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# The Morphotropic Phase Boundary in the (1-x)PbZrO<sub>3</sub>-x[0.3Bi(Zn<sup>1/2</sup>Ti<sup>1/2</sup>)<sub>2</sub>O<sub>3</sub>-0.7PbTiO<sub>3</sub>] Perovskite Solid Solution

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# The Morphotropic Phase Boundary in the $(1-x)\text{PbZrO}_3-x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-0.7\text{PbTiO}_3]$ Perovskite Solid Solution

## Abstract

Ceramics in the  $(1-x)\text{PbZrO}_3-x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-0.7\text{PbTiO}_3]$  solid solution system with  $0.48 \leq x \leq 0.56$  were investigated. A morphotropic phase boundary separating rhombohedral and tetragonal perovskite phases was identified at  $x = 0.52$ . This composition displays the maximum remanent polarization  $P_r$  of  $40.7 \mu\text{C}/\text{cm}^2$  and the best piezoelectric coefficient  $d_{33}$  of  $311 \text{ pC}/\text{N}$  in the pseudo-binary system. However, the Curie temperature  $T_c$  for this MPB composition is  $291 \text{ }^\circ\text{C}$ , much lower than initially expected.

## Keywords

Morphotropic phase boundary, piezoelectric properties,  $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ , PZT

## Disciplines

Ceramic Materials | Engineering Physics | Tribology

## Comments

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## The Morphotropic Phase Boundary in the $(1-x)\text{PbZrO}_3-x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-0.7\text{PbTiO}_3]$ Perovskite Solid Solution

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**Abstract** Ceramics in the  $(1-x)\text{PbZrO}_3-x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-0.7\text{PbTiO}_3]$  solid solution system with  $0.48 \leq x \leq 0.56$  were investigated. A morphotropic phase boundary separating rhombohedral and tetragonal perovskite phases was identified at  $x = 0.52$ . This composition displays the maximum remanent polarization  $P_r$  of  $40.7 \mu\text{C}/\text{cm}^2$  and the best piezoelectric coefficient  $d_{33}$  of  $311 \text{ pC}/\text{N}$  in the pseudo-binary system. However, the Curie temperature  $T_c$  for this MPB composition is  $291 \text{ }^\circ\text{C}$ , much lower than initially expected.

*Keywords:* Morphotropic phase boundary, piezoelectric properties;  $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ; PZT

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## Introduction

Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub>-based perovskite ceramics with compositions near the morphotropic phase boundary (MPB) have been widely investigated due to their excellent piezoelectric performance [1-4]. Recently the application of Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub>-based ceramics has been challenged for their relatively low Curie point (T<sub>c</sub>) and the environmental concern on Pb [5, 6]. Since Bi<sup>3+</sup> cation possesses a similar electron configuration (6s<sup>2</sup>) to that of Pb<sup>2+</sup>, it has been often used to substitute Pb<sup>2+</sup> on the A-site in the perovskite lattice to reduce the Pb-content [7-13]. Some of these Bi-substituted compositions not only display piezoelectric properties comparable to Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub>-based ceramics, but also exhibit increased Curie temperatures [5, 8, 12].

When the high Curie temperature is of primary interest, the solid solutions BiFeO<sub>3</sub>-PbTiO<sub>3</sub> and Bi(Zn<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> stand out [7, 9, 14]. In the former binary system, a morphotropic phase boundary (MPB), separating the rhombohedral and the tetragonal perovskite structure, exists at around 0.7BiFeO<sub>3</sub>-0.3PbTiO<sub>3</sub> [7, 15]. This MPB composition displays a high Curie temperature of 650 °C and a large distortion in its tetragonal phase (*c/a* ~ 1.18). However, the ceramic processing of this composition has been an issue and various dopants have been utilized to improve the ceramic density and suppress the electrical conductivity [16, 17].

Among Bi-containing perovskite compounds, Bi(Zn<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub> (BZT) is unique for its extremely large *c/a* ratio of 1.21 and a high spontaneous polarization P<sub>s</sub> of 103 μC/cm<sup>2</sup> [18]. Perovskite compound PbTiO<sub>3</sub> (PT) has been reported to form solid solutions with BZT at ambient conditions [9]. In the BZT-PT binary system, both the tetragonality and the Curie point increase with increasing amount of BZT and no morphotropic phase boundary (MPB) was observed. In particular, the composition 0.3BZT-0.7PT exhibits a high *c/a* ratio of 1.09 and a high Curie point exceeding 650°C [9].

Following our previous approach combining the binary systems of BiFeO<sub>3</sub>–PbTiO<sub>3</sub> with a high-T<sub>c</sub> and of PbZrO<sub>3</sub>–PbTiO<sub>3</sub> with high piezoelectric properties [19, 20], the present work combines the Bi(Zn<sub>1/2</sub>Ti<sub>1/2</sub>)O<sub>3</sub>–PbTiO<sub>3</sub> and PbZrO<sub>3</sub>–PbTiO<sub>3</sub> to form a ternary system, with the aim to produce ferroelectric ceramics with high Curie temperatures and good piezoelectric performance.

### **Experimental Procedure**

Ceramics of (1-*x*)PbZrO<sub>3</sub>–*x*[0.3BZT–0.7PT] with *x* = 0.48, 0.50, 0.52, 0.54 and 0.56 were synthesized by the solid state reaction method. High-purity oxide powders PbO (99.99%, Alfa Aesar), Bi<sub>2</sub>O<sub>3</sub> (99.9%, Aldrich), ZrO<sub>2</sub> (99.98%, Alfa Aesar), TiO<sub>2</sub> (99.99%, Aldrich) and ZnO (99.99%, Alfa Aesar) were used as starting materials. The mixed powders were milled in ethanol using vibratory mill for 6 hours. After that, the powders were uniaxially pressed into pellets and calcined at 850 °C for 4 hours. The calcined powders were milled again for 15 hours to reduce the particle size. Sintering was carried out at temperatures between 1113 °C and 1200 °C for 3 hours, depending on the composition.

The Archimedes' method was used to measure the density of the sintered ceramics. The phase development was examined on sintered samples with x-ray diffractometer (Siemens D-500, Bruker AXS) using Cu K $\alpha$  radiation. Grain size of the ceramics was analyzed by observing the fracture surface of sintered samples with scanning electron microscope (JEOL, JSM-606LV). For electrical measurements, sintered ceramics were ground, polished and electroded with silver coating. The temperature dependence of dielectric constant and loss tangent during heating from room temperature to 450 °C at 3 °C/min. was measured with the LCR meter (HP 4284A, Hewlett-Packard) in conjunction with a high temperature sample holder cell system (ProboStat,

NorECs). The ferroelectric hysteresis ( $P$ - $E$ ) loops were characterized by the standard ferroelectric test system (RT66A, Radiant technologies). For piezoelectric characterization, ceramic specimens were poled at 40 kV/cm at 100 °C 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).

## Results and Discussion

The compositions of  $(1-x)\text{PbZrO}_3-x[0.3\text{BZT}-0.7\text{PT}]$  with  $x = 0.48, 0.50, 0.52, 0.54$  and  $0.56$  studied in the present work are marked as red dots in the PZ–BZT–PT ternary phase diagram shown in Fig. 1. The phase diagram was originally proposed by Dwivedi and Randall based on their experimental investigations on the pseudo-binary system of  $0.1\text{BZT}-0.9[(1-x)\text{PZ}-x\text{PT}]$  [21, 22]. The X-ray diffraction patterns of the sintered ceramics are displayed in Fig. 2, where the structural transition can be observed in the splitting of the (100), (111) and (200) pseudo-cubic peaks. The obvious splitting of (100) and (200) peaks confirms a tetragonal structure for the composition  $x = 0.56$ . Both tetragonal and rhombohedral phases coexist in the composition range  $0.48 \leq x \leq 0.54$ , which could be determined as the MPB region in the present pseudo-binary system. The composition  $x = 0.52$  was found to have comparable amounts of tetragonal and rhombohedral phases, which can be referred to as the MPB center composition. Dwivedi and Randall identified  $0.1\text{BZT}-0.5\text{PZ}-0.4\text{PT}$  as the MPB composition in the  $0.1\text{BZT}-0.9[(1-x)\text{PZ}-x\text{PT}]$  pseudo-binary system [21, 22]. It is known that the MPB composition in the  $(1-x)\text{PZ}-x\text{PT}$  system is at  $x = 0.48$  [1]. The dashed line in Fig. 1 connects these three MPB compositions, forming the MPB in the PZ–BZT–PT ternary system which delineates the tetragonal from the rhombohedral perovskite phase. Our previous work on the PZ–BZT binary

system indicates that the solubility limit of BZT in PZ is ~10 mol.% and the structure of the solid solution is isostructural to the orthorhombic  $\text{PbZrO}_3$  [11]. Therefore, there is another phase boundary separating the rhombohedral and the orthorhombic perovskite phase at the  $\text{PbZrO}_3$  corner of the phase diagram. The solubility limit of BZT was observed to be 40 mol.% in PT [9] and around 15 mol.% in PZT [21, 22]. As a consequence, compositions in the shaded region are marked as “Mixed Phases.”

Based on the X-ray diffraction patterns shown in Fig. 2, the  $c/a$  ratio for the tetragonal phase in these compositions is calculated and listed in Table 1. It is found that the  $c/a$  ratio is in the range of 1.010 ~ 1.020, increasing with increasing content of (0.3BZT–0.7PT). It was noticed that the  $c/a$  ratio in (0.3BZT–0.7PT) is 1.09 [9]. Obviously, adding  $\text{PbZrO}_3$  suppresses the tetragonal distortion significantly and eventually leads to the formation of MPB.

The grain size and morphology are similar for all the sintered ceramics. The representative scanning electron microscopy micrographs of fractured surfaces of ceramics  $x = 0.48$  and  $0.56$  are shown in Fig. 3. The grain size was calculated with the linear intercept method and the average values are listed in Table 1. The micrographs also indicate that the ceramics experience an inter-granular fracture with the cracks running along grain boundaries.

The temperature dependence of dielectric constant  $\epsilon_r$  and loss tangent  $\tan\delta$  measured at 100 kHz are shown in Fig. 4. The composition  $x = 0.48$  displays the highest peak value of dielectric constant at about 22,200. In the whole temperature range of measurements, the loss tangent for all compositions remains low, less than 0.09. It is observed that the increase in (0.3BZT–0.7PT) content leads to the increase in the Curie temperature and the decrease in the peak dielectric constant and loss tangent. However, as seen from Table 1, the variation of composition in the studied range does not have a strong impact on the Curie temperature. The

compositions in the MPB region ( $x = 0.48$  through  $0.54$ ) possess close Curie temperatures ranging from  $287$  to  $293$  °C, while the composition  $x = 0.56$  with a pure tetragonal phase shows the highest Curie temperature of  $307$  °C. Also clear from Table 1, increasing content of (0.3BZT–0.7PT) enhances the room temperature  $\epsilon_r$  significantly while suppresses the loss tangent slightly.

The dielectric behavior shown in Fig. 4 is comparable to that observed in the pseudo-binary system  $0.1\text{BZT}-0.9[(1-x)\text{PZ}-x\text{PT}]$  [21,22]. It is interesting to notice the change of the Curie temperature with composition. For the three MPB compositions,  $T_c$  is  $380$  °C for  $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$  [1],  $320$  °C for  $0.1\text{BZT}-0.5\text{PZ}-0.4\text{PT}$  [21, 22],  $291$  °C for the composition  $x = 0.52$  in the present work. It is evident from Fig. 1 that the primary difference in these three MPB compositions is the content of  $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ . Obviously the increase in the content of  $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$  leads to the sharp decrease in  $T_c$ . The  $T_c$  is  $495$  °C for  $\text{PbTiO}_3$ ,  $230$  °C for  $\text{PbZrO}_3$  [1], and  $650$  °C for (0.3BZT–0.7PT) [9]. It is surprising that the  $T_c$  of the  $(1-x)\text{PZ}-x(0.3\text{BZT}-0.7\text{PT})$  pseudo-binary system is  $\sim 150$  °C lower than a linear interpolation of the Curie points of  $\text{PbZrO}_3$  and (0.3BZT–0.7PT). The unexpectedly low  $T_c$  also disappoints the initial intention to develop high- $T_c$  piezoelectric ceramics in the  $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$  ternary system. It appears that enhancing  $T_c$  with  $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$  is only effective in the solid solution with  $\text{PbTiO}_3$  [9]. Solid solutions with  $\text{PbZrO}_3$  [11],  $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  [21-23], and  $\text{BaTiO}_3$  [24] always lead to decreased  $T_c$ .

The search for high  $T_c$  piezoelectric perovskite MPB compositions often follows empirical guidelines such as a low tolerance factor in the rhombohedral end member [5]. It was later recognized that both a low tolerance factor for the rhombohedral member and a high  $T_c$  in the tetragonal phase are important [14]. The change of  $T_c$  as a function of composition in



perovskite solid solutions is often times unpredictable and shows a nonlinear dependence [14, 25, 26]. The nonlinearity was suggested to be a result of several factors, including limited solubility, cation ordering, formation of MPB, diffusion of ferroelectric phase transition, and frustration of crystal lattice [25]. First-principles calculations suggest that  $T_c$  correlates well with polarization magnitudes computed from cation displacements [26]. Recently Stringer *et al.* [14] found good correlations between the composition dependence of  $T_c$  with the spread of tolerance factor within the solid solution and the variance of the B-site ionic radius. In the  $(1-x)\text{PZ}-x(0.3\text{BZT}-0.7\text{PT})$  pseudo-binary solid solution system concerned in the present study, the change in composition  $x$  does not change the spread of the tolerance factor since the radius of  $\text{Zr}^{4+}$  is between those of  $\text{Ti}^{4+}$  and  $\text{Zn}^{2+}$  [27]. The calculation of the variance of the B-site cation radius indicates that as composition  $x$  increases from 0.48 to 0.56, it increases from 0.00336 to 0.00351 ( $\text{\AA}$ )<sup>2</sup>. This corresponds to an increase in  $T_c$  from 287 to 307 °C. The trend within the composition range of the present study appears to be consistent with previous results [14]. It should be noted that the variance of (0.3BZT–0.7PT), the tetragonal end member with a  $T_c$  of 650 °C, is 0.00232 ( $\text{\AA}$ )<sup>2</sup>. Obviously the variance parameter cannot explain the significantly decreased  $T_c$  compared to the end member (0.3BZT–0.7PT).

Figure 5 displays polarization vs. electric field hysteresis loops of unpoled  $(1-x)\text{PZ}-x(0.3\text{BZT}-0.7\text{PT})$  ceramics measured with a frequency of 4 Hz at room temperature. Well-defined square-shaped hysteresis loops were observed for all the compositions. The coercive field  $E_c$  and the remanent polarization  $P_r$  from the measurement are listed in Table 1. It is observed that  $E_c$  increases monotonically with increasing  $x$ . This trend is believed to be associated the increasing  $c/a$  ratio with increasing  $x$ . It was shown previously that a higher  $c/a$  ratio of ferroelectric perovskite leads to higher internal stresses, making the domain switching

more difficult [20, 28]. In contrast, the remanent polarization  $P_r$  initially increases then decreases with  $x$ , showing the maximum value of  $40.7 \mu\text{C}/\text{cm}^2$  in the MPB center composition of  $x = 0.52$ . Apparently the coexistence of roughly equal amounts of rhombohedral and tetragonal phases in this composition facilitates the domain switching processing and maximizes the switchable polarization.

The piezoelectric coefficient  $d_{33}$  measured at room temperature from the poled ceramics of  $(1-x)\text{PZ}-x(0.3\text{BZT}-0.7\text{PT})$  is displayed in Fig. 6. The variation of  $d_{33}$  with composition  $x$  follows the same trend as that in remanent polarization  $P_r$ : it reaches the maximum  $311 \text{ pC}/\text{N}$  in the MPB center composition  $x = 0.52$ . Again, the observation proves that the MPB is extremely critical to piezoelectric performance. Compared to the value ( $300 \text{ pC}/\text{N}$ ) measured in the MPB composition  $0.1\text{BZT}-0.5\text{PZ}-0.4\text{PT}$  [21, 22], the slightly higher  $d_{33}$  observed in the composition  $x = 0.52$  in present work can be attributed to the higher content of  $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$  and the lower Curie temperature.

## Conclusions

The  $\text{PbZrO}_3$ - $\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ - $\text{PbTiO}_3$  ternary solid solution system was investigated along the pseudo-binary line  $(1-x)\text{PZ}-x(0.3\text{BZT}-0.7\text{PT})$ . An MPB separating the rhombohedral and tetragonal perovskite phases was observed to center at the composition  $0.48\text{PbZrO}_3$ - $0.156\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ - $0.364\text{PbTiO}_3$ . Although the composition  $(0.3\text{BZT}-0.7\text{PT})$  displays a high  $T_c$  of  $650 \text{ }^\circ\text{C}$ , its solid solution with  $\text{PbZrO}_3$  significantly shifts the Curie temperature to lower values. For the MPB composition  $[0.48\text{PbZrO}_3$ - $0.156\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ - $0.364\text{PbTiO}_3]$ ,  $T_c$  drops to  $291 \text{ }^\circ\text{C}$ . However, a large  $P_r$  of  $40.7 \mu\text{C}/\text{cm}^2$  and a high  $d_{33}$  of  $311 \text{ pC}/\text{N}$  were observed in this composition.

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**Table 1** Structure and properties of the  $(1-x)\text{PbZrO}_3-x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3-0.7\text{PbTiO}_3]$  ceramics.

The properties of the MPB composition  $x = 0.52$  are highlighted in bold.

$x$	$\rho$ (g/cm <sup>3</sup> )	$c/a$	Grain size ( $\mu\text{m}$ )	100 kHz, 25 °C		$T_c$ (°C)	$E_c$ (kV/cm)	$P_r$ ( $\mu\text{C}/\text{cm}^2$ )	$d_{33}$ (pC/N)
				$\epsilon_r$	$\tan\delta$				
0.48	7.418	1.010	4.3	729	0.052	287	14.5	29.0	106
0.50	7.517	1.018	3.4	946	0.049	291	16.4	34.1	159
<b>0.52</b>	<b>7.547</b>	<b>1.019</b>	<b>3.8</b>	<b>1080</b>	<b>0.049</b>	<b>291</b>	<b>17.0</b>	<b>40.7</b>	<b>311</b>
0.54	7.587	1.020	3.9	1160	0.042	293	21.5	34.1	213
0.56	7.637	1.020	4.2	1020	0.031	307	28.9	24.9	134

**Fig. 1** The  $\text{PbZrO}_3\text{--Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--PbTiO}_3$  ternary phase diagram revised from Ref. [22]. The compositions studied in the present work are marked as red dots. The compositions marked by green squares are reported in Ref. [21, 22]. The curved dashed line connecting the three MPB compositions represents the MPB in the ternary system, separating the rhombohedral (R) from the tetragonal (T) perovskite phase. The symbol “O” in the upper corner close to  $\text{PbZrO}_3$  stands for the orthorhombic phase.

**Fig. 2** The X-ray diffraction patterns of sintered ceramics of  $(1-x)\text{PbZrO}_3\text{--}x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.7\text{PbTiO}_3]$ .

**Fig. 3** Scanning electron microscopy micrographs of sintered ceramics of  $(1-x)\text{PbZrO}_3\text{--}x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.7\text{PbTiO}_3]$ . (a)  $x = 0.48$ , and (b)  $x = 0.56$ .

**Fig. 4** (a) Dielectric constant  $\epsilon_r$  and (b) loss tangent  $\tan\delta$  measured at 100 kHz as a function of temperature in sintered ceramics of  $(1-x)\text{PbZrO}_3\text{--}x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.7\text{PbTiO}_3]$ .

**Fig. 5** Polarization vs. electric field hysteresis loops measured at room temperature at 4 Hz in sintered ceramics of  $(1-x)\text{PbZrO}_3\text{--}x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.7\text{PbTiO}_3]$ .

**Fig. 6** Piezoelectric coefficient  $d_{33}$  measured at room temperature in poled ceramics of  $(1-x)\text{PbZrO}_3\text{--}x[0.3\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.7\text{PbTiO}_3]$ . The dashed line is guide for the eye.

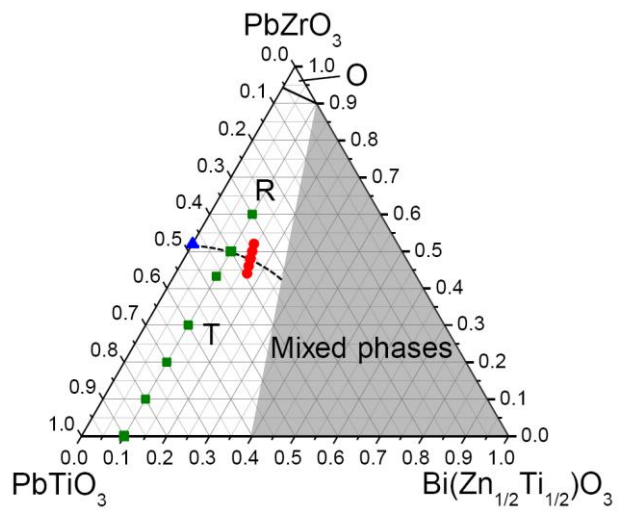


Fig. 1

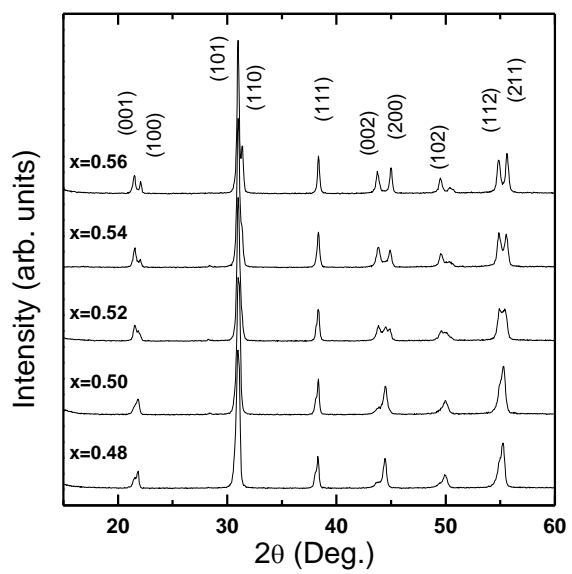


Fig. 2



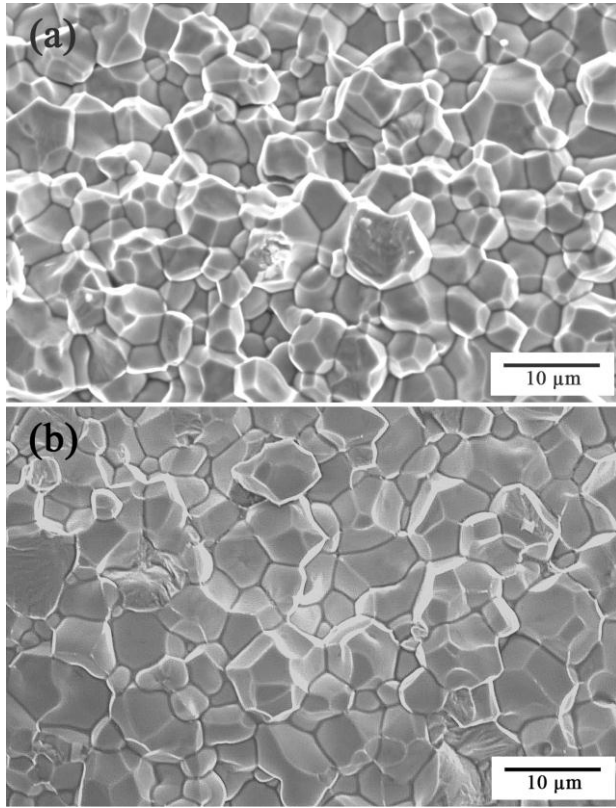


Fig. 3

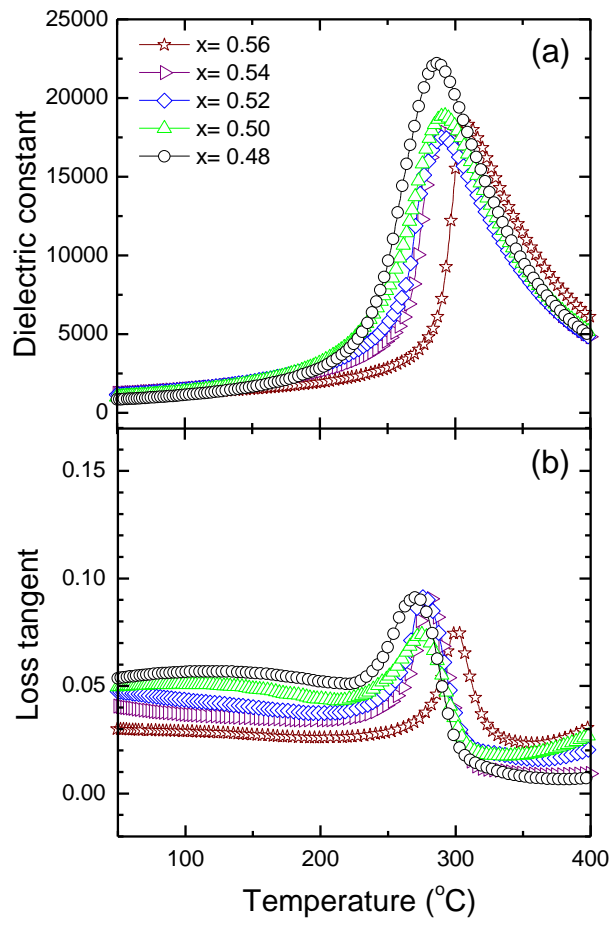


Fig. 4

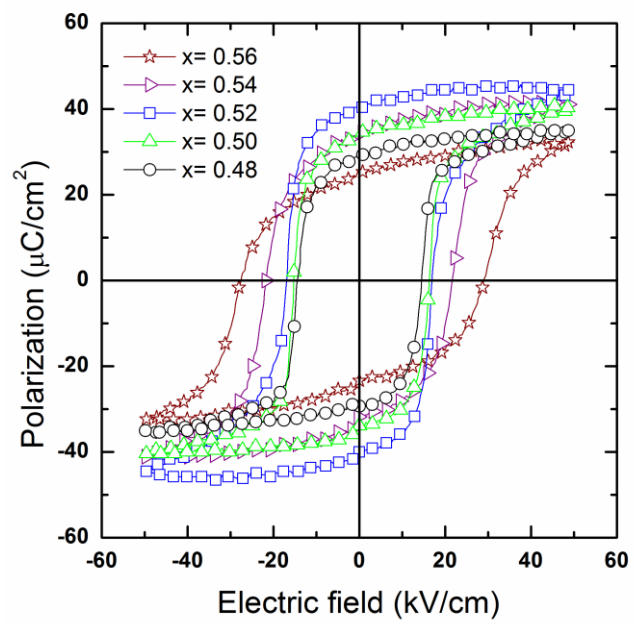


Fig. 5

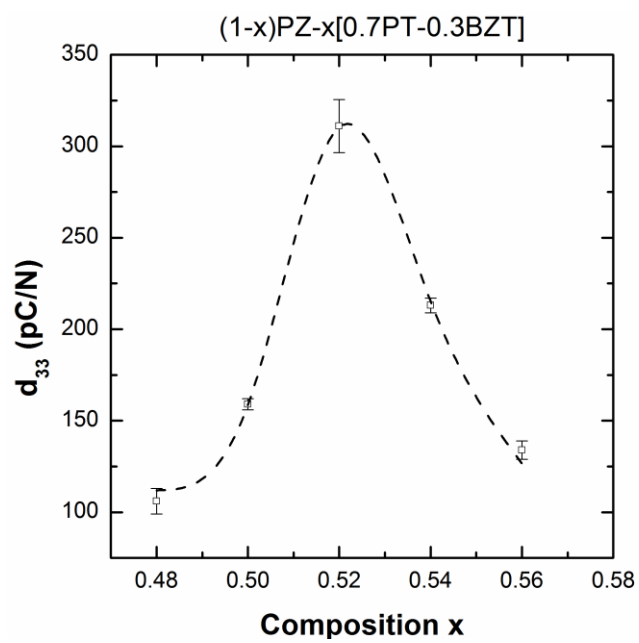


Fig. 6