Piezoelectric Ceramics with Compositions at the Morphotropic Phase Boundary in the BiFeO3–PbZrO3–PbTiO3 Ternary System

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Abstract
Since ceramics in the PbZrO$_3$–PbTiO$_3$ binary system display excellent piezoelectric properties and those in BiFeO$_3$–PbTiO$_3$ exhibit high Curie temperatures, morphotropic phase boundary (MPB) compositions in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary solid solution system are investigated for the development of piezoelectric ceramics for high temperature applications. It is found that the MPB compositions in the ternary system deviate away from the mixture of two binary MPB compositions 0.70BiFeO$_3$–0.30PbTiO$_3$ and 0.52PbZrO$_3$–0.48PbTiO$_3$. With decreasing amount of BiFeO$_3$ in the MPB compositions in the ternary system, the Curie temperature $T_C$ is observed to decrease while the piezoelectric coefficient $d_{33}$ is found to increase. Accompanied with this trend are the decrease in the $c/a$ ratio of the tetragonal phase, the increase in the dielectric constant and the decrease in the loss tangent of the ceramics at room temperature. It is further noticed that the compositions in the rhombohedral-rich side of MPB exhibit slightly better piezoelectric properties. An example of such compositions is 0.511BiFeO$_3$–0.326PbZrO$_3$–0.163PbTiO$_3$, with $T_C$ of 431°C, $d_{33}$ of 101 pC/N, and the electromechanical coupling factor $k_p$ of 0.50.

Keywords
Institute for Combinatorial Discovery, Piezoelectric ceramics, Morphotropic phase boundary, electrical properties, BiFeO$_3$–PbZrO$_3$–PbTiO$_3$

Disciplines
Ceramic Materials | Engineering Physics | Thermodynamics

Comments

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Piezoelectric Ceramics with Compositions at the Morphotropic Phase Boundary in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ Ternary System

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This work was supported by the Air Force Office of Scientific Research through Grant FA9550-08-1-0316.

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Abstract

Since ceramics in the PbZrO$_3$–PbTiO$_3$ binary system display excellent piezoelectric properties and those in BiFeO$_3$–PbTiO$_3$ exhibit high Curie temperatures, morphotropic phase boundary (MPB) compositions in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary solid solution system are investigated for the development of piezoelectric ceramics for high temperature applications. It is found that the MPB compositions in the ternary system deviate away from the mixture of two binary MPB compositions 0.70BiFeO$_3$–0.30PbTiO$_3$ and 0.52PbZrO$_3$–0.48PbTiO$_3$. With decreasing amount of BiFeO$_3$ in the MPB compositions in the ternary system, the Curie temperature $T_C$ is observed to decrease while the piezoelectric coefficient $d_{33}$ is found to increase. Accompanied with this trend are the decrease in the $c/a$ ratio of the tetragonal phase, the increase in the dielectric constant and the decrease in the loss tangent of the ceramics at room temperature. It is further noticed that the compositions in the rhombohedral-rich side of MPB exhibit slightly better piezoelectric properties. An example of such compositions is 0.511BiFeO$_3$–0.326PbZrO$_3$–0.163PbTiO$_3$, with $T_C$ of 431 °C, $d_{33}$ of 101 pC/N, and the electromechanical coupling factor $k_p$ of 0.50.

*Keywords:* Piezoelectric ceramics; Morphotropic phase boundary; electrical properties; BiFeO$_3$–PbZrO$_3$–PbTiO$_3$. 
I. Introduction

BiFeO$_3$–PbTiO$_3$ binary system is of great interest for high temperature applications due to the high Curie temperature (630 °C) at the MPB composition.$^1$ However, the large coercive field of the ceramic leads to unsaturated hysteresis loops and the leakage current hinders the poling process.$^{2-5}$ Various cations have been employed to suppress the dielectric loss in BiFeO$_3$ and BiFeO$_3$-based ceramics.$^6$-$^{10}$ However, only limited success has been achieved in enhancing their dielectric, ferroelectric and piezoelectric properties. Another peculiar aspect of the MPB composition in the BiFeO$_3$–PbTiO$_3$ system is its extremely high tetragonality ($c/a = 1.18$).$^1$ The large tetragonal distortion was suggested to be responsible for the high internal stresses in the ceramic and the high resistance in domain switching under electric fields.$^{11,12}$ The high internal stress could lead the ceramic to shred during processing. Reduction in tetragonality by chemical modification seems always to be accompanied with decrease in the Curie temperature.$^{13}$

In our previous study, PbZrO$_3$ was introduced to the BiFeO$_3$–PbTiO$_3$ solid solution for the development of ceramics with combined high Curie temperatures and high piezoelectric properties.$^{14}$ In order to preserve the high Curie temperature, MPB compositions near the BiFeO$_3$–PbTiO$_3$ side in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary system were investigated. The study showed that the dielectric loss was suppressed and saturated hysteresis loop could be observed at relatively low electric fields in these MPB compositions. However, the piezoelectric coefficient $d_{33}$ achieved was moderate (64 pC/N).$^{14}$ The present investigation is a follow-up study, expanding the search for the MPB compositions in a much wider range in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary system. Electrical properties in the tetragonal phase-rich and the rhombohedral phase-rich MPB compositions are compared.
II. Experimental Procedure

Ceramics in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary system were prepared by the mixed oxide solid state reaction method. Powders of Bi$_2$O$_3$ (99.9995%, Alfa Aesar), Fe$_2$O$_3$ (99.99%, Alfa Aesar), PbO (99.99%, Alfa Aesar), TiO$_2$ (99.99%, Aldrich) and ZrO$_2$ (99.978%, Alfa Aesar) were mixed and milled with a vibratory mill in ethanol for 6 hours. To compensate the evaporation loss in the subsequent high temperature processing, 2 mol.% excess of PbO and 1 mol.% excess of Bi$_2$O$_3$ were included. After drying, the mixed powder was pressed as a pellet and calcined at 850 °C for 4 hours. The calcined pellet was ground and milled for 15 hours again and then uniaxially pressed into disks at 180 MPa with 2 wt.% polyvinyl alcohol aqueous solution as binder. The pressed disk was buried in the powder with the same composition and sintered at 1075 °C for 2 hours.

The Archimedes’ method was employed to determine the density of sintered pellets. The grain morphology of as-sintered pellets was observed by scanning electronic microscope (JEOL JSM-606LV, Peabody, MA). After removal of the surface layer of the sintered pellets, the phase development was analyzed using X-ray diffractometer with Cu-K$\alpha$ radiation (Siemens D-500, Bruker AXS, Madison, WI). For electrical characterization, sintered pellets were polished and electroded with a thin layer of silver. An LCR meter (HP 4284A, Agilent Technologies, Palo Alto, CA) in conjunction with a high temperature sample holder cell system (ProboStat, NorECs AS, Oslo, Norway) was used to measure the temperature dependence of dielectric constant and loss tangent during heating from room temperature to 600 °C at the rate of 4 °C/min. The polarization vs. electric field hysteretic loops were measured with the standardized ferroelectric test system (RT-66A, Radiant Technologies, Albuquerque, NM) at room temperature at ~4 Hz. For piezoelectric characterization, the ceramic specimens were poled under 70 kV/cm at room
temperature for 30 minutes. The piezoelectric coefficient $d_{33}$ was measured 24 hours after poling with a piezo-$d_{33}$ meter (ZJ-4B, Shanghai Institute of Ceramics, China). The temperature dependence of the planar coupling factor, $k_p$, of the poled specimens was measured by an impedance analyzer (HP 4194A, Agilent Technologies, Palo Alto, CA) in conjunction with an environmental test chamber (Delta Design 9015, Delta Design, Poway, CA).

III. Results

The strategy for identifying the MPB compositions in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary system in the present study is schematically shown in Fig. 1. Four initial compositions, denoted as D0, E0, F0, and G0, were selected from the straight line connecting 0.70BiFeO$_3$–0.30PbTiO$_3$ and 0.52PbZrO$_3$–0.48PbTiO$_3$ (They are the MPB compositions in the binary systems). Expanding from our previous study where compositions A0, B0 and C0 contained 5, 10, and 15 mol.% of 0.52PbZrO$_3$–0.48PbTiO$_3$, respectively, the compositions D0, E0, F0 and G0 in the present work contain 20, 30, 40, and 50 mol.% of 0.52PbZrO$_3$–0.48PbTiO$_3$, respectively. X-ray diffraction analysis indicates that only D0 sits in the tetragonal side of the MPB while the other three compositions are in pure tetragonal phase (Fig. 2). The next step in locating the MPB compositions in the ternary system was to reduce the content of PbTiO$_3$ while maintaining the molar ratio between BiFeO$_3$ and PbZrO$_3$ in the four initial compositions, as schematically shown in Fig. 1(b). Initially the change in PbTiO$_3$ content was at a greater step size. When the composition is in the MPB region, the step size for varying PbTiO$_3$ content was controlled around 0.7 mol.%.

X-ray diffraction patterns of all four series of compositions with reduced PbTiO$_3$ contents from their corresponding initial compositions D0, E0, F0, and G0 were recorded and analyzed.
The pseudocubic (200) diffraction peak was focused to determine the MPB separating the rhombohedral and the tetragonal perovskite phase. As shown in Fig. 3, compositions D0, E1, F1, G1 are in the tetragonal side while D2, E3, F3, G3 are in the rhombohedral side of the MPB region in the ternary system. In between are the compositions D1, E2, F2, G2, which are referred to as the “MPB center composition” hereafter. The exact contents of these MPB compositions, together with the initial compositions, are listed in Table 1. Further semiquantitative analysis was performed on the pseudocubic (200) diffraction peaks shown in Fig. 3. Their intensity profiles were deconvoluted with the pseudo-Voigt function. The intensity ratio was employed to estimate the volume ratio between the rhombohedral (R) and the tetragonal (T) phase according to:

$$\frac{R}{T} = \frac{I_{R200}}{I_{T002} + I_{T200}}$$

where $I_{R200}$ represents the integrated intensity of the deconvoluted rhombohedral (200) peak, while $I_{T200}$ and $I_{T002}$ are the intensity of the deconvoluted tetragonal (200) and (002) peaks, respectively. The results, listed in Table 2, confirm that $R/T$ ratio is close to 1 in the MPB center compositions D1, E2, F2, and G2. The ratio $R/T$ is less than 1 in compositions D0, E1, F1, G1 and greater than 1 in D2, E3, F3, and G3.

The sintered pellets of all compositions are of high quality. Density measurement with the Archimedes’ method indicates that the relative density value for all the sintered pellets is between 93% and 96%. Scanning electron microscopy (SEM) examination confirms the high density and indicates a uniform grain size. Figure 4 shows the SEM micrographs of the surfaces of as-sintered pellets for the four MPB center compositions. The grain sizes were determined with the linear intercept method and the average values are 2.6, 3.2, 3.5 and 3.0 µm for D1, E2,
F2 and G2, respectively. It is seen that the grain size in composition D1 is slightly smaller than the other three compositions. However, the grain size and morphology are almost the same for compositions within each composition series.

The dielectric property of the four MPB center compositions was characterized and is displayed in Fig. 5. From Fig. 5(a) where the dielectric constant, $\varepsilon_r$, measured at 100 kHz is shown, ceramics D1 and E2 exhibit a sharp ferroelectric to paraelectric transition, while F2 and G2 display a broad peak. The ceramic E2 shows the highest peak value of $\varepsilon_r$. The Curie temperature, $T_C$, for ceramics D1, E2, F2, and G2 is determined to be 494, 438, 393 and 361 °C, respectively. The ceramic D1 still shows a high loss tangent at temperatures above 100 °C, but a progressive suppression of tan$\delta$ is evident in compositions E2, F2, and G2. The Curie temperature $T_C$, the $\varepsilon_r$ and tan$\delta$ at room temperature for all 12 compositions are summarized in Table 2. It is noticed that $T_C$ of the MPB center compositions are slightly higher than that of both R-rich and T-rich MPB compositions in the same series. The room temperature tan$\delta$ value remains low and almost unchanged for all compositions. However, the $\varepsilon_r$ at room temperature apparently increases as the composition changes from series D to series G.

Figure 6 shows the polarization vs. electric field hysteresis loops under 80 kV/cm, measured at 4 Hz for all specimens. Note that the polarization scale for composition D and E series is the same. The scale for F and G series is the same but is larger than that of D and E. It is evident that saturated hysteresis loops can be obtained in compositions in series F and G while only unsaturated loops are seen in series D and E. It also appears that a higher rhombohedral to tetragonal phase ratio ($R/T$) corresponds to a higher remanent polarization, $P_r$, within the same composition series. However, there is not an obvious trend for the coercive field, $E_c$. Figure 6
also reveals slightly distorted hysteresis loops in ceramics E1, F1, and G1 with tetragonal phase rich, suggesting that large amounts of tetragonal phase may hamper the motion of domain walls and lead to smaller polarizations. The remanent polarization \( P_r \) and the coercive field \( E_c \) measured from hysteresis loops shown in Fig. 6 are listed in Table 2. It should be pointed out that, strictly speaking, the values in Table 2 from unsaturated loops are not the real physical property \( P_r \) and \( E_c \) since they can be quite different under different measuring peak fields.

The measured piezoelectric coefficient \( d_{33} \) for all 12 compositions are also tabulated in Table 2. The beneficial effect of a higher \( R/T \) ratio on remanent polarization is also seen on \( d_{33} \). This can be better appreciated from the plot displayed in Fig. 7. The rhombohedral phase rich MPB compositions (D2, E3, F3, G3) display \( d_{33} \) values even higher than their corresponding MPB center compositions, especially in series D. In addition, progressive improvements in \( d_{33} \) are seen in composition series D, E, F, and G: Series G displays the best \( d_{33} \) with a value of 132 pC/N in the rhombohedral phase rich composition G3. It should be noted that these samples were poled at room temperature for the \( d_{33} \) measurement. It is very likely that higher values of \( d_{33} \) could be observed in these ceramics if poled at a higher temperature.

Since compositions D2, E3, F3, and G3 display the highest \( d_{33} \) in each composition series, these four compositions were selected to further evaluate their potential for high temperature piezoelectric applications. The temperature dependence of the planar coupling factor \( k_p \) in these four compositions was measured from room temperature to 200 °C and the results are displayed in Fig. 8. The \( k_p \) at room temperature is 0.49, 0.50, 0.63 and 0.65 for D2, E3, F3, and G3, respectively. These values are comparable to lead zirconate titanate (PZT) ceramics and are much higher than pure and modified BiFeO\(_3\)-PbTiO\(_3\) solid solutions.\(^{15-17}\) Except composition
D2, these compositions maintain a stable $k_p$ up to at least 200 °C. Composition D2 appeared to lose its piezoelectricity at 200 °C due to the high dielectric loss at this temperature (The loss tangent of D2 is similar to that of D1 which is shown in Fig. 5b). Additional measurements at temperatures above 200 °C are needed to identify the upper limit of the working temperature for these compositions in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary system.

IV. Discussion

In piezoelectric ceramics, a higher piezoelectric coefficient $d_{33}$ is generally observed in a composition with a lower Curie temperature.\textsuperscript{18-20} It has been speculated that this trend is resulted from the higher dielectric permittivity in compositions with lower Curie temperatures.\textsuperscript{18,19} This trend is observed again in the present study, as shown in Fig. 9. However, in this BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary system, the lattice distortion in the tetragonal phase, as manifested in the $c/a$ ratio, may also influence the piezoelectric property. It is evident from Fig. 9 (and also Fig. 3) that the $c/a$ ratio decreases considerably as the Curie temperature $T_C$ decreases. For example, from composition D1 ($T_C = 494$ °C) to E2 ($T_C = 438$ °C), the increase of $d_{33}$ from 60 pC/N to 99 pC/N is accompanied with a drop of $c/a$ from 1.07 to 1.04. It is argued that higher tetragonality introduces larger internal stresses during cooling after sintering, which could limit ferroelectric domain wall motion.\textsuperscript{11,12} In addition, switching between $a$ and $c$ lattice parameters during domain polarization switching under applied electric fields is definitely easier in compositions with a lower $c/a$ ratio. This explains that the hysteresis loops in ceramics D1 and E2 remained unsaturated even under high electric fields (Fig. 6). Compared to the tetragonal phase, the rhombohedral perovskite phase induces lower internal stresses at the ferroelectric/paraelectric
phase transition and a smaller lattice distortion is resulted from ferroelectric polarization switching. Therefore, domain walls are more mobile in compositions with a lower $c/a$ in the tetragonal phase and a higher volume fraction of the rhombohedral phase. These ceramics will have a higher efficiency in the poling process. As a result, larger remanent polarizations and higher piezoelectric coefficients are anticipated.

The present study indicates that combining two MPB compositions in the binary BiFeO$_3$–PbTiO$_3$ and PbZrO$_3$–PbTiO$_3$ systems at different proportions does not lead to the MPB compositions in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary system. Identifying the MPB compositions in the ternary system requires a time-consuming trial and error approach. Figure 10 shows the exact locations of these MPB compositions in part of the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary phase diagram. For the sake of completeness, composition series A, B, and C reported in our previous study$^{14}$ which contain 5, 10 and 15 mol.% of 0.52PbZrO$_3$–0.48PbTiO$_3$ respectively, are also depicted in Fig. 10. Compositions further away from BiFeO$_3$ (beyond series G) were not explored because the $T_C$ in series G is already lower than that in PZT ceramics. The MPB in this portion of the ternary system is the line connecting the circles. The area above this MPB in the PbTiO$_3$ side is the tetragonal phase field, while that in the lower part is the rhombohedral field. Moving along the MPB from A toward G can be thought as adding the content of PZT to BiFeO$_3$–PbTiO$_3$. Figure 11 clearly shows that adding PZT to BiFeO$_3$–PbTiO$_3$ increases the room temperature dielectric constant gradually and significantly suppresses the dielectric loss. The enhanced dielectric permittivity is an important contributor to the high piezoelectric coefficient $d_{33}$. Again, it should be noted that the piezoelectric property is enhanced at the price of decreased Curie temperature. A good compromise between Curie temperature and
piezoelectric property seems to occur in the ceramic E3 with $T_C$ of 431 °C, $d_{33}$ of 101 pC/N and $k_p$ of 0.50 at room temperature.

V. Conclusions

The BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary solid solution system was thoroughly 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$_3$. Adding PZT to BiFeO$_3$–PbTiO$_3$ decreases the Curie temperature, enhances the room temperature dielectric permittivity, significantly suppresses the dielectric loss, considerably increases the remanent polarization, and improves the piezoelectric property. A higher rhombohedral/tetragonal phase ratio in the MPB region appears to be favorable for the ferroelectric and piezoelectric properties.

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High Temperature Morphotrophic Phase Boundary Piezoelectrics Based on Bi(Me)O₃-PbTiO₃
Fig. 1. The strategy for identifying the MPB compositions in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary solid solution system. (a) The first step was to mix 0.70BiFeO$_3$–0.30PbTiO$_3$ with 0.52PbZrO$_3$–0.48PbTiO$_3$ at 20 mol.% (D0), 30 mol.% (E0), 40 mol.% (F0), and 50 mol.% (G0). (b) A close look at the boxed area in (a) to show the second step where the content of PbTiO$_3$ was reduced while the molar ratio between BiFeO$_3$ and PbZrO$_3$ was maintained.

Fig. 2. Phase development in the ceramics D0, E0, F0, and G0 sintered at 1075 °C. These compositions are either tetragonal phase rich (D0) or of pure tetragonal phase (E0, F0, G0). The diffraction peaks are indexed on the basis of a tetragonal unit cell.

Fig. 3. Close examination of the pseudocubic (200) diffraction peak in sintered ceramics of (a) D0, D1, and D2, (b) E1, E2, and E3, (c) F1, F2, and F3, (d) G1, G2, and G3. Compositions D1, E2, F2 and G2 are referred to as the MPB center compositions containing approximately equal amount of rhombohedral and tetragonal phases. T denotes tetragonal while R for rhombohedral perovskite phase, respectively. Note the display range of 2θ is the same for four panels and the decrease in the c/a ratio is obvious.

Fig. 4. SEM micrographs of the surfaces of sintered pellets with MPB center compositions. (a) D1, (b) E2, (c) F2, and (d) G2.

Fig. 5. Temperature dependence of dielectric properties measured at 100 kHz during heating in MPB center compositions D1, E2, F2, and G2. (a) Dielectric constant $\varepsilon_r$, (b) loss tangent $\tan \delta$.

Fig. 6. The polarization vs. electric field hysteresis loops measured at room temperature at ~4 Hz in all compositions. (a) The D series, (b) the E series, (c) the F series, and (d) the G series.

Fig. 7. The influence of the rhombohedral/tetragonal phase ratio (R/T) upon the piezoelectric coefficient $d_{33}$ for the four series of compositions.
Fig. 8. The evolution of the planar coupling factor $k_p$ of ceramics D2, E3, F3 and G3 during heating up to 200 °C.

Fig. 9. The correlation of $d_{33}$ and $c/a$ with the Curie temperature $T_C$ in the MPB center compositions D1, E2, F2 and G2.

Fig. 10. The exact locations of the MPB center compositions in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary system. The MPB region in the ternary system deviates from the thin dashed line which connects the two binary MPB compositions.

Fig. 11. The change of room temperature dielectric properties measured at 100 kHz with composition from series A to G.
Table 1. Compositions in molar fractions of the ceramics investigated in the present study. Bold font denotes the MPB center compositions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>BiFeO$_3$</th>
<th>PbTiO$_3$</th>
<th>PbZrO$_3$</th>
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</thead>
<tbody>
<tr>
<td>D0</td>
<td>0.560</td>
<td>0.336</td>
<td>0.104</td>
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<tr>
<td><strong>D1</strong></td>
<td><strong>0.566</strong></td>
<td><strong>0.329</strong></td>
<td><strong>0.105</strong></td>
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<tr>
<td>D2</td>
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<td>0.106</td>
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<tr>
<td>E0</td>
<td>0.490</td>
<td>0.354</td>
<td>0.156</td>
</tr>
<tr>
<td>E1</td>
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<td>0.340</td>
<td>0.159</td>
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<tr>
<td><strong>E2</strong></td>
<td><strong>0.506</strong></td>
<td><strong>0.333</strong></td>
<td><strong>0.161</strong></td>
</tr>
<tr>
<td>E3</td>
<td>0.511</td>
<td>0.326</td>
<td>0.163</td>
</tr>
<tr>
<td>F0</td>
<td>0.420</td>
<td>0.372</td>
<td>0.208</td>
</tr>
<tr>
<td>F1</td>
<td>0.440</td>
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<td><strong>F2</strong></td>
<td><strong>0.445</strong></td>
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<tr>
<td>F3</td>
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<tr>
<td>G0</td>
<td>0.350</td>
<td>0.390</td>
<td>0.260</td>
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<tr>
<td>G1</td>
<td>0.368</td>
<td>0.359</td>
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<tr>
<td><strong>G2</strong></td>
<td><strong>0.372</strong></td>
<td><strong>0.351</strong></td>
<td><strong>0.277</strong></td>
</tr>
<tr>
<td>G3</td>
<td>0.377</td>
<td>0.343</td>
<td>0.280</td>
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Table 2. The rhombohedral/tetragonal phase ratio \(R/T\), Curie temperature \(T_C\), dielectric constant \(\varepsilon_r\) and \(\tan \delta\) (100 kHz) at room temperature, remanent polarization \(P_r\), coercive field \(E_c\), and piezoelectric coefficient \(d_{33}\) of compositions investigated in the BiFeO\(_3\)–PbZrO\(_3\)–PbTiO\(_3\) ternary system. Bold font denotes the MPB center compositions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>(R/T)</th>
<th>(T_C) (°C)</th>
<th>(\varepsilon_r) at RT</th>
<th>(\tan \delta) at RT</th>
<th>(P_r) (µC/cm(^2))</th>
<th>(E_c) (kV/cm)</th>
<th>(d_{33}) (pC/N)</th>
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<tbody>
<tr>
<td>D0</td>
<td>0.5</td>
<td>492</td>
<td>264</td>
<td>0.0041</td>
<td>0.7</td>
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<td>263</td>
<td>0.0038</td>
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<td>21.5</td>
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<tr>
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<td>0.6</td>
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<td>0.0040</td>
<td>1.4</td>
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<tr>
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Fig. 1. The compositions studied in the BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary phase diagram. (a) Four compositions (D0, E0, F0, G0) on the straight line connecting the two MPB compositions in binary BiFeO$_3$–PbTiO$_3$ and PbZrO$_3$–PbTiO$_3$ systems are initially prepared, which contain 20, 30, 40 and 50 mol% of 0.52PbZrO$_3$–0.48PbTiO$_3$ respectively. (b) A close look to the selected region to indicate additional compositions prepared to locate the MPB compositions.
Fig. 2. Phase formation in the ceramics D0, E0, F0 and G0 sintered at 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.
Fig. 3. Change in phase formation driven by composition variation around MPB in the sintered ceramics (a) D0, D1 and D2, (b) E1, E2 and E3, (c) F1, F2 and F3, (d) G1, G2 and G3. D1, E2, F2 and G2 are determined as the MPB composition containing approximately equal amounts of rhombohedral and tetragonal phases. T denotes tetragonal while R for rhombohedral perovskite phase, respectively.
Fig. 4. SEM micrographs of the surfaces of sintered pellets with MPB compositions (a) D1, (b) E2, (c) F2 and (d) G2
Fig. 5. Temperature dependence of dielectric properties measured at 100 kHz during heating in MPB compositions D1, E2, F2 and G2 (a) dielectric constant $\varepsilon_r$, (b) loss tangent $\tan \delta$. 
Fig. 6. The polarization vs. electric field hysteresis loops measured at room temperature at 4Hz in compositions with varied rhombohedral/tetragonal phase ratio: (a) D0~D2, (b) E1~E3, (c) F1~F3 and (d) G1~G3.
Fig. 7. The influence of rhombohedral/tetragonal phase ratio upon the $d_{33}$ of ceramics poled at room temperature under 70kV for 30 mins. T denotes tetragonal while R for rhombohedral perovskite phase, respectively.
Fig. 8. The temperature dependence of planar coupling coefficient $k_p$ of ceramics D2, E3, F3 and G3 during heating up to 200°C. D2 was decoupled at 200°C, therefore no data is presented.
Fig. 9. The correlation of Curie temperature $T_C$ of MPB compositions D1, E2, F2 and G2 with piezoelectric coefficient $d_{33}$ of ceramics poled at 70kV/cm and tetragonality $c/a$. 
Fig. 10. The real MPB compositions for BiFeO$_3$–PbZrO$_3$–PbTiO$_3$ ternary system, which deviate from the straight line connecting the two MPB compositions in binary BiFeO$_3$–PbTiO$_3$ and PbZrO$_3$–PbTiO$_3$ systems.
Fig. 11 The change of room temperature dielectric properties measured at 100kHz with the Curie temperature in BiFeO₃–PbZrO₃–PbTiO₃ system