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Normal-Relaxor-Diffuse Ferroelectric Phase Transition and Electrical Properties of $Bi(Mg_{1/2}Ti_{1/2})_3$–$PbZrO_3$–$PbTiO_3$ Solid Solution Ceramics Near the Morphotropic Phase Boundary

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Perovskite-type xBi$(Mg_{1/2}Ti_{1/2})O_3$–$(0.56 - x)$PbZrO$_3$–0.44PbTiO$_3$ (xBMT–PZ–PT) ternary solid solution ceramics were synthesized via a conventional solid-state reaction method. The phase transition behaviors, dielectric, ferroelectric, and piezoelectric properties were investigated as a function of the BMT content. The X-ray diffraction analysis showed that the tetragonality of xBMT–PZ–PT was enhanced with increasing the BMT content, and a morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases was identified approximately in the composition of $x = 0.08$. In addition, the dielectric diffuseness and frequency dispersion behavior were induced with the addition of BMT and a normal-relaxor-diffuse ferroelectric transformation was observed from the PZ-rich side to the BMT-rich side. The electrical properties of xBMT–PZ–PT ceramics exhibit obviously compositional dependence. The $x = 0.08$ composition not only possessed the optimum properties with $\varepsilon^T_{33}/\varepsilon_0 = 1450$, $Q_m = 69$, $d_{33} = 390$ pC/N, $k_p = 0.46$, $P_r = 30$ μC/cm^2, $E_c = 1.4$ kV/mm, $T_c = 325$°C, and a strain of 0.174% ($d_{33}^* = 436$ pm/V) under an electric field of 4 kV/mm as a result of the coexistence of two ferroelectric phases near the MPB, but also owned a good thermal-depolarization behavior with a d_{33} value of >315 pC/N up to 290°C and a frequency-insensitive strain behavior.

I. Introduction

Lead-based perovskite structured binary piezoelectric ceramics, such as $PbZrO_3$–$PbTiO_3$ (PZT), have been widely investigated and used for actuators and sensors due to their excellent piezoelectric performances.[1,2] The high piezoelectric activity should be achieved near a morphotropic phase boundary (MPB) where two adjacent phases with different lattice distortions in a phase diagram have equal Gibbs free energies.[3–5] On the other hand, forming a ternary solid solution between PZT and some lead-based relaxor ferroelectrics is an important route to further improve their electrical properties, such as $Pb(Me_{1/3}Nb_{2/3})O_3$-type (Me: Mg^{2+}, Zn^{2+}, Ni^{2+}, etc.) complex perovskites, because these relaxor ferroelectrics might have better dielectric properties.[6–8] Recently, however, the application of lead-based ceramics has been challenged for their relatively low Curie points (T_c) and brought about serious lead pollution due to their high toxicity. Thus, the lead-free and low-lead content piezoelectric ceramics have attracted much attention. Unfortunately, the currently focused lead-free ferroelectric systems such as titanate- or niobate-based compositions have exhibited either processing difficulties or stability issues of piezoelectric properties,[9] which could make them quite hard to be applied in industry. In contrast, it should be meaningful and applicable to develop lead-reduced piezoelectric ceramics to satisfy the requirements of industry.

Nowdays, bismuth-based compositions are widely considered as nontoxic substitutes for lead-based compositions. Indeed, Bi^{3+} and Pb^{2+} possess the same lone-pair electronic configurations and majority of the Bi-containing oxygen octahedral compounds are known to demonstrate good ferroelectric properties.[10] Bi-based perovskites compounds such as $BiMeO_3$, in which Me are cations with an valence of +3 (Me:Fe^{3+}, Sc^{3+}, $Ni_{1/2}Ti_{1/2}$, $Mg_{1/2}Ti_{1/2}$, and $Zn_{1/2}Ti_{1/2}$, etc.) are typical lead-free ferroelectrics and have been largely investigated in recent years.[11–15] Among the $BiMeO_3$ members, $Bi(Mg_{1/2}Ti_{1/2})O_3$ (BMT) shows a structure of rhombohedral symmetry at room temperature and needs to be synthesized under high-pressure and high-temperature conditions.[16] Recently, it has been shown that BMT can be stabilized in the solid solutions with other perovskite end members. For instance, $(1 - x)$BMT–xPT is one of the most promising candidates for high-temperature applications due to its high T_c (478°C, $x = 0.37$), reasonable piezoelectric properties (e.g., $d_{33} = 225$ pC/N, $k_p = 0.38$) and low cost.[17–20] Nevertheless, there are still a few disadvantages in this system such as relatively high conductivity and high coercive fields, which make it hard to be well poled. So if we combine BMT–PT with PZT, it is reasonable to believe that excellent electrical properties can be achieved near the MPB region of a new ternary solid solution system of BMT–PZ–PT. Although this ternary system was studied by Chen *et al.*[21] and Fu *et al.*[22] in terms of its electrostrains under a high external electric field, yet, a full study on their phase transformation behavior and compositional dependence of dielectric, ferroelectric, and piezoelectric properties has been still missing.

In this work, a new MPB composition system of xBi$(Mg_{1/2}Ti_{1/2})O_3$–$(0.56 - x)$PbZrO$_3$–0.44PbTiO$_3$ (xBMT–PZ–PT) was constructed by substituting BMT for PZ at a fixed content of PT. The purpose of this study was then to identify how the phase structure of xBMT–PZ–PT changes with the BMT content and simultaneously to explore the composition dependence of electrical properties. The thermal stability and frequency dependence of piezoelectric and electromechanical properties were investigated as well.

II. Experimental Procedures

The xBMT–$(0.56 - x)$PZ–0.44PT (xBMT–PZ–PT, $x = 0$–0.56) ceramics were synthesized by a conventional solid-state reaction method using high-purity oxides: Bi_2O_3(≥99.0%), PbO (≥99.0%), ZrO_2(≥99.0%), TiO_2(≥99.0%), and $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$(≥99.0%) as raw materials. The powders were weighted and ball-milled with ethanol and zirconia media for

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4 h, then the slurry was dried at 100°C and calcined twice in a closed alumina crucible at 850°C for 2 h. After calcination, the mixture was ball-milled again for 6 h with 0.5 wt% PVB as a binder. The granulated powder was uniaxially pressed into disks with a diameter of 10 mm and a thickness of 1 mm. The compacted disks were sintered in the temperature range 1050°C–1200°C for 2 h. To minimize the vaporization of Bi and Pb, sample disks were buried in the sacrificial powder of the same composition. For the electrical measurements, silver paste was painted on major sides of the disks and then fired at 650°C for 30 min as the electrodes. The specimens were polarized in a silicone oil bath at 100°C under a dc field of 3–4 kV/mm for 15 min.

The phase structures were analyzed at room temperature by the X-ray diffractometer (XRD, D/Mzx-rB; Rigaku, Tokyo, Japan) with Cu$K_{\alpha 1}$ radiation. The dielectric properties were measured at various frequencies using an LCR meter (Agilent E4980A, Santa Clara, CA) in a temperature range 25°C–550°C and at a frequency range 0.1 kHz–1 MHz. The piezoelectric strain constant d_{33} of poled samples was measured by a Belincourt-meter (YE2703A; Sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p and the mechanical quality factor Q_m were determined by a resonance–antiresonance method with an impedance analyzer (PV70A; Beijing Band ERA Co. Ltd., Beijing, China). A ferroelectric test system (Precision LC, Radiant Technologies, Inc. Albuquerque, NM) was used to measure the polarization–electric field (P–E) hysteresis loops and electric-field-induced strain (S–E) curves. Thermal depoling experiments were conducted by annealing the poled samples at various temperatures for 15 min 24 h after poling, cooling to room temperature, and then measuring their d_{33} and k_p values.

III. Results and Discussion

Figure 1 shows a schematic phase diagram of the BMT–PZ–PT ternary system based on the work of Jaffe *et al.*[1] and Randall *et al.*[17] in which the blue dashed line stands for the approximate position of the MPB for the BMT–PZ–PT ternary system. The selected compositions were plotted as red dots and located on both sides of the MPB by fixing a PT content of 44%. It is thus expected that the substitution of BMT for PZ was found to induce a morphotropic phase structural transformation from rhombohedral to tetragonal ferroelectric phases. Figure 2 illustrates the room-temperature XRD patterns of xBMT–PZ–PT ceramics. As can be seen, all compositions demonstrate a pure perovskite structure without any deleterious phases in terms of typical diffraction patterns as shown in Fig. 2(a). This indicates that Bi^{3+} and ($Mg_{1/2}{}^{2+}Ti_{1/2}{}^{4+}$) can diffuse completely into the PZT matrix lattice to form a homogeneous solid solution. Moreover, a phase transition from rhombohedral to tetragonal with an increase in the BMT content was detected. The difference between these two phase structures can be characterized by the (200)-diffraction peaks around 45°. Figure 2(b) presents the (200)-diffraction peaks at 43°–47°. It is observed that there was no observable peak splitting for the compositions with $x \leq 0.06$, indicating that these compositions have a pure rhombohedral symmetry. When $x \geq 0.1$, the (200) peak tends to split and the splitting becomes more and more obvious, generally suggesting that a tetragonal structure appears and becomes stronger. Figure 2(c) shows the (200) diffraction peaks of the $x = 0.04$, 0.08, and 0.14 compositions. The fitting analysis of the diffraction peak profiles was carried out by using pseudo-Voigt peak shape function. The symmetry of the samples can be well established from the peak splitting and the relative intensity of these reflection lines. It can be clearly seen that a transition from a rhombohedral phase for the $x = 0.04$ samples to a tetragonal phase for the $x = 0.14$ sample. The $(002)_T/(200)_T$ and $(200)_R$ peaks could be simultaneously detected in the $x = 0.08$ sample. From the above results, it is clear that the phase structure of xBMT–PZ–PT ceramics changes from the rhombohedral structure to the tetragonal structure with increasing the BMT content. The $x = 0.08$ sample should be an MPB composition with a coexistence of both rhombohedral and tetragonal phases.

Figure 3 shows the temperature and frequency dependencies of the dielectric permittivity and loss tangent of the unpoled xBMT–PZ–PT ceramics. From Figs. 3(a)–(g), it can be obviously seen that the dielectric behavior of the xBMT–PZ–PT ceramics changes drastically with the addition of BMT. The PZ–PT ($x = 0$) binary composition exhibits an evident normal ferroelectric phase transition behavior. With increasing the BMT content, the ternary solid solution exhibits more relaxor-like characteristics, showing that the dielectric peaks at the dielectric maxima become more diffuse and more frequency-dependent. The diffuseness of the phase transition can be described by the modified Curie-Weiss law,[23] which can be expressed as $1/\varepsilon - 1/\varepsilon_m = C^{-1}(T - T_m)^{\gamma}$ where ε_m is the maximum value of the dielectric permittivity at the transition temperature T_m, C is the Curie-like constant, and γ is the degree of diffuseness which varies between 1 for a normal ferroelectric and 2 for an ideal relaxor ferroelectric. The γ value of different compositions can be determined from the slopes of linearly fitted lines as shown in Fig. 3(h). It can be seen that the γ value of the xBMT–PZ–PT ternary solid solution increases with increasing the BMT content as $x < 0.56$, which indicates that the relaxor characteristics becomes more distinct. There are two mechanisms for the observed relaxor behavior. One is attributed to the inhomogeneous distribution of B-site cations in an ABO_3 perovskite structure and another is attributed to the defect relaxation related to oxygen vacancies.[24] When $x = 0.56$, The BMT–PT binary composition owns $\gamma = 1.77$ but $\Delta T_{relax} = 0$, which is defined as the difference between T_m values measured at 1 kHz and1 MHz,[25] indicating that this composition owns a typical diffuse phase transition behavior with no frequency dispersion. This is usually considered as an intermediate state between normal ferroelectrics and relaxor ferroelectrics.[26] The above change means that there is a normal-relaxor-diffuse ferroelectric transformation in the studied compositions from the PZ-rich side to the BMT-rich side. In addition, the corresponding loss tangent was found to decrease with increasing the BMT content unless the pure BMT–PT. A relatively high loss tangent was also previously reported for pure BMT-PT sample.[17,22] Nevertheless, the loss value can retain less than 0.07 in the temperature range from room temperature to ~250°C at a frequency of over 1 kHz, suggesting a potential for high-temperature applications. However, the loss value significantly increases at higher temperatures, which is possibly attributed to the formation

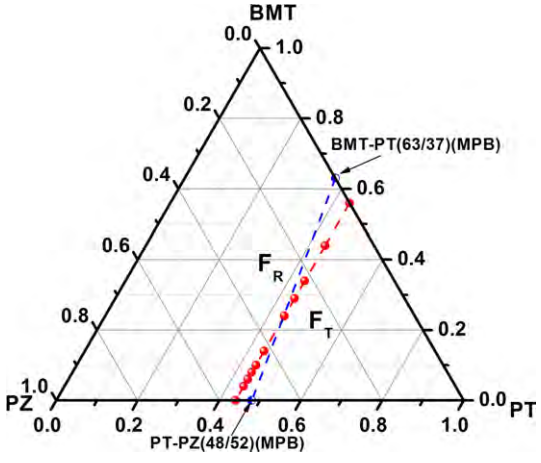

Fig. 1. Schematic phase diagram of BMT–PZ–PT ternary system.

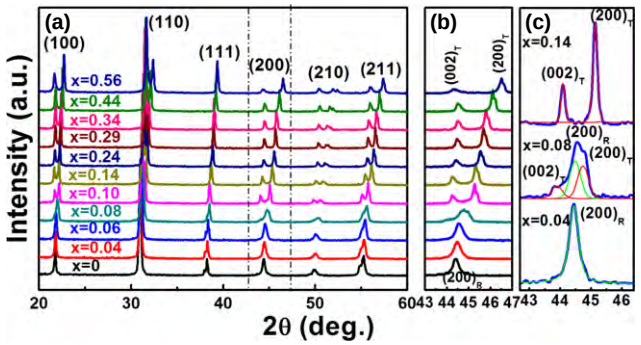

Fig. 2. (a) Room-temperature XRD full patterns of *x*BMT–PZ–PT ceramics, (b) Locally enlarged diffraction peaks in the 2θ range 43°–47°, and (c) Peak fitting analysis for the compositions with $x = 0.04$, 0.08, and 0.14.

of thermally activated space charges. This conduction feature has been also reported in $BiScO_3$–PT ceramics.[27] The volatilization of Bi and Pb during sintering might be one of reasons for highly conductive characteristics of *x*BMT–PZ–PT ceramics. This drawback would degrade the piezoelectric and electromechanical properties of this system to a certain degree considering the difficultly in electrical poling.

Figure 4(a) presents the dielectric permittivity ε_r at a fixed frequency of 10 kHz as a function of temperature for some typical unpoled *x*BMT–PZ–PT ceramics. For pure PZ–PT, a narrow peak was found for a normal ferroelectric ceramic. As the amount of BMT (x) was increased, the dielectric peak was found to become broader and broader, indicating a typical relaxor ferroelectric behavior as discussed above in Fig. 3. This is possibly as a result of the increase in random fields caused by the enhanced cation disorder degree at both A-sites and B-sites ions.[28] Moreover, it can be seen from Fig. 4(b) that the dielectric maxima ε_m reaches a maximum value at $x = 0.08$, indicating that the phase coexisted composition usually exhibits an enhanced dielectric property. In comparison, the variation in T_m does not show particular trend with increasing the BMT content. It first decreases from 358°C for $x = 0$ sample up to 285°C for the $x = 0.24$ sample, and then starts to increase afterwards. Generally, the

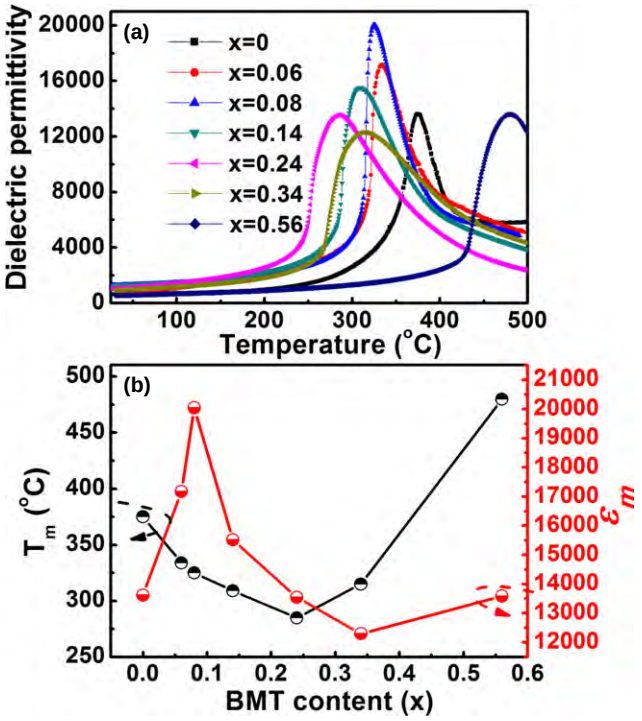

Fig. 4. (a) Dielectric permittivity versus temperature curves measured at 10 kHz for *x*BMT–PZ–PT ceramics as indicated, (b) The corresponding T_m and ε_m values as a function of the BMT content.

decline in T_m corresponds to a decrease in tetragonality for a couple of perovskite solid solution ceramics, such as PZT and $BiMeO_3$–PT systems. It seems that the addition of BMT tends to enhance the tetragonality [see Fig. 2(a)], which should be responsible for the increase in T_m as $x \geq 0.24$. As $x < 0.24$, the variation in T_m in this study cannot be well explained in the same way. There are probably two competitive causes responsible for the change in the T_m value in the studied ternary system. The rhombohedral to tetragonal ferroelectric phase transition was usually accompanied by a rise of the T_m value as observed in a fewer perovskite-structured

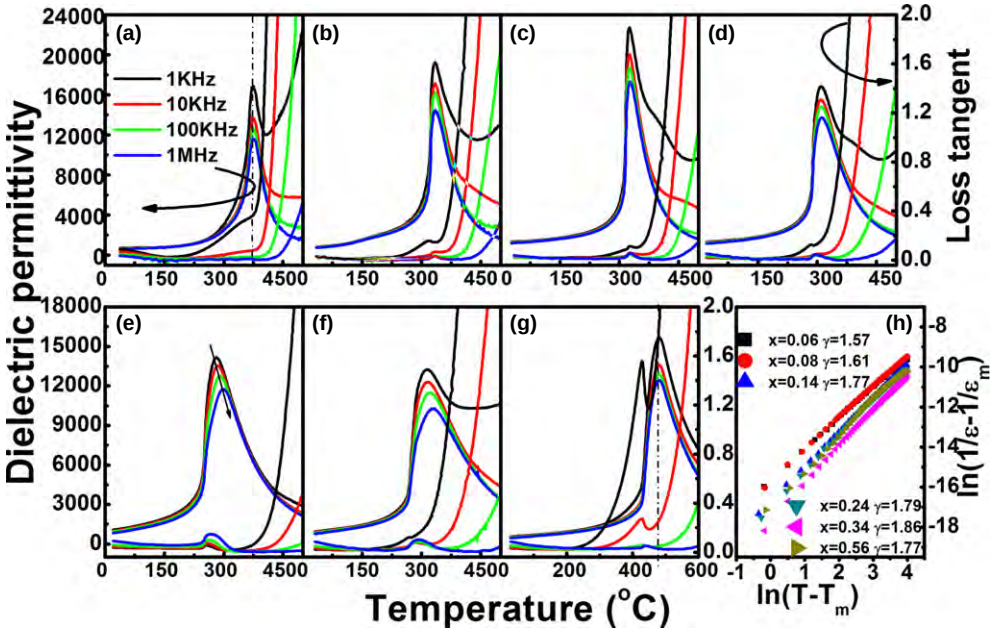

Fig. 3. Dielectric permittivity and loss tangent for selected *x*BMT–PZ–PT ceramics as a function of temperature and frequency: (a) $x = 0$, (b) $x = 0.06$, (c) $x = 0.08$, (d) $x = 0.14$, (e) $x = 0.24$, (f) $x = 0.34$, (g) $x = 0.56$, and (h) a plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ as a function of $\ln(T - T_m)$ at 10 kHz for selected samples.

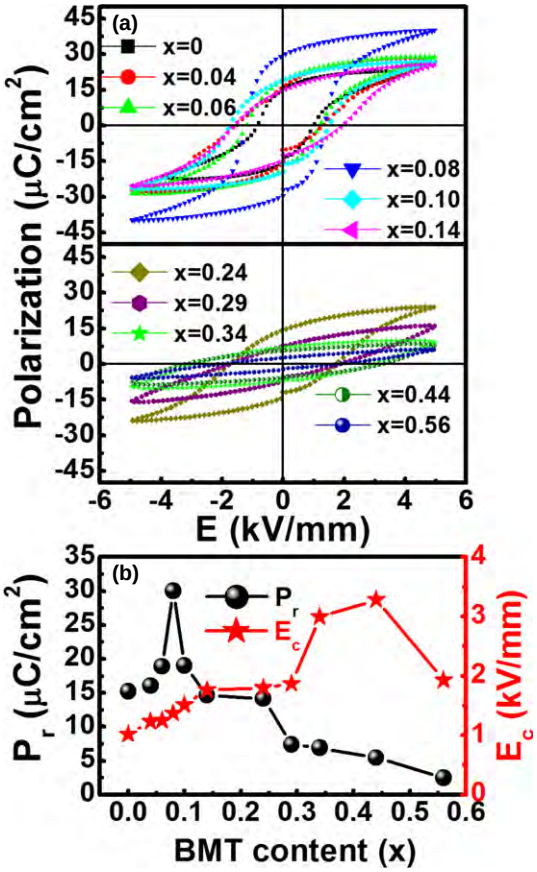

Fig. 5. (a) *P–E* hysteresis loops of the *x*BMT–PZ–PT ceramics, (b) The values of P_r and E_c as a function of the BMT content.

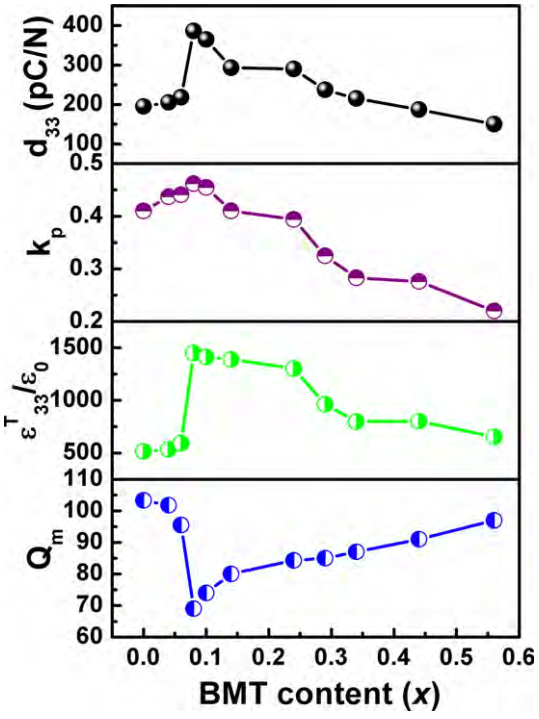

Fig. 6. Dielectric and piezoelectric properties of poled *x*BMT–PZ–PT ceramics sintered at optimum temperatures as a function of the BMT content.

piezoelectric ceramics, basically because of the enhanced tetragonality. Moreover, the observed composition-induced normal to relaxor phase transition usually tends to reduce the T_m values because of the weakening of the ferroelectric order degree.[29] The first reason might be dominant for the $x > 0.24$ samples, and the second reason might mainly contribute to the $x < 0.24$ compositions.

The ferroelectricity of *x*BMT–PZ–PT ceramics was characterized by measuring *P–E* hysteresis loops at 1 Hz at room temperature, as shown in Fig. 5(a). The remanent polarization (P_r) and the coercive fields (E_c) values as a function of BMT content (x) are given in Fig. 5(b). It can be observed from the shape of the hysteresis loops that all samples are of typical ferroelectrics and changes markedly with the addition of BMT. The $x = 0$ sample (0.56PZ–0.44PT) prepared in this study showed similar both ferroelectric and piezoelectric properties to those reported previously for similar compositions.[30,31] The P_r value was found to firstly increase and reach a maximum value of 30 μC/cm² at $x = 0.08$, and then decrease rapidly upon increasing x. Due to the coexistence of ferroelectric rhombohedral and tetragonal phases in the MPB region, The highest P_r value can be expected due to the summation of the possible crystallographic orientations, eight <111> spontaneous polarization directions in a rhombohedral phase and six <001> directions in a tetragonal phase, which make the domain switching easier.[32] Meanwhile, E_c was found to increase from 1.02 to 3.28 kV/mm from the $x = 0$ sample to the $x = 0.44$ sample, which should be generally attributed to the enhanced tetragonality based on the fact that the domain walls are partially clamped in tetragonal phases by larger local internal stresses from the structural distortion in the polarization process (large c/a ratio). A relatively low E_c value was observed for the $x = 0.56$ sample probably because this composition usually has a high leakage current in addition to its high tetragonality,[18] such that the *P–E* loop was poorly saturated.

Figure 6 shows the dielectric and piezoelectric properties for poled *x*BMT–PZ–PT solid solution ceramics sintered at their optimum temperatures. It can be seen that the dielectric and piezoelectric properties exhibit obviously compositional dependences. With increasing the BMT content, they first dramatically increase with x, and reach the maxima at $x = 0.08$, after that start to decline. Therefore it can be confident that the MPB plays a crucial role in improving piezoelectric properties. The reason may be that the multiple polarization states can be more susceptibly switched along the direction of the external electric field, making the

Table I. Dielectric and Piezoelectric Properties of $BiMeO_3$–PZ–PT Ternary Solid Solution Ceramics

Compounds	MPB (x)	T_c (°C)	k_p	d_{33} (pC/N)	$\varepsilon^T_{33}/\varepsilon_0$	Ref.
$(0.9 - x)$BMT–xPT–0.1PZ	0.4	~450	–	260	–	[21]
xBZT–$(1 - x)PZ_{0.56}T_{0.44}$	0.18	~260		365	1430	[28]
xBZT–$(1 - x)PZ_{0.52}T_{0.48}$	0.15	–	0.45	319	1325	[33]
x(0.3BZT–0.7PT)–$(1 - x)$PZ	0.52	~291	–	311	1080	[34]
0.1BZT–0.9[xPT–$(1 - x)$PZ)]	0.445	~320	0.45	300	978	[35]
xBNT–$(0.9 - x)$PT–0.1PZ	0.47	~295	–	317	1100	[36]
0.511BFO–0.326PZ–0.163PT	–	~431	0.5	101	371	[37]
xBMT–$(0.56 - x)$PZ–0.44PT	0.08	~325	0.46	390	1450	This study

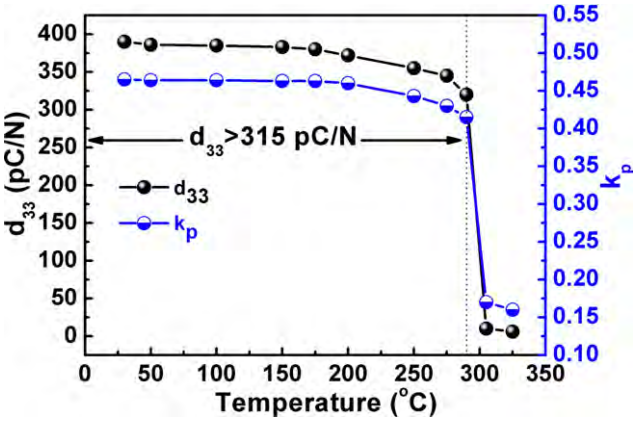

Fig. 7. The thermal stability of d_{33} and k_p values for the poled $x = 0.08$ sample.

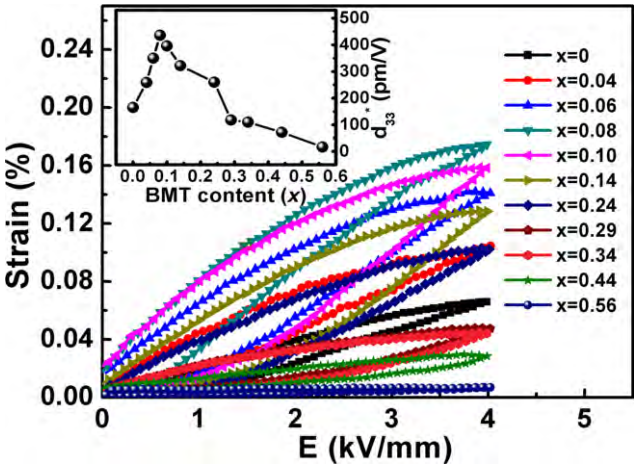

Fig. 8. Unipolar strain curves at 1 Hz for xBMT–PZ–PT ceramics with different BMT contents and the inset shows the normalized strain d_{33}^* as a function of the BMT content.

materials more electrically active, and thereby enhancing the piezoelectric response. By comparison, Q_m shows an opposite tendency with increasing x. The best dielectric and piezoelectric properties of $\varepsilon_{33}^T/\varepsilon_0 = 1450$, $Q_m = 69$, $d_{33} = 390$ pC/N, and $k_p = 0.46$ appear in the composition with $x = 0.08$, which are superior to those of pure Pb$(Zr_{0.52}Ti_{0.48})O_3$[1] and 0.63BMT–0.37PT.[17] The comparison of the electrical properties between $BiMeO_3$–PZ–PT systems such as BZT–PZ–PT[27,33–35] and $Bi(Ni_{1/2}Ti_{1/2})O_3$ (BNT)–PZ–PT[36] was made in Table I. Although $BiFeO_3$ (BFO)–PZ–PT[37] system was reported to have a much higher T_c value, yet, its dielectric and piezoelectric properties are relatively low. It can be seen that the BMT–PZ–PT system possesses relatively high T_c and high piezoelectric properties. Figure 7 reveals the thermal stability of d_{33} and k_p values for the $x = 0.08$ sample. The sample is open-circuited during annealing, but short-circuited before d_{33} and k_p values are remeasured at each chosen temperature (T_a). This is an easy and convenient method for evaluating the thermal stability of piezoelectric properties. It should be also good enough to compare the property response since the samples in the current method may experience more heating cycles than in the in-situ measurement. It can be seen that the d_{33} and k_p values decrease only slightly with increasing depoling temperature ($T_a \leq 290$°C), and begin to sharply drop with further increasing T_a ($T_a > 290$°C) due to the fact that T_a is approaching the T_c (325°C). Nevertheless, a high d_{33} value (>315 pC/N) can be maintained in the T_a range 30°C–290°C, demonstrating a good thermal stability of piezoelectric properties for the studied composition.

Figure 8 presents the unipolar electric-field-induced strain curves of xBMT–PZ–PT ceramics, measured under a relatively low electric field of 4 kV/mm at room temperature. The normalized strain d_{33}^*, which was defined as S_{max}/E_{max} where S_{max} is the strain value at the maximum electric field (E_{max}), was summarized in the inset of Fig. 8. An obviously composition-dependent strain behavior was observed in xBMT–PZ–PT ceramics with varying BMT content, and it generally shows a comparably small hysteresis with a nearly linear increase with the electric field. Similar to the remnant polarization and piezoelectric property, the unipolar strain first increases significantly with the increase in the BMT content and then reaches the maxima of 0.174% at $x = 0.08$, finally starts to decrease. It is probably due to the easy polarization switching around the MPB composition by the coexistence of rhombohedral and tetragonal phases.[32] In addition, the normalized strain d_{33}^* shows the same trend (see inset of Fig. 8), and the highest d_{33}^* of 436 pm/V was obtained at the MPB composition of $x = 0.08$, which shows a great potential for the design of piezoelectric actuators. For a better understanding of the strain behavior of the $x = 0.08$ sample, the frequency dependence of the strain values and the corresponding d_{33}^* were also measured. The results indicate that the $x = 0.08$ sample exhibited a frequency-insensitive strain behavior. Its value ranges only between 0.168% and 0.178% as frequency increases from 0.5 to 40 Hz and the normalized strain d_{33}^* varies between 419 and 445 pm/V.

IV. Conclusions

A new piezoelectric composition system of xBMT–$(0.56 - x)$PZ–0.44PT (xBMT–PZ–PT) was constructed by substituting BMT for PZ and fabricated by a conventional mixed-oxide method. The phase transitional behaviors and composition-dependent electrical properties were investigated as a function of the BMT content. The XRD results indicate that the ternary system undergoes a gradual phase structural transformation with changing the BMT content. Consequently, an MPB was identified at $x = 0.08$, which was also confirmed by corresponding dielectric, piezoelectric, and ferroelectric properties. With increasing the BMT content, the dielectric diffuseness and frequency dispersion behavior were induced and the solid solutions were found to exhibit a normal-relaxor-diffuse ferroelectric transformation from the PZ-rich side to the BMT-rich side. The $x = 0.08$ composition possessed the optimum properties of $\varepsilon^T_{33}/\varepsilon_0 = 1450$, $Q_m = 69$, $d_{33} = 390$ pC/N, $k_p = 0.46$, $P_r = 30$ μC/cm^2, $E_c = 1.4$ kV/mm and $T_c = 325$°C, and a strain with 0.174% ($d_{33}^* = 436$ pm/V) under an electric field of 4 kV/mm was obtained. Furthermore, the $x = 0.08$ sample exhibited a good thermal-depolarization behavior with a d_{33} value of >315 pC/N) up to 290°C, and a frequency-insensitive strain behavior. These results demonstrate that this ternary system could be a good piezoelectric material with reduced lead content and interesting electrical properties.

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