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Structure, piezoelectric, and ferroelectric properties of BaZrO$_3$ substituted Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-PbTiO$_3$ perovskite

Longlong Fan, Jun Chen, Huajun Kang, Laijun Liu, Liang Fang, Jinxia Deng, Ranbo Yu, and Xianran Xing

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Structure, piezoelectric, and ferroelectric properties of BaZrO$_3$ substituted Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-PbTiO$_3$ perovskite

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The structure and electric properties of (0.9-x)Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-xPbTiO$_3$-0.1BaZrO$_3$ (0.45 ≤ x ≤ 0.53) ceramics were investigated. The morphotropic phase boundary between tetragonal ferroelectric and pseudo-cubic relaxor phases is ascertainment at x = 0.50. The BaZrO$_3$ substitution can much reduce the coercive field of Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-PbTiO$_3$. The studies on temperature dependence of both ferroelectric and dielectric constant indicate a direct evidence for the antiferroelectric relaxor phase, which was ever suggested in the binary system of Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-PbTiO$_3$. The phase transition of ferroelectric to antiferroelectric relaxor produces the thermal depoling below the Curie temperature. The ceramic of BMT-0.47PT-0.1BZ exhibits a high strain 0.37% and a large-signal $d_{33}$ (530 pm/V) in the antiferroelectric-relaxor phase. BaZrO$_3$ substituted Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$-PbTiO$_3$ shows an analogous phase diagram to that of lead-free (Bi,Na)TiO$_3$-BaTiO$_3$. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4722286]

I. INTRODUCTION

Recently, the Bi-based perovskite structures BiMe$_2$O$_3$-PbTiO$_3$ solid solutions are popularly studied due to the high Curie temperature ($T_C$). It was ever suggested that the $T_C$ of the compositions in the vicinity of the morphotropic phase boundary (MPB) of BiMe$_2$O$_3$-PbTiO$_3$ was linear related to the tolerance factor (t) of the end member BiMe$_2$O$_3$ compound. BiScO$_3$-PbTiO$_3$ (BS-PT) has a low t of 0.907 (Refs. 1 and 2) and exhibits an excellent high temperature piezoelectric performance. $T_C$ at the MPB is as high as $T_C$ ≈ 450 °C and piezoelectric parameter $d_{33}$ is 460 pC/N. But, the utility of BS-PT is limited by the high cost of Sc$_2$O$_3$. As an analogy Bi-based compound, it is found that the Bi(Mg$_{1/3}$Ti$_{1/3}$)O$_3$-PbTiO$_3$ (BMT-PT) system has a similarly high $T_C$ (478 °C) at the MPB composition to BS-PT system, however with a relatively lower piezoelectric coefficient. 3 This may be induced by the core-shell microstructure and the oxygen octahedral rotations. The study on the temperature dependence of ferroelectric properties of BMT-PT shows that strain, remanent polarization ($P_r$), and the maximum polarization ($P_{max}$) increase with increasing temperature, and a large value of large-signal $d_{33}$ (500 pm/V) could be obtained at high temperature. The enhanced piezoelectric property is due to the fact that domains can be easier switched with the reduced tetragonality as the temperature is raised. 4

For the application of piezoelectric actuators, the electric field induced strain is an important parameter. The strain behavior of the piezoelectric ceramics is related to the crystal structure, domain configuration, and so on. 5–8 The antiferroelectric order can obviously enhance the strain level not only for lead but also lead-free piezoelectrics. For example, a field induced high strain could be achieved by the phase transition between antiferroelectric and ferroelectric orders in (Pb, La)(Ti, Zr, Sn)O$_3$ system. 9 As for the BMT-PT, the end member Bi(Mg$_{1/3}$Ti$_{1/3}$)O$_3$, which only can be synthesized by high pressure method, is expected to be antiferroelectric structure (Pnnm) analogue to PbZrO$_3$. However, there is no direct polarization to manifest the order of antiferroelectric property. 10 In this study, we introduce perovskite BaZrO$_3$ into the BMT-PT system to form a ternary system. The addition of BaZrO$_3$ could reduce the tetragonality that will improve the domain mobility to raise the piezoelectric properties. Furthermore, the dielectric spectrum of Ba-based piezoelectric ceramics 11–13 exhibits that the ceramics possesses relaxor character at the MPB compositions, and the dielectric loss is lower at high temperature, which could improve the resistance of piezoelectric ceramics at high temperature.

In this work, 10 mol. % BaZrO$_3$ content is added into the BMT-PT system, forming (0.9-x)Bi(Mg$_{1/3}$Ti$_{1/3}$)O$_3$-xPbTiO$_3$-0.1BaZrO$_3$ (abbreviated as BMT-xPT-0.1BZ). The structure and piezoelectric and ferroelectric properties were investigated. In order to explore phase transition, the temperature dependence of dielectric and ferroelectric properties were applied. The large-signal $d_{33}$ is much enhanced near the MPB composition. A kind of antiferroelectric-relaxor (AFE-relaxor) phase transition is also found, which contributes to the thermal depoling.

II. EXPERIMENT

The BMT-xPT-0.1BZ polycrystalline specimens were prepared by the conventional solid-state reaction method. A
stoichiometric amount of Bi₂O₃, PbO, BaCO₃, 4MgCO₃·Mg(OH)₂·5H₂O, TiO₂, and ZrO₂ were mixed by ball mill in alcohol for 12 h. After drying, the mixed powder was calcined at 900 °C for 4 h. The calcined powder was ground and milled in ethanol again for 12 h to reduce the particle size. Then, the dried slurry was uniaxially pressed into the cylindrical pellets with a diameter of 10 mm and thickness of 3 mm with polyvinyl alcohol at a pressure of 300 MPa. The pellets were then sintered at 1150 °C for 2 h. Protective powder of the same composition was placed around the pellets to minimize the evaporation loss of PbO and Bi₂O₃ during the high temperature sintering.

The room temperature x-ray diffractometer equipped with Cu-Kα radiation was used to analyze the phase structure. The fracture microstructure of the sintered sample was examined by scanning electron microscope. The sintered pellets were ground and polished to a thickness of ~0.6 mm and then electroded with silver paste for the measurements of electrical characteristics. The piezoelectric coefficient d₃₃ was measured after poling 24 h with piezo-d₃₃ meter (China Academy of Acoustics, ZJ-3). The poled samples for piezoelectric measurements were poled under a field of 70 kV/cm in silicon oil at 50 °C for 12 min. The temperature dependence of dielectric spectrum was measured on both poled and unpoled pellets using an impedance analyzer (4294 A). The polarization and longitudinal strain vs. electric field hysteresis loops were characterized by a ferroelectricity analyzer (TF Analyzer 1000) at a frequency of 1 Hz. For the measurement of the temperature dependence of polarization and strain, the temperature range was from room temperature to 160 °C with a step-length of 15 °C.

III. RESULTS AND DISCUSSION

The room temperature x-ray diffraction (XRD) patterns of powders from the crushed ceramics of BMT-x PT-0.1BZ, with 0.45 ≤ x ≤ 0.53, are shown in Fig. 1(a). All of the samples are in the pure perovskite phase. For the composition of x ≤ 0.47, its crystal structure is pseudo-cubic where no splitting of any peaks can be detected. Since the BMT-PT system was indexed in the rhombohedral phase (R3c) by TEM investigation, we also specify these compositions with upper Bi(Mg₁/₂Ti₁/₂)O₃ content as the rhombohedral phase. Tetragonal phase (T) is observed for x = 0.53 as displayed by the splitting of [100] and [200] peaks. It indicates that a phase change from T to R can be detected in the range of 0.48 ≤ x ≤ 0.51. With decreasing content of PbTiO₃, it is evidenced that the relative intensity of the (200) peak of the T phase to that of R phase near 2θ = 45° decreases. The MPB is around the composition of BMT-0.50PT-0.1BZ. As shown in Fig. 1(b), the electric field can induce a phase transition from the R to T from the XRD profile of the poled and unpoled BMT-0.48PT-0.1BZ ceramics. It is evidenced that [200] peaks split and the relative ratio of (002)/(200) peak intensity is strengthened in the poled ceramic of BMT-0.48PT-0.1BZ.

The fracture surface of BMT-0.48PT-0.1BZ is shown in Fig. 2, it can be found that the ceramic is well densified with an average grain size of ~4 μm.

For the BMT-x PT-0.1BZ ceramics with 0.45 ≤ x ≤ 0.53, the ferroelectric hysteresis loops are shown in Fig. 3. Well saturated polarization vs. electric field, P(E), loops can be obtained for the ceramics measured with an E-field of 70 kV/cm at 1 Hz. For the compositions with x ≥ 0.48, typical P(E) hysteresis loops of ferroelectric materials are shown. While the PT content decreases to x = 0.47, the loop
becomes obviously constricted, showing an antiferroelectric character. As shown in Fig. 3(b), the \( P_r \) changes slightly in the upper range of PT content. It is 31.8 \( \mu \text{C/cm}^2 \) at the MPB composition. While \( x \) decreases to 0.47, the \( P_r \) suddenly reduces to 6.21 \( \mu \text{C/cm}^2 \). This is similar to the change of the composition dependence of coercive field \( (E_C) \). For the antiferroelectric-like loops, we will also use \( E_C \) to identify their ferroelectricity instead of transition field \( (E_A-F) \).\(^9\) The \( E_C \) decreases dramatically from 33.4 kV/cm for the \( x = 0.48 \) to 8.3 kV/cm for the \( x = 0.47 \), which might be due to the fact that the phase transition from FE to AFE state.\(^{14}\) It needs to note that the result of polarization agrees well with the XRD pattern for the composition of \( x = 0.48 \). The well maintained \( P_r \) of \( x = 0.48 \) indicates that the transition for \( R \) to \( T \) phase can be stabilized even after unloading electric field.

The bipolar and unipolar strain vs. electric field, \( S(E) \), curves are plotted in Fig. 4. Agreeing to the above \( P(E) \) loops, the compositions of BMT-\( x \)PT-0.1BZ with \( x \geq 0.48 \) exhibit an archetypal butterfly shape curve. However, the \( S(E) \) curves of BMT-0.47PT-0.1BZ and BMT-0.45PT-0.1BZ, which are in the \( R \) phase, totally differ to the ferroelectric one; the negative part of the strain curve becomes flatter. This behavior could be attributed to the antiferroelectric order.\(^{14,15}\) According to the non-zero coercive field and remnant polarization for the composition of \( x \leq 0.47 \), it could be supposed that they are in antiferroelectric phase mixed with ferroelectric phase. The antiferroelectric order profits the large strain near the MPB.\(^9,14\) Corresponding to the total strains of the bipolar \( S(E) \) curves, the maximum strain of the unipolar \( S(E) \) reaches as high as \( 0.37\% \) at the composition of \( x = 0.47 \), as shown in Fig. 4(b). It is known that the unipolar displacement is related to the extrinsic effect of domain switching and intrinsic piezoelectric effect. The hysteresis of unipolar strain is attributed to the non-180\(^\circ\) domain switching.\(^{14,16}\) The lower hysteresis of BMT-0.48PT-0.1BZ (9.4\%) than that of BMT-PT38 (24\%) (Ref. 4) indicates that the BaZrO\(_3\) substitution could dramatically reduce the

![FIG. 3. (a) \( P(E) \) loops and (b) \( P_r \) and \( E_C \) for the BMT-\( x \)PT-0.1BZ with \( 0.45 \leq x \leq 0.53 \).](image)

![FIG. 4. (a) Bipolar and (b) unipolar strain curves vs. E-field of BMT-\( x \)PT-0.1BZ with \( 0.45 \leq x \leq 0.53 \).](image)

![FIG. 5. Small and large-signal \( d_{33} \) for the BMT-\( x \)PT-0.1BZ with \( 0.45 \leq x \leq 0.53 \).](image)
extrinsic effect from the domain-switching, which is better for the application of actuator.

The piezoelectric properties as a function of PT content for the BMT-xPT-0.1BZ samples are shown in Fig. 5. For the compositions of $x \geq 0.48$, both small and large-signal $d_{33}$ decrease with increasing amount of PT. The maximum of small-signal $d_{33}$ value reaches 227 pC/N at the composition of $x = 0.48$. This value is similar to the MPB composition of BMT-PT fabricated with the precursor of MgTiO$_3$. As $x$ reduces to 0.47, the large-signal $d_{33}$ reaches to the maximum value (520 pm/V), meanwhile the small-signal one diminishes nearly. This agrees well with the result of ferroelectric measurement that there is an FE-AFE phase transition at $x = 0.47$.

FIG. 6. Dielectric constant and loss as a function of temperature in the frequency range of 1 kHz to 1 MHz for the BMT-xPT-0.1BZ ($x = 0.53, 0.5, 0.48, 0.47,$ and $0.45$). (a), (c), (e), (g), and (h) are data for the unpoled ceramics, while (b), (d), and (f) are data for the poled ceramics.
In order to utilize the high temperature application of piezoelectric materials, not only the Curie temperature but also the depoling temperature are significant. Fig. 6 shows the temperature dependence of dielectric permittivity measured at different frequencies (1 kHz-1 MHz) on the unpoled and poled BMT-xPT-0.1BZ ceramics ($x = 0.45, 0.47, 0.48, 0.50,$ and $0.53$). Both unpoled and poled specimens display two dielectric anomalies for the ceramics with $x \geq 0.48$. The temperature of the first anomaly is the depolarization temperature ($T_d$), which corresponds to the transition from the ferroelectric state to antiferroelectric one (FE-AFE). The temperature at which the dielectric constant reaches the maximum value ($T_m$) corresponds to the antiferroelectric-paraelectric (AFE-PE) transition. It can be seen that both FE-AFE and AFE-PE phase transitions occur in a wide temperature range, and the dielectric peaks at $T_d$ and $T_m$ (Fig. 6(a)) are frequency dependence, which indicates that the BMT-xPT-0.1BZ possesses a relaxor character. Especially, the FE-AFE phase transition temperature is widened, and the relaxor property is enhanced with the decrease in the PT content. This relaxor property may derive from the BMT-PT system. For the compositions of BMT-PT in the $R$ phase, microdomain structures related to strong frequency dispersion are mainly observed. It is similar to the BNT-BT where the nanodomains appear at the MPB composition and their volumes increase with increasing BaTiO$_3$ content. With increasing temperature, the nanodomains increase also. The increase in the volume of nanodomains broadens the FE-AFE phase transition temperature range. Therefore, the similar dielectric properties could hypothesize that the BMT-xPT-0.1BZ behaves a similar domain structure to the BNT-BT.

For the poled ceramics, both the dielectric constant and dielectric loss vary sharply at $T_d$, as shown in Figs. 6(b), 6(d), and 6(f). We can identify the $T_d$ according to the dielectric loss on poled pellet. The $T_d$ and $T_m$ are about 140°C and 300°C for the BMT-0.48PT-0.1BZ, respectively. The $T_m$ is lower than that of the BMT-PT system. It has been known that the high $T_c$ of PbTiO$_3$-BiFeO$_3$ is associated with the strong hybridization between the Pb/Bi and O. The replacement of ionic Ba$^{2+}$ to Pb$^{2+}$/Bi$^{3+}$ would weaken such hybridization, resulting in the decrease in the $T_m$. It is the same with the ionic Sr-substitution in the Bi(Ni,Ti)O$_3$-PT system. Even through the Curie temperature is reduced, the dielectric loss can be much reduced at high temperature up to 400°C. The addition of BaZrO$_3$ benefits in the improvement of resistivity of BMT-PT.

In order to further confirm the exact phase transition of FE-AFE suggested from the results of dielectric property, the temperature dependence of $P(E)$ and $S(E)$ curves for the BMT-0.48PT-0.1BZ were employed. As shown in Fig. 7(a), for the BMT-0.48PT-0.1BZ, the $P-E$ loops display that the $P_{max}$ of the sample is invariant, but the $P_r$ slightly decreases as a function of temperature below 130°C. When the temperature is above 145°C, the hysteresis loop becomes “pinched” similar to that of antiferroelectric materials. With further increase in temperature, the $P_r$ keeps continuing to weaken. The antiferroelectric order is enhanced, while the ferroelectric order is depressed. However, the $P_r$ is still non-zero at 160°C, when the electric field is completely unloaded. It suggests that the sample possesses both ferroelectric and antiferroelectric orders above the $T_d$. Similar to the BNT-BT, the broadened temperature range of phase transition from the FE to AFE state could be associated with the coexistence of ferroelectric and antiferroelectric domains. It needs to note that the FE-AFE phase transition manifested by the temperature dependent $P(E)$ loops is in a good agreement with the result of dielectric constant on the poled pellet. Therefore, the phase between the $T_d$ and $T_m$ could be concluded to be antiferroelectric-relaxor (AFE-relaxor), which was suggested in the lead-free BNT-BT system. It has been known that the AFE-relaxor phase in the BNT-BT is caused by the fact that the nanomorphology structure of Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ (Pmmn) analogous to PbZrO$_3$ may also attribute to the property of the AFE-relaxor in the BNT-PT based system. The existence of AFE $P4bm$ phase embeds in the ferroelectric $R3c$ matrix. The orthorhombic structure of Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ (Pmmn) analogous to PbZrO$_3$ may also attribute to the property of the AFE-relaxor in the BNT-PT based system. From the dielectric and ferroelectric properties as a function of composition and temperature and XRD data, a composition and temperature phase diagram could be designed for the poled BMT-xPT-0.1BZ ceramics with 0.45 ≤ $x$ ≤ 0.53 (Fig. 8). The phases at $T < T_d$ and $T > T_m$ are classical ferroelectric phase and cubic phase.
respectively. The phase in $T_d < T < T_m$ is thought to be the AFE-relaxor similar to BNT-BT.\textsuperscript{19–21} In the composition between the 0.48 and the MPB ($x = 0.50$), the AFE-relaxor phase can be transformed into the ferroelectric $T$ phase by electric poling and stabilized below the $T_d$.

**IV. CONCLUSIONS**

The pure perovskite phase of BMT-$x$PT-0.1BZ can be fabricated by conventional solid reaction. The position of MPB composition is BMT-0.50PT-0.1BZ for the crushed unpoled ceramic powder. The substitution of BaZrO$_3$ reduces the $E_C$ and improves the electric resistance at high temperature. With the addition of BaZrO$_3$, the AFE-relaxor is induced in the BMT-PT. For the BMT-0.48PT-0.1BZ, the phase transition temperatures of $T_d$ and $T_m$ are 140°C and 300°C, respectively. In the AFE-relaxor phase of BMT-0.47PT-0.1BZ, the unipolar strain is 0.37%, and the large signal $d_{33}$ is 530 pm/V.

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