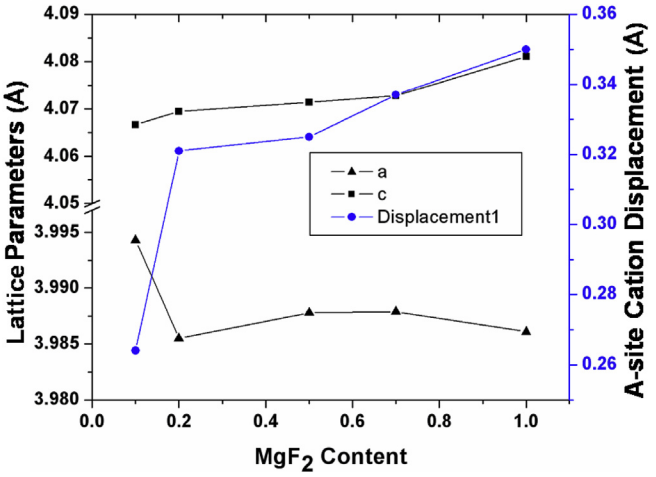

Fig. 3. Rietveld refined lattice parameters and A-site cation displacement of tetragonal phase with different amounts of MgF_2 BS-PT.