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$BiFeO_3$–$PbZrO_3$–$PbTiO_3$ ternary system for high Curie temperature piezoceramics

Wei Hu, Xiaoli Tan*, Krishna Rajan

Department of Materials Science and Engineering & Institute for Combinatorial Discovery, Iowa State University, Ames, IA 50011, USA

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Abstract

$BiFeO_3$–$PbZrO_3$–$PbTiO_3$ ternary solid solution system was investigated for the development of piezoelectric ceramics with high Curie temperatures. The search for the morphotropic phase boundary (MPB) compositions in this ternary system started from mixing two MPB compositions: $0.70BiFeO_3$–$0.30PbTiO_3$ and $0.52PbZrO_3$–$0.48PbTiO_3$. The content of $PbTiO_3$ was then further fine tuned in order to reach the appropriate volume fraction between the rhombohedral and tetragonal phases in the sintered ceramics. It was observed that the sintering temperature has a profound impact on the density, grain morphology, dielectric and ferroelectric properties of the ceramics. The composition that displays the best combined structure and properties was identified to be $0.648BiFeO_3$–$0.053PbZrO_3$–$0.299PbTiO_3$, with a Curie temperature T_C of 560 °C, a remanent polarization P_r of 15.0 μC/cm^2, and a piezoelectric coefficient d_{33} of 64 pC/N.

Keywords: Sintering; Dielectric properties; Ferroelectric properties

1. Introduction

Searching for ferroelectric ceramics with a high Curie temperature has been a continuous task in the field of electroceramics due to the demand from high temperature piezoelectric applications.[1,2] The previous work reported in the literature was primarily focused on binary solid solution systems between two perovskite compounds,[2–4] such as $BiScO_3$–$PbTiO_3$,[5,6] $Bi(Mg_{1/2}Ti_{1/2})O_3$–$PbTiO_3$[7,8] and $BiInO_3$–$PbTiO_3$.[9,10] In these binary systems, the dielectric and piezoelectric performances were observed to peak at the morphotropic phase boundary (MPB) composition where a composition-induced phase transition occurs.[11] The MPB composition, usually a very narrow composition range, displays a specific Curie temperature in the binary solid solution. In contrast, the MPB in a ternary system corresponds to a continuous range of composition, providing adjustability in the Curie temperature and allowing a further degree of freedom in optimizing the properties.

The $BiFeO_3$–$PbTiO_3$ (BF–PT) binary system exhibits a high Curie temperature (630 °C) and a large tetragonality at the MPB composition and has been investigated for high-temperature piezoelectric applications.[12–16] However, the high leakage current makes it difficult to pole the ceramic and the high coercive field leads to unsaturated hysteresis loops even at very high electric fields.[16–18] In the mean time, the well-known $PbZrO_3$–$PbTiO_3$ (PZT) ceramics have demonstrated excellent dielectric and piezoelectric performances but the Curie temperature at the MPB composition (380 °C) is low for some applications.[2,11] In the present work, binary systems of $BiFeO_3$–$PbTiO_3$ and $PbZrO_3$–$PbTiO_3$ are combined to form a ternary system, with the aim to produce ferroelectric ceramics with high Curie temperatures and excellent piezoelectric properties.

2. Experimental

Ceramic samples in the BF–PZ–PT ternary system were prepared by the solid state reaction method. A stoichiometric amount of Bi_2O_3 (99.9%, Aldrich), Fe_2O_3 (99.99%, Alfa Aesar), PbO (99.99%, Alfa Aesar), TiO_2 (99.99%, Aldrich), ZrO_2 (99.978%, Alfa Aesar) were mixed with vibratory mill in ethanol for 6 h. After drying, the mixed powder was pressed and calcined in covered crucibles at 850 °C for 5 h. The as-calcined powder was ground and milled in ethanol again for 15 h to reduce

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* Corresponding author. Tel.: +1 515 294 3355; fax: +1 515 294 5444.
E-mail address: xtan@iastate.edu (X. Tan).

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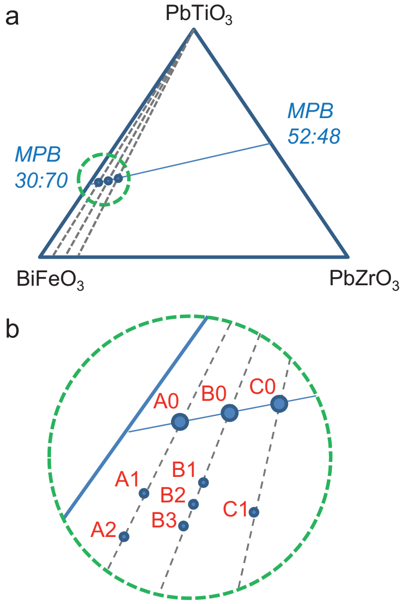

Fig. 1. The compositions studied in the $BiFeO_3$–$PbZrO_3$–$PbTiO_3$ ternary phase diagram. (a) Three compositions (A0, B0, C0) on the straight line connecting the two MPB compositions in binary $BiFeO_3$–$PbTiO_3$ and $PbZrO_3$–$PbTiO_3$ systems are initially prepared. In order to preserve the high Curie temperature, compositions close to the $BiFeO_3$–$PbTiO_3$ side are focused. (b) A close look to the circled region to indicate additional compositions prepared to locate the MPB compositions.

the particle size. Then the dried slurry was pressed at 300 MPa to form cylindrical pellets with 10% poly vinyl alcohol (PVA) solution as binder and sintered at temperatures between 975 and 1075 °C for 4 h. Protective powder of the same composition was placed around the pellets to minimize the evaporation loss of PbO and Bi_2O_3.

The phase development after sintering was analyzed using X-ray diffractometer with Cu-Kα radiation. The Archimedes' method was employed to determine the density of sintered pellets. Scanning electron microscopy (SEM) was used to examine the grain morphology in the as-sintered pellets. For dielectric and ferroelectric measurements, sintered pellets were polished and electroded with silver paste. An LCR meter (HP-4284A, Hewlett-Packard) in conjunction with a high temperature sample holder cell system (ProboStat, NorECs) was used to measure the temperature dependence of dielectric constant and loss tangent during heating from room temperature to 700 °C at the rate of 4 °C/min. The polarization vs. electric field hysteretic loops were characterized by the RT-66A standardized ferroelectric test system (Radiant technologies) at room temperature at ~4 Hz. A high voltage source-measure unit (Keithley 237) was used to measure the leakage current at room temperature. The piezoelectric coefficient d_{33} was measured 24 h after poling with a piezo-d_{33} meter (ZJ-4B, Shanghai Institute of Ceramics, China).

3. Results and discussion

The compositions prepared in the BF–PZ–PT ternary system for this study are schematically shown in Fig. 1. Three initial compositions A0, B0 and C0 were selected from the straight line connecting the two MPB compositions of 0.70BF–0.30PT and 0.52PZ–0.48PT. In order to preserve the high Curie temperature observed in 0.70BF–0.30PT, the ceramics of A0, B0, and C0 contain 5 mol.%, 10 mol.%, and 15 mol.% of (0.52PZ–0.48PT), respectively. However, X-ray diffraction analysis (Fig. 2) indicates that these three compositions sit in the tetragonal side of the MPB in the ternary system. The results indicate that the MPB in the BF–PZ–PT ternary system deviates away from the straight line connecting the two MPB compositions of 0.70BF–0.30PT and 0.52PZ–0.48PT. It was also noticed that the large internal stresses in A0 and B0 due to the high fraction of the tetragonal phase make the sintered pellets easy to break. In order to maintain the physical integrity and reach the MPB composition, the content of the tetragonal phase needs to be reduced. This was realized through the decrease in the PT content while maintaining a constant molar ratio between BF and PZ. Accordingly, compositions A1, A2, B1, B2, B3, and C1 were synthesized (Fig. 1b). The exact compositions of these prepared ceramics are listed in Table 1. Indeed, as can be seen from Fig. 2, the volume fraction of the rhombohedral phase increases at the expense of the tetragonal phase in these sintered ceramics when PT content is reduced. Three compositions A2, B2 and C1 were identified as the MPB compositions in the ternary system and were selected for further investigation.

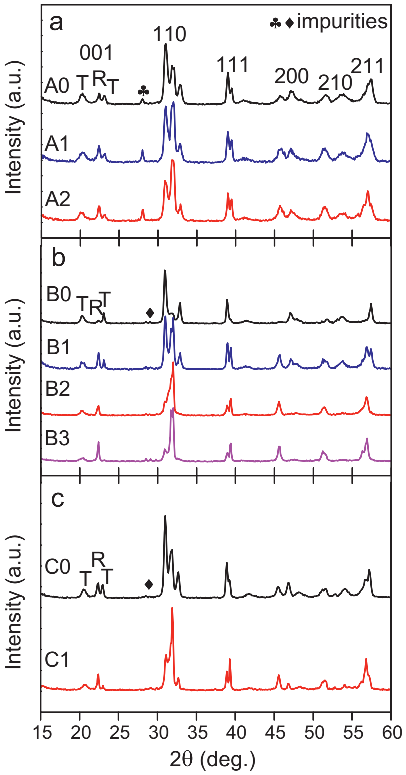

Fig. 2. Phase formation in the ceramics sintered at the same temperature (a) 1050 °C, (b) 1075 °C, and (c) 1075 °C. The diffraction peaks are indexed on the basis of the pseudocubic perovskite structure. T denotes tetragonal while R for rhombohedral perovskite phase, respectively.

It is interesting to note that, in addition to chemical composition, sintering temperature is also capable of altering the volume fraction between the rhombohedral and tetragonal phases in the

Table 1
Compositions investigated in the BF–PZ–PT ternary solid solution system. Bold font denotes the MPB compositions.

Composition	$BiFeO_3$	$PbTiO_3$	$PbZrO_3$
A0	0.665	0.309	0.026
A1	0.680	0.293	0.027
A2	**0.686**	**0.287**	**0.027**
B0	0.560	0.336	0.104
B1	0.645	0.302	0.053
B2	**0.648**	**0.299**	**0.053**
B3	0.650	0.296	0.054
C0	0.595	0.327	0.078
C1	**0.615**	**0.304**	**0.081**

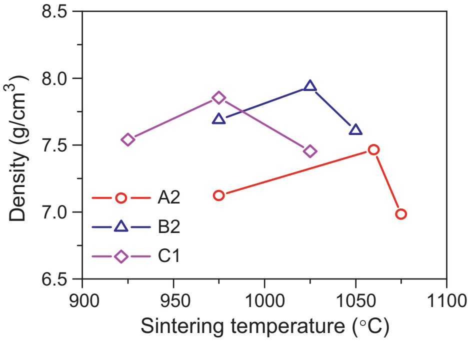

Fig. 4. Ceramic density as a function of sintering temperature in MPB compositions A2, B2 and C1.

BF–PZ–PT ternary system. Fig. 3 shows the X-ray diffraction patterns of the selected compositions A2, B2, and C1 sintered at different temperatures. Especially in the compositions A2 and B2, obvious changes in the relative intensity of R and T peaks are observed. Associated with the change in the phase ratio is the change in the impurity phases, as seen in Fig. 3. It appears that the evaporation loss of Bi_2O_3 and PbO at high temperature during sintering dictates the phase ratio and the impurity phases. In compositions A2 and B2, the impurity phase formed at lower sintering temperatures is identified as $Bi_{46}Fe_2O_{72}$.[19] However, the impurity phase at higher temperatures cannot be determined conclusively due to the very low peak intensity. It could be either $Bi_2Fe_4O_9$ or $Pb_2Bi_6O_{11}$.[17] Fig. 3 shows that the impurity phase abruptly changed in the composition A2 at 1075 °C and B2 at 1050 °C. In contrast, only negligible amount of impurity phase was found in the composition C1 at all sintering temperatures.

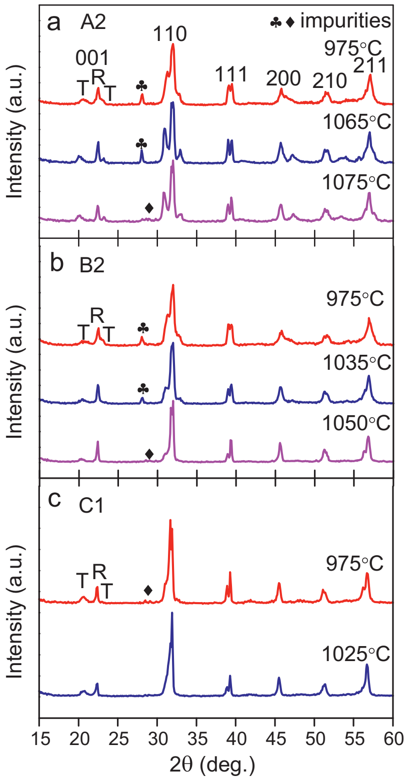

Fig. 3. Influence of sintering temperature on the phase formation in MPB compositions (a) A2, (b) B2 and (c) C1. The X-ray diffraction peaks are indexed on the basis of the pseudocubic perovskite structure.

The density of sintered pellets of compositions A2, B2 and C1 is displayed in Fig. 4. It is noted that for all three compositions, the density initially increases with increasing sintering temperature and then decreases. For compositions A2 and B2, this transition corresponds to the change of the impurity phase. The decomposition of Bi-compounds and/or the evaporation loss of Bi_2O_3 and PbO influence the density of the sintered pellets. Fig. 5 shows the SEM micrographs of pellets sintered at various temperatures. For all the compositions (A2, B2, C1) the grain size generally increases with sintering temperature. At certain temperatures, 1075 °C for A2 and 1050 °C for B2, abrupt and significant grain growth was detected, along with drastic changes in the grain morphology. It should be noted that this change in the grain morphology corresponds well with the change in the impurity phase (Fig. 3) and the density (Fig. 4). It is seen in Fig. 3 that the composition C1, sintered at both 975 and 1025 °C, contains the same impurity phase as that in the composition A2 sintered at 1075 °C and the composition B2 sintered at 1050 °C. Consistent with this, the grain morphology of C1 is similar to that of A2 at 1075 °C and B2 at 1050 °C (Fig. 5). It appears that the significant grain growth in A2, B2, and C1 during sintering was assisted by the formation of the impurities along grain boundaries, as evidenced by the backscatter image shown in Fig. 5(i).

The strong influence of sintering temperature on the phase formation and microstructure in the BF–PZ–PT ternary ceramics is also confirmed in their dielectric properties. Dielectric measurements were made on pellets of the MPB compositions A2, B2 and C1. Fig. 6 shows the temperature dependence of dielectric constant, ε_r, and loss tangent, tan δ, measured at 100 kHz. For compositions A2 and B2, significant difference in dielectric properties is observed in ceramics sintered at close temperatures. Although drastic change in the grain size and morphology was detected, the different impurity phases are believed to be the primary factor dictating the dielectric behavior. Ceramics sintered at lower temperatures with the $Bi_{46}Fe_2O_{72}$ impurity phase display a relatively higher dielectric constant at low temperatures and a diffuse transition around T_C. In contrast, ceramics sintered at higher temperatures with either $Bi_2Fe_4O_9$ or $Pb_2Bi_6O_{11}$ impurity phase show a sharp transition at T_C. The Curie temperatures

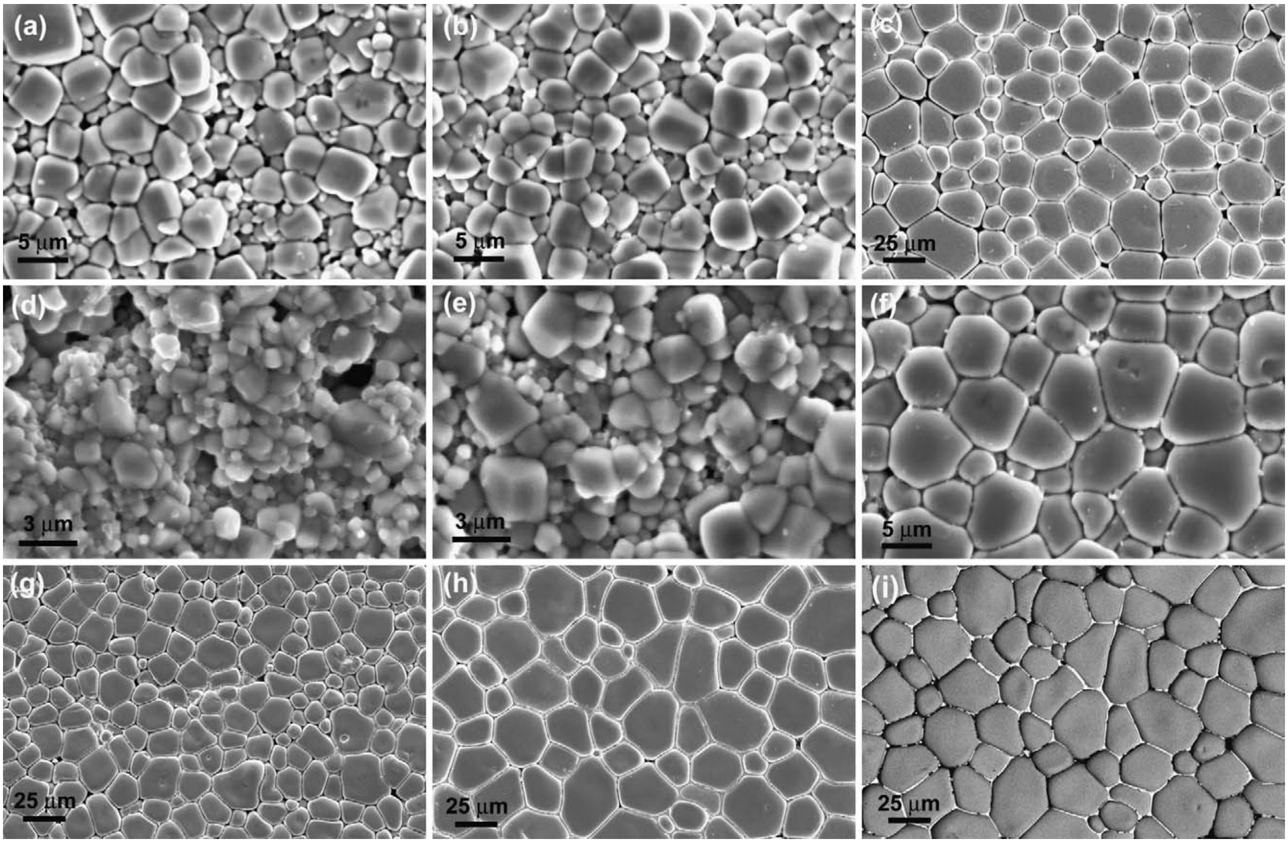

Fig. 5. SEM micrographs of the surfaces of MPB compositions A2 sintered at (a) 975 °C, (b) 1065 °C, (c) 1075 °C; B2 sintered at (d) 975 °C, (e) 1035 °C, (f) 1050 °C; and C1 sintered at (g) 975 °C, (h) 1025 °C. (i) SEM micrograph in the backscatter mode for (h) to indicate the grain boundary impurity phase.

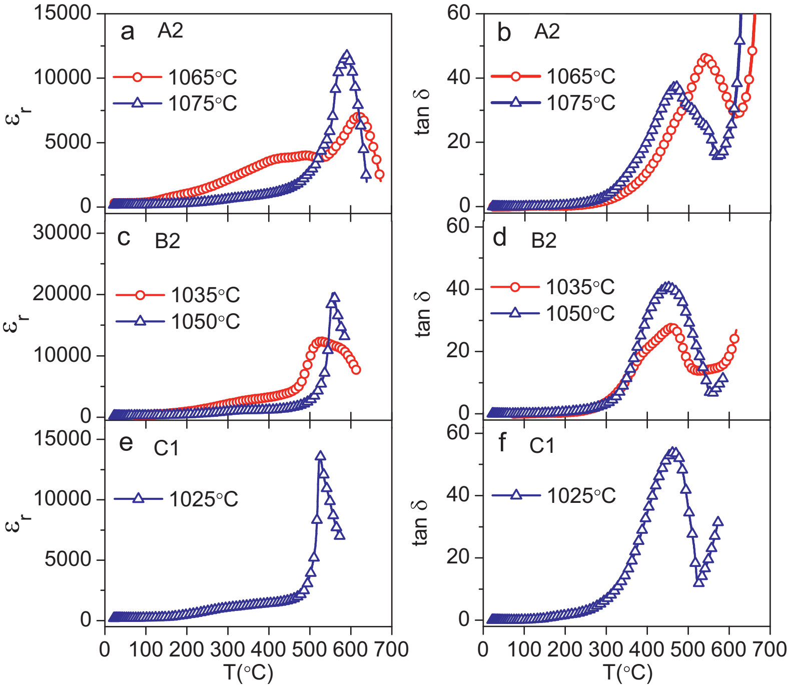

Fig. 6. Temperature dependence of dielectric properties measured at 100 kHz during heating in MPB composition A2 (a) dielectric constant ε_r, (b) loss tangent tan δ; composition B2 (c) ε_r, (d) tan δ; and composition C1 (e) ε_r, (f) tan δ.

Table 2
Comparison of the room temperature dielectric properties of the ternary BF–PZ–PT ceramics with the binary 0.67BF–0.33PT ceramic. The MPB ceramics A2, B2 and C1 were sintered at 1075, 1050, and 1025 °C, respectively.

Composition	T_C (°C)		1 kHz	10 kHz	100 kHz	1 MHz
A2	590	ε_r	225	219	214	208
		tan δ	0.044	0.019	0.019	0.028
B2	560	ε_r	237	232	229	222
		tan δ	0.025	0.014	0.013	0.016
C1	525	ε_r	285	283	280	277
		tan δ	0.008	0.007	0.008	0.012
0.67BF–0.33PT[13]	610	ε_r	117	105	101	99
		tan δ	0.185	0.056	0.025	0.040

T_C determined by the sharp anomalies on the ε_r vs. T curves are 590, 560 and 525 °C for A2, B2 and C1, respectively. Table 2 compares the room temperature dielectric properties of A2, B2 and C1 with a binary composition 0.67BF–0.33PT reported in literature.[13] It is evident that adding (PZ–PT) to (BF–PT) suppresses the dielectric loss and enhances the dielectric constant.

The Curie temperature in perovskite ferroelectric oxides is correlated with the room temperature lattice distortion.[2, 20] In the BF–PZ–PT ternary system, the lattice distortion can be represented by the *c*/*a* ratio of the tetragonal phase in the MPB compositions A2, B2 and C1. As shown in Fig. 7, a good correlation between the Curie temperature and the *c*/*a* ratio is present. It suggests that when the perovskite structure displays more distortion (greater *c*/*a*), more energy is needed to transform to the parent cubic structure, leading to a higher Curie temperature.

Fig. 8 shows the polarization vs. electric field hysteresis loops of ceramics A2, B2, and C1 sintered at different temperatures. Due to the suppressed dielectric loss in A2 and B2 sintered at lower temperatures, strong electric fields up to 70 kV/cm could be applied. Especially in ceramic B2 sintered at 1035 °C, a saturated P vs. E loop was recorded with a coercive field of 28.2 kV/cm and a remanent polarization of 15.0 μC/cm^2. It is noted that in a previous report on the MPB composition in the binary BF–PT system, the hysteresis loop displayed a much lower polarization and was still unsaturated even at 150 kV/cm.[16]

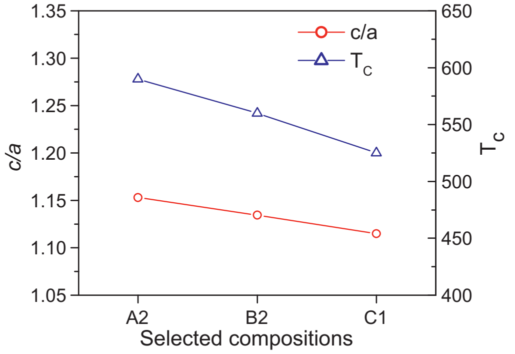

Fig. 7. The correlation between the *c*/*a* in the tetragonal phase and the Curie temperature in MPB compositions.

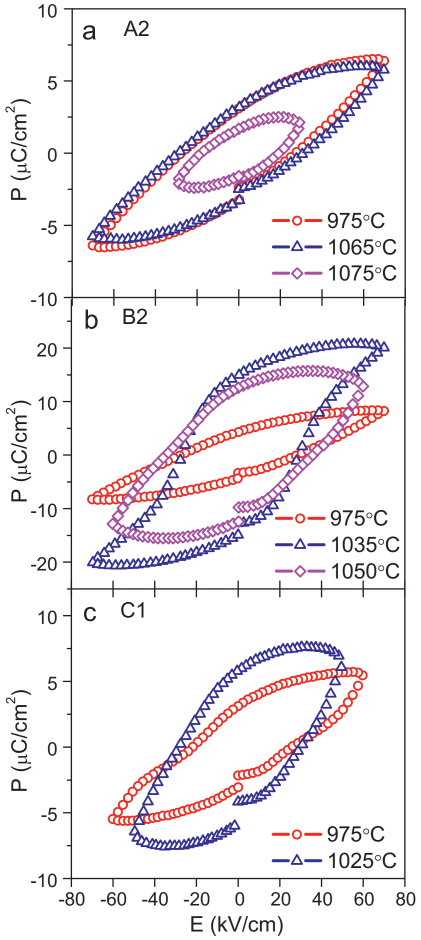

Fig. 8. The polarization vs. electric field hysteresis loops measured at room temperature at 4 Hz in MPB compositions A2, B2, and C1 sintered at different temperatures. (a) A2, (b) B2, and (c) C1.

Although higher sintering temperatures (1075 °C for A2, 1050 °C for B2 and 1025 °C for C1) demonstrated beneficial effects for a sharp phase transition at T_C (Fig. 6), they are detrimental to ferroelectric properties. The impurity phase along the grain boundaries [Fig. 5(i)] leads to a high leakage current under strong electric fields. The results are consistent with the dielectric loss measurement at room temperature at a low frequency (Fig. 9). At 20 Hz, the loss tangent decreases with increasing sintering temperature initially and then abruptly increases to high values when a different impurity phase was formed along grain boundaries at higher sintering temperatures. The low frequency dielectric loss is due to the space charge which is apparently related to the impurity phase along grain boundaries. Sehirlioglu et al. reported previously that excess Bi_2O_3 would enhance the resistivity and ferroelectric properties in $BiScO_3$–$PbTiO_3$.[21] It is speculated that the Bi-rich $Bi_{46}Fe_2O_{72}$ impurity phase formed under lower sintering temperatures is also critical to good ferroelectric properties in the BF–PZ–PT ternary solid solution system.

The severely distorted polarization vs. electric field hysteresis loops for the ceramic C1 (Fig. 8) suggest that it may have

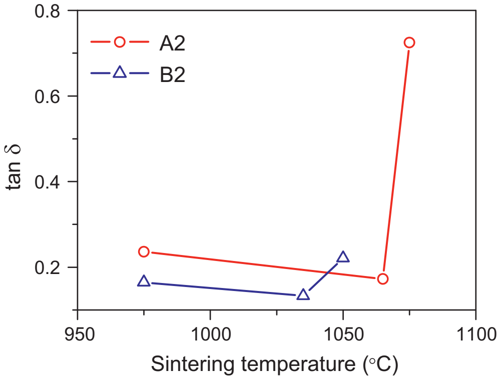

Fig. 9. Influence of sintering temperature on room temperature dielectric loss tangent (measured at 20 Hz) in MPB compositions A2 and B2.

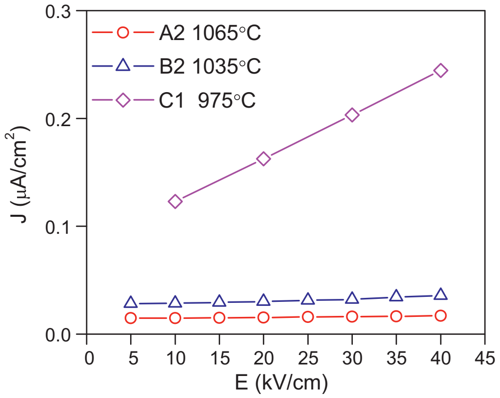

Fig. 10. Leakage current measured at room temperature on ceramics A2 (sintered at 1065 °C), B2 (sintered at 1035 °C), and C1 (sintered at 975 °C).

a high leakage current. Indeed, experimental measurements at room temperature on ceramics A2 (sintered at 1065 °C), B2 (sintered at 1035 °C), and C1 (sintered at 975 °C) confirmed this. As shown in Fig. 10, the leakage current from the ceramic C1 increases considerably as the applied electric field increases. At 40 kV/cm, it is about one order of magnitude higher than those from ceramics A2 and B2. The low leakage current from A2 and B2 allowed them to be poled. Both ceramics were poled at room temperature under 70 kV/cm for 1 h. For the ceramic A2 sintered at 1065 °C, d_{33} was 17 pC/N. The low piezoelectric coefficient can be attributed to the ultrahigh *c*/*a* ratio in this ceramic (Fig. 7), which suppresses contributions from domain wall motion.[20] For the ceramic B2 (sintered at 1035 °C) d_{33} was measured to be 64 pC/N. This value is comparable to previous results obtained from the $BiFeO_3$–$PbTiO_3$ ceramics.[15]

4. Conclusions

The $BiFeO_3$–$PbZrO_3$–$PbTiO_3$ ternary solid solution system was investigated for the development of piezoelectric ceramics with high Curie temperatures. The MPB compositions in the ternary system were found to deviate away from the mixture of two binary MPB compositions $0.70BiFeO_3$–$0.30PbTiO_3$ and $0.52PbZrO_3$–$0.48PbTiO_3$. The sintering temperature was observed to influence the rhombohedral/tetragonal phase ratio in the sintered ceramics. It was further revealed that the formation of impurity phases, ceramic density, grain morphology, dielectric as well as ferroelectric properties are all very sensitive to the sintering temperature. Although the ceramics sintered at higher temperatures exhibit good dielectric properties with a sharp paraelectric/ferroelectric transition, the impurity phase along the grain boundaries is obviously detrimental to the ferroelectric properties. To obtain ceramics with excellent piezoelectric performances and high Curie temperatures, the processing conditions need to be further optimized.

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