Piezoelectric properties of high Curie temperature barium titanate–bismuth perovskite-type oxide system ceramics

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Barium titanate (BaTiO$_3$, BT)—bismuth magnesium titanium oxide [Bi(Mg$_{0.5}$Ti$_{0.5}$)O$_3$, BMT] system ceramics were prepared in an ambient atmosphere in order to increase the Curie temperature (T$_c$) of BT above 132 °C. A single perovskite phase was observed for BT–BMT ceramics with BMT compositions less than 50 mol %, and their relative densities were greater than 94%. Synchrotron measured x-ray diffraction patterns revealed that all the cations in the ceramics were homogeneously distributed. The temperature dependence of the dielectric properties revealed that the BT–BMT system ceramics exhibited relaxorlike characteristics with a dielectric maximum temperature as high as 360 °C for the 0.5BT–0.5BMT ceramic. The apparent piezoelectric constant (d^*) was 60 pC/N for the 0.4BT–0.6BMT ceramic. Based upon these results, the BT–BMT system shows potential as a new type of lead-free material for high T$_c$ piezoelectric applications. © *2010 American Institute of Physics*. [doi:10.1063/1.3481390]

I. INTRODUCTION

Lead-free piezoelectrics have become highly desirable materials from the viewpoint of providing a materials solution to environmental problems associated with using conventional lead containing piezoelectrics such as Pb(Zr,Ti)O$_3$ (PZT) ceramics.[1] However, their piezoelectric properties are very poor compared with those of PZT ceramics.[2] Therefore, many researchers have attempted to improve the piezoelectric properties of lead-free ferroelectrics by materials development and gradually improvements have been achieved.[1–4] Recently, chemically modified potassium niobate (KNbO$_3$, KN)—sodium niobate (NaNbO$_3$) solid solution ceramics have been reported as new lead-free piezoelectrics with a new morphotropic phase boundary (MPB), and their reported piezoelectric properties are similar to those of PZT ceramics.[5,6]

For actuator device applications at off-resonance, there are two important parameters, i.e., piezoelectric constant (d) and Curie temperature (T$_c$). For example, barium titanate (BaTiO$_3$, BT) ceramics is a typical lead-free ferroelectric material, and its piezoelectric constant, d_{33}, of 191 pC/N was reported.[2] One method to improve the piezoelectric properties of this material is by domain engineering. Recently, higher d_{33} values of 350 pC/N (Ref. 7) and 460 pC/N (Ref. 8) were reported for fine-grained BT ceramics with high 90° domain wall densities. Moreover, for the [110] grain-oriented BT ceramics, even higher d_{33} values up to 788 pC/N was reported by Wada *et al.*[9] However, its measured T$_c$ was only 132 °C, and this low T$_c$ value made its piezoelectric appli-

cations limited to transducers for use in water. Therefore, it is important to increase the T$_c$ of BT ceramics to over 300 °C, which is higher than the melting point of lead-free solder.

In the literature, there are reports of perovskite materials with higher T$_c$ values such as KN with a T$_c$ of 435 °C and bismuth ferrite (BiFeO$_3$) with a T$_c$ of 830 °C.[10] In addition, some researchers have already investigated solid solution system ceramics between BT and the above perovskite materials.[11,12] Currently, new bismuth perovskite materials with higher T$_c$ have become widely investigated, such as bismuth chromium oxide (BiCrO$_3$) with T$_c$ of 470 °C,[13] bismuth manganese oxide (BiMnO$_3$) with T$_c$ of 500 °C,[14] and bismuth cobalt oxide (BiCoO$_3$) with T$_c$ over 1 000 °C.[15] The preparation of these bismuth perovskite materials require a high pressure over 6 GPa and a high sintering temperature over 1 000 °C and their high leakage current makes poling treatment difficult or in some cases impossible.

Recently, material researchers have focused their attention on tetragonal bismuth zinc titanium oxide [Bi(Zn$_{0.5}$Ti$_{0.5}$)O$_3$, BZT] which exhibits T$_c$ values over 700 °C.[16] This is because it is expected that BZT has a relatively low leakage current owing to low leakage current elements such as Ti and Zn ions as compared to high leakage current elements with mixed valence states such as Co, Fe, and Cr ions. However, to prepare BZT ceramics, high pressure over 6 GPa and high temperature over 900 °C are required. Recently, Huang and Cann[17] prepared lead-free BT–BZT solid solution system ceramics at atmospheric pressure, and reported that this system remained a solid solution up to 34 mol % of BZT and a maximum T$_c$ of 160 °C. Furthermore, Yamato *et al.* prepared BT–BZT system ceramics using oxide nanoparticles as raw materials in air, and reported

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that the system solid solution limit was 50 mol % of BZT and the maximum T_c was approximately 230 °C.[18] Moreover, they also reported higher loss tangent values over 10% at room temperature for 0.5BT–0.5BZT ceramics, and this high loss tangent still made poling treatment very difficult. For BT–BZT ceramics, it has been proposed that a possible reason for the high loss tangent may be Bi vacancies and multivalence Zn ions. Therefore, if Zn ions can be replaced by more valence-stable ions such as Mg, new lead-free piezoelectric materials with low loss tangent may be achieved. Khalyavin *et al.*[19] prepared single crystal of bismuth magnesium titanium oxide $[Bi(Mg_{0.5}Ti_{0.5})O_3,$ BMT] under a high pressure of 6 GPa and this crystal structure was assigned to be orthorhombic (*Pnnm*). This symmetry is exactly the same as that of antiferroelectric lead zirconate ($PbZrO_3$). Suchomel and Davis[20] prepared lead titanate ($PbTiO_3$) and BMT solid solution system ceramics in atmosphere and reported that this system exhibited a MPB between tetragonal and rhombohedral. We believe that it is very important to more closely investigate this new lead-free BT–BMT solid solution system.

Therefore, in this study, the BT–BMT system ceramics with various chemical compositions were prepared using nanoparticles under atmospheric conditions and their piezoelectric properties were investigated.

II. EXPERIMENTAL PROCEDURE

The BT–BMT ceramics were prepared by a conventional sintering method in air. Bi_2O_3 (Rare Metallic Co., LTD., >99.999%), TiO_2 (Ishihara Sangyo Kaisha LTD., >99.9%, size: 7 nm), MgO (Ube Materials Industries Co., LTD., >99.9%, size: 20 nm), and $BaCO_3$ (Ube Materials Industries Co., LTD., >99.9%, size: 40 nm) were weighed to prepare proper molar ratios of $(1-x)BT-xBMT$ $(0<x<0.7)$. The powders were mixed with ethanol and ball-milled for 16 h. The mixture was dried, calcined at 950 °C for 6 h, and then crushed. 2 wt % polyvinyl butyral was added to the powders, and they were ball-milled further for 16 h. The dried powders were sieved and then uniaxially pressed into green pellets at room temperature. After the binder was burned out at 700 °C for 10 h, the pellets were sintered at various temperatures between 975 and 1290 °C for 2 h.

The density was measured by the Archimedes method. The crystal structure and lattice parameters were determined by x-ray diffraction (XRD) (Rigaku RINT2000, Cu $K\alpha$, 50 kV, 30 mA) and using a high-intensity synchrotron XRD on beam line BL02B2 at the synchrotron radiation facility, SPring-8, Japan. The diffraction patterns were analyzed by the Rietveld method using TOPAS software (Bruker axs, Version 2.1). For electric measurements, the ceramics were polished and cut into sizes of $2 \times 2 \times 0.5$ mm³. Silver electrodes were painted and fired on the top and bottom surfaces with an area of 2×2 mm². The dielectric properties were measured at various frequencies from 0.1 to 10 MHz at temperatures between 20 and 450 °C using an impedance analyzer (Agilent, HP4294A). The polarization versus electric-field (P-E) and strain versus electric-field (S-E) curves were measured at room temperature and 0.1 and 1 Hz using a ferro-
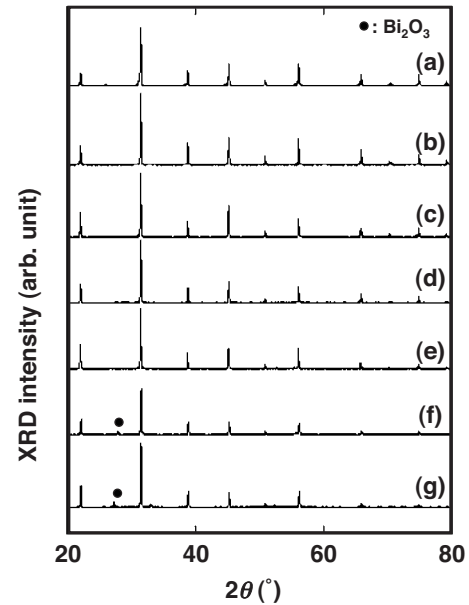

FIG. 1. XRD patterns measured at room temperature for (a) 0.9BT–0.1BMT, (b) 0.8BT–0.2BMT, (c) 0.7BT–0.3BMT, (d) 0.6BT–0.4BMT, (e) 0.5BT–0.5BMT, (f) 0.4BT–0.6BMT, and (g) 0.3BT–0.7BMT ceramics.

electric characteristic evaluation system. A slope of the S-E curve measured at the field amplitude of 70 kV/cm was defined as an apparent piezoelectric constant (d^*).

III. RESULTS AND DISCUSSION

A. Preparation of BT–BMT system ceramics by conventional sintering method

The optimum sintering temperatures were investigated for the BT–BMT ceramics, since the sintering temperature was expected to decrease with increasing Bi composition. Thus, optimum sintering temperatures of two chemical compositions; BT and 0.5BT–0.5BMT were initially determined based on the density and dielectric loss tangent at 300 Hz, room temperature, and then those of other compositions were linearly estimated. Sintered pellets were orange-colored and their relative densities were always greater than 94%. Figure 1 shows XRD patterns of the BT–BMT ceramics. The XRD peaks of the perovskite phase was clearly observed for all the BT–BMT ceramics, although small amounts of Bi_2O_3 were
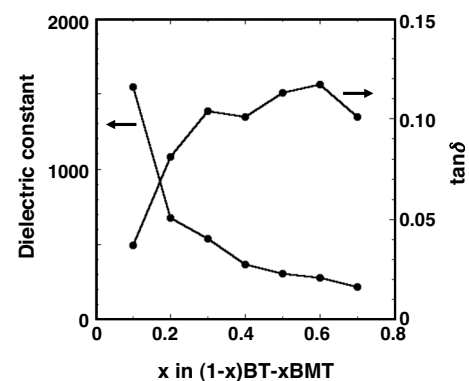

FIG. 2. The BMT composition dependence of dielectric constant and loss tangent measured at 100 kHz and room temperature for the BT–BMT ceramics.
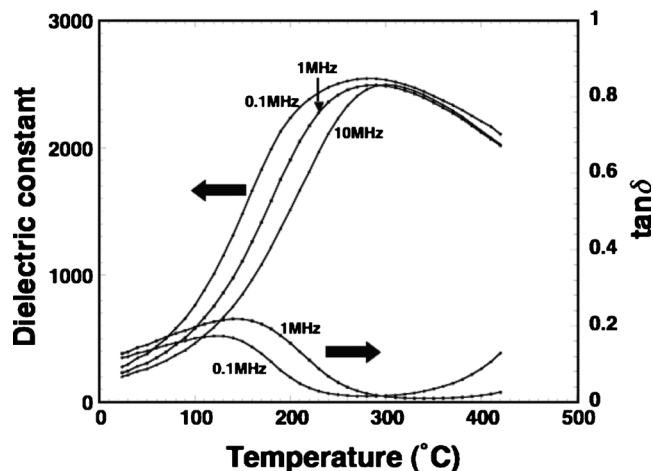
FIG. 3. Temperature dependence of the dielectric constant and loss tangent for the 0.4BT–0.6BMT ceramic.

observed for the BMT-rich ceramics with BMT contents over 60 mol %. Therefore, the perovskite single phase was stable for BMT contents below 60 mol %. For BT–BZT ceramics, the perovskite single phases was reported to be stable for BZT compositions below 50 mol %.[18] This suggests that the perovskite phase of BT–BMT is more stable than that of BT–BZT, but, the mechanism remains unclear at present.

Crystalline homogeneity of the BT–BMT ceramics was evaluated via synchrotron XRD measurement performed at high temperature of 475 °C. The crystal structure for all the BT–BMT ceramics was assigned to be cubic and a full width at half maximum (FWHM) of the 222 peaks for the BT–BMT ceramics was much smaller than that of pure BT ceramics, which suggests that all the cations in the ceramics were homogeneously distributed. This is because that if there is inhomogeneous distribution of the cations in the ceramics, their FWHM is usually broader than that of pure BT. Next, synchrotron XRD measurements were performed at room temperature. The 222 peaks at room temperature were found to be symmetric or very slightly asymmetric, which corresponds to a crystal structure that is either pseudocubic or
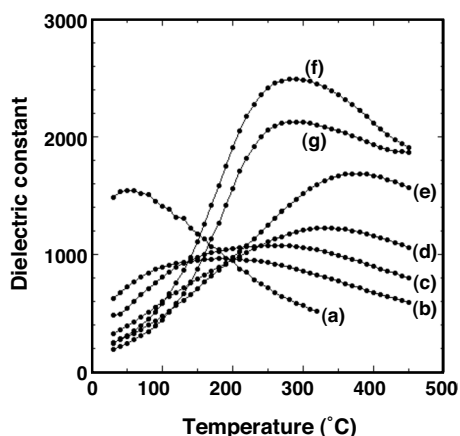

FIG. 4. Temperature dependence of the dielectric constant measured at 1 MHz for (a) 0.9BT–0.1BMT, (b) 0.8BT–0.2BMT, (c) 0.7BT–0.3BMT, (d) 0.6BT–0.4BMT, (e) 0.5BT–0.5BMT, (f) 0.4BT–0.6BMT, and (g) 0.3BT–0.7BMT ceramics.
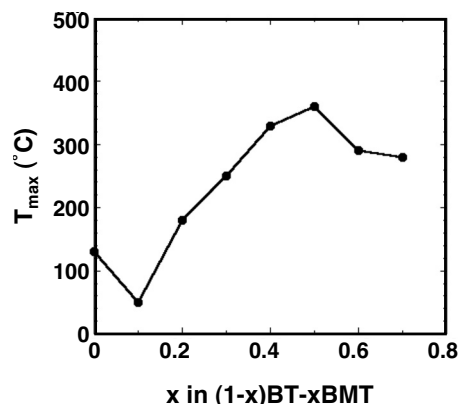

FIG. 5. The BMT composition dependence of T_{max} for the BT–BMT ceramics.

rhombohedral, respectively. Further investigation is required to determine a more refined crystal structure.

B. Dielectric properties of BT–BMT system ceramics

The room temperature dielectric properties for the BT–BMT ceramics measured at 100 kHz are shown in Fig. 2. With increasing BMT contents, the dielectric constant decreased from 1500 to 2000, while the loss tangent increased and saturated at around 10%. From a previous report on BT–BZT ceramics, the loss tangent was reported to be about
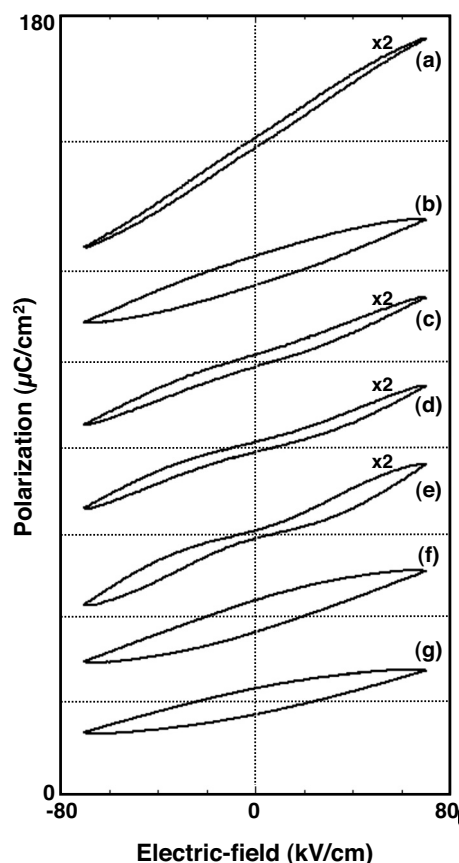

FIG. 6. P-E hysteresis loops measured at 1 Hz and room temperature for (a) 0.9BT–0.1BMT, (b) 0.8BT–0.2BMT, (c) 0.7BT–0.3BMT, (d) 0.6BT–0.4BMT, (e) 0.5BT–0.5BMT, (f) 0.4BT–0.6BMT, and (g) 0.3BT–0.7BMT ceramics.
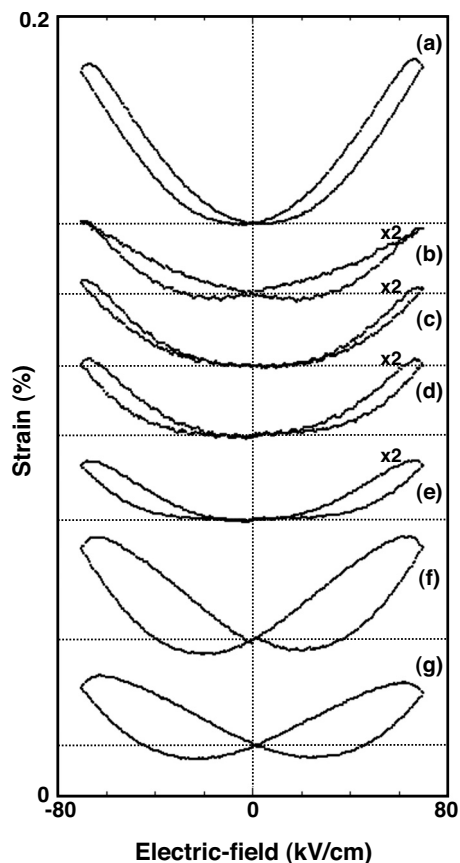
FIG. 7. S-E curves measured at 1 Hz and room temperature for (a) 0.9B–0.1BMT, (b) 0.8BT–0.2BMT, (c) 0.7BT–0.3BMT, (d) 0.6BT–0.4BMT, (e) 0.5BT–0.5BMT, (f) 0.4BT–0.6BMT, and (g) 0.3BT–0.7BMT ceramics.
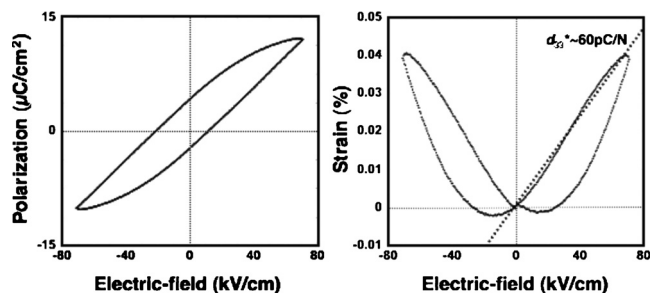

FIG. 8. P-E hysteresis loop and S-E curve measured at 0.1 Hz and room temperature for the 0.4BT–0.6BMT ceramic.

S-E behaviors were ferroelectric for BMT contents below 20 and over 60 mol %. On the other hand, the double P-E and S-E loops for BMT contents from 30 to 50 mol % suggest that these ceramics may be either antiferroelectric or ferroelectric with domain walls pinned by defects. For our case, the latter mechanism was likely to correspond to the response due to high concentration of the bismuth vacancies, coupling with the oxygen vacancies which pinned and depinned the domain wall.

Among the BT–BMT ceramics with T_{max} higher than 200 °C, the maximum strain was obtained for the 0.4BT–0.6BMT ceramics. The P-E hysteresis loop and S-E curve of the 0.4BT–0.6BMT ceramics were measured at 0.1 Hz and room temperature, as shown in Fig. 8. The remanent polarization was around 3.5 $\mu C/cm^2$, while the apparent piezoelectric constant d^* was around 60 pC/N. It should be noted that this d^* value of 60 pC/N was measured using the sample with high loss tangent of around 12% at 100 kHz. Thus, if a dielectric loss lower than 5% is achieved for the BT–BMT ceramics, much larger electric strain may be obtained. At present, we are working to improve crystal quality by means of inhibition of vaporization of bismuth oxide.

IV. CONCLUSIONS

In this study, BT–BMT ceramics were investigated in order to synthesize new high T_c lead-free piezoelectric materials. Optimization of the calcination and sintering conditions resulted in the formation of a single perovskite phase and their densities were greater than 94%. The BT–BMT ceramics exhibited high loss tangents of around 10%. The temperature dependence of the dielectric constant revealed that the maximum T_{max} was 360 °C for the 0.5BT–0.5BMT ceramics. The apparent piezoelectric constant d^* was approximately 60 pC/N for the 0.4BT–0.6BMT ceramics. Based upon these results, the BT–BMT system shows potential as a new type of lead-free material for high T_c piezoelectric applications.

15%.[18] This reduction in the loss tangent was smaller than expected. This suggests that for BT–BMT and BT–BZT systems, the high loss tangent may originate from bismuth vacancies or other defects.

Figure 3 shows the temperature dependence of the dielectric constant and loss tangent for the 0.4BT–0.6BMT ceramics measured at various frequencies. A strong dielectric dispersion, or frequency dependence of the dielectric properties was observed, indicating the BT–BMT system shows characteristics similar to known relaxor materials based on the polar nanoregions.[21] Figure 4 shows the temperature dependence of the dielectric constant measured at 1 MHz for a series of BT–BMT ceramics. For BMT compositions below 50 mol %, the dielectric maximum temperature measured at 1 MHz (T_{max}) increased with increasing BMT contents, while for BMT contents over 50 mol %, the T_{max} decreased with increasing BMT contents, as shown in Fig. 5. At present, we cannot explain this abnormal phenomena regarding the shift in T_{max}. For the BT–BMT system, the maximum T_{max} was found to be 360 °C for the 0.5BT–0.5BMT ceramics, which suggests a potential use of these ceramics for high T_c piezoelectric applications.

C. High electric-field properties of BT–BMT ceramics

Figures 6 and 7 show P-E and S-E curves measured at 1 Hz and room temperature for a series of the BT–BMT ceramics of various compositions, respectively. The P-E and

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