Nonlinear ferroelectric and dielectric properties of Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$-PbTiO$_3$ perovskite solid solutions

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ABSTRACT

Polycrystalline samples of Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$-PbTiO$_3$ (BMT-PT) solid solutions exhibit high ferroelectric Curie temperatures and are promising materials for high temperature piezoelectric devices. A morphotropic phase boundary (MPB) between ferroelectric rhombohedral and tetragonal phases occurs between BMT-PT ratio of 70-30 and 65-35 compositions. In the present investigation, ceramics having BMT-PT ratios in the range from 70-30 to 50-50 were prepared by a conventional solid state reaction method. The change of crystal structure as a function of composition and temperature has been studied using high temperature X-ray diffraction. Polarisation-Electric field hysteresis curves at different temperatures show antiferroelectric behaviour for x = 0.30, 0.35 and 0.40 compositions while 0.45 and 0.50 show a ferroelectric behavior. Copyright © 2012 VBRI Press.

Keywords: Bi-based perovskites; morphotropic phase boundary; nonlinear ferroelectric

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Introduction

Investigations of ferroelectric perovskite-type compounds with different distributions of the 6- or 12-fold coordination cations have been studied in detail as these materials are involved in the fabrication of many devices, e.g. capacitors, piezoelectric ultrasonic tranducers, electrostrictive actuators, SAW substrates, etc [**1-3**]. These materials have high electromechanical characteristics which can be controlled either by doping or compositional change. The latter is connected in some cases with the onset of cationic disorder, the magnitude of which strongly influences the properties, mainly due to the dependence of the nature of the phase transition on the cationic distribution. However, most of these materials are made from lead bearing compounds, e.g. lead zirconate titanate (PZT), lead magnesium niobate (PMN), etc. So for environmental, health and social reasons, manufacturers are more and more constrained to reduce and ultimately eliminate the lead content of their materials.

The origin of the enhanced piezoelectric response in perovskite PZT is the result of lone pair electrons in the Pb^{2+} hybrid orbitals [**4**] and the existence of a morphotropic phase boundary (MPB) between two ferroelectric phases [**5**]. Bi^{3+} is an excellent candidate for the substitution of Pb in the PZT system since it has a similar electronic structure

and is less toxic as compared to its Pb counterpart. There are numerous Bi-based perovskite ceramics that can be used in solid solutions [**6-11**]. Recently for high temperature applications, new piezoelectric ceramics of the general formula $(1-x)BiMeO_3–xPbTiO_3$ (Me^{3+} = Sc, In, Y, Yb, Fe, Ga, etc.) with paraelectric–ferroelectric phase transition temperature higher than lead zirconate titanate (PZT) and its contemporary compositions have been reported [**9**], [**12**], [**13**] and [**14**]. Alternative lower cost systems, for example $BiFeO_3–PbTiO_3$ and $BiGaO_3–PbTiO_3$ have been investigated by other researchers in order to identify particular compositions that merit further development for use in high temperature piezoelectric devices [**15-18**]. Some of these reports have been concerned with the use of bismuth based complex perovskites, including $Bi(Mg_{0.5}Ti_{0.5})O_3$ (BMT) and $Bi(Mg_{0.5}Zr_{0.5})O_3$ (BMZ) [**19-25**]. BMT-PT system in particular has shown significant promise with respect to a relatively high Curie temperature ($T_c \sim 450$ °C) and high remanent polarisation ($P_r \sim 0.38$ C m^{-2}) [**22**]. These materials show high temperature ferroelectric–paraelectric phase transitions but the piezoelectric and dielectric properties were limited or unknown due to their high electrical conductivity. Through systematic research, a number of MPB systems based on $Bi(M)O_3$-$PbTiO_3$ ($M = Ti^{4+}$, Sc^{3+}, Zn^{2+}, Nb^{5+}) have been discovered [**10,11**]. Bi-based perovskite, $Bi(Mg_{1/2}Ti_{1/2})O_3$ designated as BMT, exhibits a high Tc with an enhanced tetragonality through solid solution with $PbTiO_3$ (PT) [**26**]. Solid solutions made from BMT and tetragonal titanates such as $PbTiO_3$ near their respective MPB would be excellent candidates as low-lead or lead-free piezoelectric materials [**14**]. In this paper we will present experimental results and interpretation of nonlinear ferroelectric and dielectric properties of $Bi(Mg_{1/2}Ti_{1/2})O_3$-$PbTiO_3$ perovskite solid solutions.

Experimental

Suitable stoichiometric amounts of high purity oxides of Bi_2O_3, MgO, PbO and TiO_2 were used as starting materials according to the formula $(1-x)Bi(Mg_{1/2}Ti_{1/2})O_3$-$xPbTiO_3$ for x = 0.30, 0.35, 0.40, 0.45 and 0.50 or 70-30, 65-35, 60-40, 55-45 and 50-50 compositions. Weighted source powders were mixed by ball milling for ~24 hrs using ZrO_2 balls and isopropanol as a media. The mixed powders were dried and calcined for 2 hrs at ~700 ºC. The grinding process was repeated for ~8 hrs in presence of PVA+PEG as binding liquid. After grinding the powders were uniaxially pressed into pellets of approximately 10 mm diameter and sintered at a temperature of 1000/1100 ºC for 2 hrs. The densities of the sintered pellets, measured by the Archimedes method, were > 95% of the theoretical value. X-ray diffraction analysis was performed on a PW3710 Philips diffractometer with a high termperature attachment using CuKα (λ=0.15405 nm) radiation (Room temperature to 700 ºC) in order to identify the crystalline phases present in the system. Sintered pellets were polished to a 1 μm finish and thermally etched for 30 min at a temperature of 900 °C. The microstructure and energy dispersive spectroscopy of the fractured surfaces was examined by scanning electron microscopy using a Philips XL30FEG. For electrical measurements, the polished samples were coated with silver

paste (DuPont type 7474) fired at 800 ºC for 15 minutes and aged overnight at 100 ºC. Dielectric measurements as a function of frequency (100 Hz-1 MHz) and temperature (20 to 600 ºC) were carried out by using a HP 4192A Impedance analyzer. Ferroelectric polarisation-electric field measurements were performed as a function of temperature under silicone oil using a computer-controlled function generator (HP 33120A) and a high voltage amplifier (Chevin Research HVA1B). A current amplifier was used to measure the induced current, which was then integrated numerically to yield the charge Q and then the polarization P as surface charge density. The applied field and induced current waveforms were downloaded to a PC using a 16-bit A/D card. The measurements were carried out using a 'burst mode' waveform comprising four complete sinusoidal cycles.
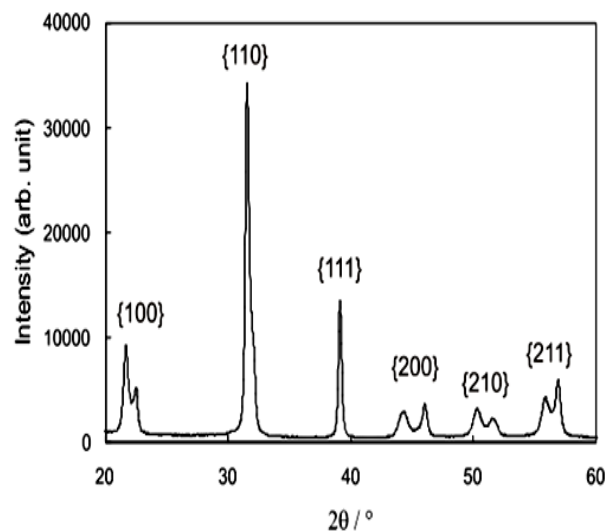

Fig. 1. XRD patterns obtained for BMT-PT ceramics for 50-50 composition.

Results and discussion

Room temperature X-ray diffraction (XRD) pattern of a typical composition x=0.50 shown in **Fig. 1**, exhibits a tetragonal symmetry. **Fig. 2 a, b, c, d and e** show XRD patterns of the BMT-xPT (70-30, 65-35, 60-40, 55-45 and 50-50) ceramics recorded at different temperatures for 2θ= 40º to 60º. Although the XRD profiles for the various x values were carried over a wide range of 2θ =10º to 90º but 2θ= 40º to 60º was selected to plot the XRD pattern to check the splitting of (200), (210) and (211) tetragonal phase *(T)*. The ceramics for all compositions were found to be single phase with minor impurity phase and were indexed according to a pseudo-cubic perovskite structure. A slight asymmetry in the (200) reflection suggests development of the tetragonal phase *(T)* for x=0.35 with increase in temperature. More detailed inspection of the (200), (200) and (211) peaks in F**ig. 2** illustrates the changes in crystal symmetry as a function of temperature in all compositions except x = 0.30. The splitting of the {200} reflection into separate (200) and (002) peaks for x = 0.35 to 0.50 compositions indicate that the ceramics were tetragonal, with an increase in c/a ratio. On the basis of previous results [**27**], it was anticipated that the MPB

should occur at approximately x = 0.38 BMT-PT and therefore that the x = 0.30 composition should be rhombohedral. However, the exact MPB composition is difficult to determine. The broadening of the diffraction peak is most likely due to the presence of some residual tetragonal phase. Also, the (111) reflection did not show the splitting associated with the rhombohedral distortion; this can be attributed to a combination of the very small distortion of the rhombohedral structure and the limited resolution of the diffractometer system used in the present study.
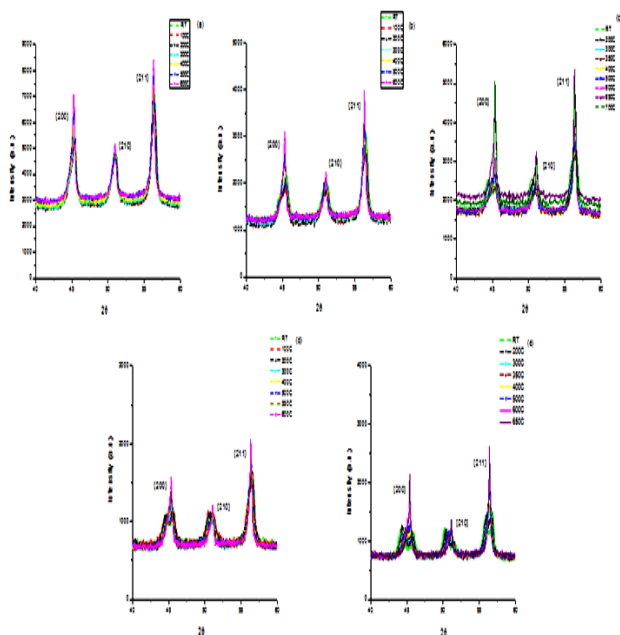
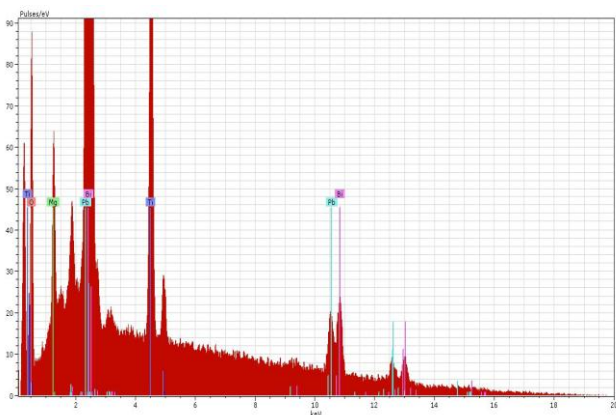**Fig. 2.** (a-e). XRD patterns of BMT-xPT (x=0.30, 0.35,0.40, 0.45 and 0.50) at different temperatures.

Fig. 3. Show the EDS picture for BMT-PT 50-50 ceramic.

Fig. 3 shows the Energy dispersive spectrograph (EDS) for a typical composition with x = 0.50 composition**.** EDS analysis of individual grains in different compositions indicates a homogeneous distribution of all the basic elements in the ceramics. All peaks obtained in the EDS spectra are labelled with different color. The microstructure of the 50-50 BMT-PT ceramic is illustrated by the scanning electron micrograph (SEM) in **Fig. 4.** All the ceramics

examined during the present study exhibited similar dense and fine-grained microstructures; with average grain sizes in the range from 1.5 to 2 μm.

Fig. 5 shows the dielectric-temperature ($\varepsilon_r^/$–T) and ($\varepsilon_r^{//}$–T) variation of the BMT-0.40PT system at different frequencies. The dielectric behaviour in the low temperature region was characterized by a significant frequency-dependence, with both the permittivity and loss reducing with increasing frequency. $\varepsilon_r^/$ increased, while tanδ reduced with increasing temperature up to 250 °C. Beyond this point, the permittivity became relatively frequency-independent, while the loss tangent increased sharply at low frequencies due to increasing electrical conductivity.
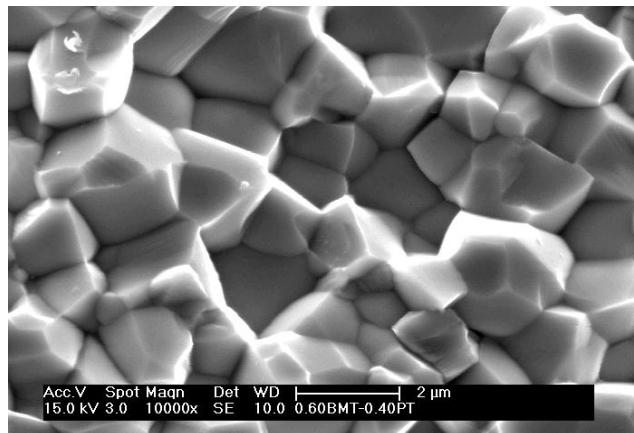

Fig. 4. Show the SEM micrograph illustrating typical microstructure for BMT-PT 60-40 ceramic.

The temperature dependence of the dielectric permittivity and loss for the BMT-PT ceramic for all compositions are shown in **Fig. 6a** and **b**. The position of the lower temperature 'shoulder' in the $\varepsilon_r^/$–T relationship, associated with the relaxor-like transition, was lowest for the x = 0.40 composition at approximately 150 °C, increasing to around 300 °C for the x=0.50 BMT-PT ceramic. The higher temperature peak in $\varepsilon_r^/$ at a temperature around 500 °C did not show any significant variation with composition. The broadening or diffuseness of peak occurs mainly due to compositional fluctuation and/or substitution disordering in the arrangement of cations in one or more crystallographic sites of the BMT–PT structure. The value of peak dielectric permitivity increases initially with the increase of concentration and again it decreases with increases of concentration.

The anomalies were observed both on heating and cooling. There have been several contradictions as reported by different workers, in the dielectric permittivity-temperature relationships in BMT-PT ceramics. Both Randall [27] and Moure [28] reported the existence of two peaks for certain BMT-PT compositions. Moure suggested that the lower temperature peak might be associated with a ferroelectric to antiferroelectric phase transformation, similar to that observed in $(Bi_{0.5}Na_{0.5})TiO_3$-$BaTiO_3$ (BNT-BT) ceramics [29]. Suchomel [30] observed only one broad dielectric peak, which narrowed and increased in Curie temperature as the PT content increased. The loss of dielectric dispersion at a temperature around 200 ^{0}C is

similar to that observed in relaxor ferroelectrics and points to the occurrence of a diffuse phase transformation around this point. The origin of the relaxor behaviour is most likely associated with the disorder of the Mg and Ti cations in the complex perovskite BMT. A broad peak in dielectric permittivity was also observed around 500 ^{0}C, which indicates the presence of a second higher temperature phase transformation. The further increase of permittivity at temperatures above 550 ^{0}C is attributed to space-charge polarisation, associated with the very high dielectric loss caused by increasing electrical conductivity. The differences in behaviour reported by different authors could be a result of the variations in processing methods employed.

Ferroelectric polarization and Electric field hysteresis (P-E) curves of BMT-PT compositions are shown in **Fig. 7(a-e)**. It is obvious from the **Figs** for x = 0.30, 0.35 and 0.40, that the hysteresis loops get constricted at the center with increase in temperature, which is most prominent for x = 0.40 composition. These loops were unsaturated at room temperature (RT), but showed an increasingly 'pinched' appearance with increasing temperature, indicating the development of antiferroelectric behaviour. P–E loops are more predominant at low temperatures. The onset of typical ferroelectric bevaviour with respect to temperature could be seen for x = 0.45 composition. BMT-PT (x = 0.50) ceramic exhibited typical ferroelectric behaviour at temperatures from RT to 150 °C, as illustrated by the polarisation-electric field (P-E) loops presented in **Fig. 7e**.

Fig. 5. Changes of (a) real part of dielectric permittivity and (b) loss tangent as a function of temperature for BMT-PT 60-40 ceramic.
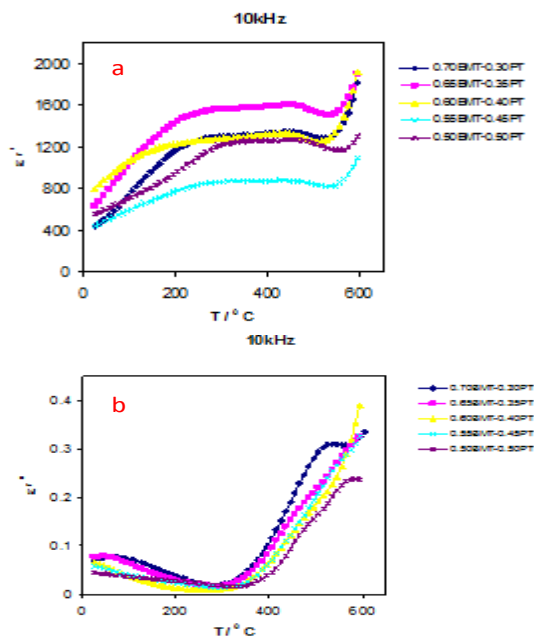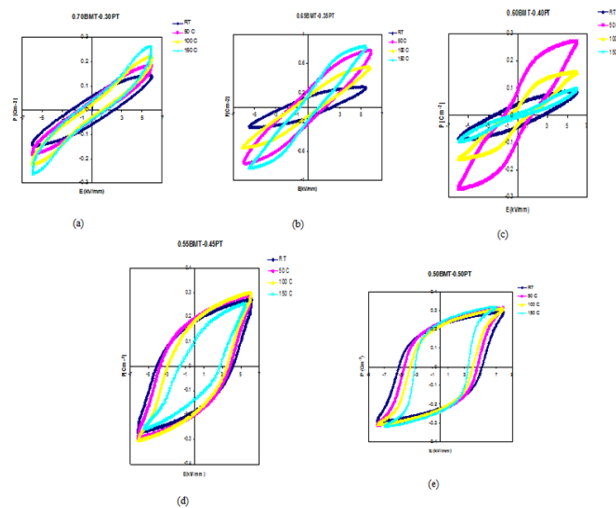

Fig. 6. Changes of (a) real part of dielectric permittivity and (b) loss tangent as a function of temperature for BMT-PT ceramics with various compositions, at a frequency of 10 kHz.

Fig. 7. Polarisation-Electric Field (P-E) hysteresis loops obtained for (a) x=0.30, (b) 0.35, (c) 0.40, (d) 0.45 and (e) 0.50 BMT-PT ceramics at various temperatures.

With increase in temperature, the tips of the ferroelectric loops (x = 0.50) sharpened and the loops became more and more square. The ferroelectric coercive field was approximately 5.5 MV m^{-1} at RT, reducing to around 3.6 MV m^{-1} at 150 °C. The remanent polarisation was in the region of 0.26 C m^{-2}. In this case, the ferroelectric behaviour starts to become less clear because the electrical response is dominated by the conduction effects. The change in the ferroelectric behaviour for these compositions with temperature can be corelated with the dielectric curves reported above (**Fig. 5**), which appeared to show the presence of two phase transformations. The first of these, in the range 150 to 300 °C exhibits frequency-dependent behaviour, which can be attributed to a transformation from a relaxor ferroelectric to an antiferroelectric phase. The occurrence of antiferroelectric characteristics at temperatures below that of the dielectric peak (or shoulder in this case) is consistent with the behaviour of relaxor ferroelectrics, which usually develop strong ferroelectric characteristics only at temperatures well below that of the dielectric maximum [31]. The identification of an intermediate antiferroelectric phase in the BMT-PT system is consistent with the behaviour of other complex perovskites such as BNT-BT [29]. Furthermore, it was shown [32] that Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$

ceramics, prepared in a metastable state by high pressure/high temperature processing, have an antiferroelectric-like crystal structure, similar to that of PbZrO$_3$. Therefore, the observed antiferroelectric behaviour of BMT-PT ceramics can be anticipated by considering the crystal structure of BMT. With increase in temperature, the tips of the ferroelectric loops (x = 0.50) sharpened and the loops became more and more square.

Conclusion

Ceramics of Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-PbTiO$_3$ has been successfully processed by conventional sintering from powders synthesised by direct solid-state reaction of the constituent oxides. Single phase Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-PbTiO$_3$ is formed in the bulk, with density >95% and grain sizes in the range from 1.5 to 2 μm. The crystal structure transformed from rhombohedral to tetragonal with temperature for all compositions except for BMT-PT (70-30). Dielectric permittivity presented two maxima with temperature one associated with the relaxor-like transition, which was lowest for the x = 0.40 composition at approximately 150 °C, increasing to around 300 °C for the x = 0.50 BMT-PT ceramic. The higher temperature peak in $\varepsilon_r^/$ at a temperature around 500 °C did not show any significant variation with composition. Ferroelectric hysteresis curves show an antiferroelectric behaviour for 70-30, 65-35 and 60-40 BMT-PT ceramic samples with increase in temperature while the typical ferroelectric behaviour for 50-50 BMT-PT composition was clearly exhibited.

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