

Investigation of dipolar defects in $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ single crystals using different poling methods

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The temperature dependence of piezoelectric, pyroelectric, and dielectric properties have been measured for [001] and [111] oriented $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ (PZN-8%PT) and $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$ (PZN-4.5%PT) single crystals poled by two different poling methods, i.e., room temperature (RT) poling and poling through field cooling (FC). Compared with the RT poling case, some interesting features have been found in the FC poled [001] oriented crystal but not in the [111] oriented crystal. These features include the enhancement of piezoelectric properties, lowering of the transition temperature from rhombohedral to tetragonal phase, increasing the amplitude of the spontaneous polarization in the tetragonal phase region, and the decrease of the dielectric constants in the tetragonal phase. These results revealed that the dipolar defects in the crystals are formed between the *B* and *O* sites in the ABO_3 perovskite structure. © 2007 American Institute of Physics. [DOI: 10.1063/1.2401043]

I. INTRODUCTION

Due to the remarkable piezoelectric and electromechanical properties in domain engineered $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PZN-*x*PT) single crystals, they have been studied extensively in recent years for potential applications in many electromechanical devices, such as transducers and actuators.^{1,2} PZN-PT system is a complete solid solution relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})$ and ferroelectric PT and there is a morphotropic phase boundary (MPB) between tetragonal and rhombohedral phases near 8%PT composition at room temperature. It was found that [001] poled rhombohedral phase crystals close to the MPB composition have the maximum piezoelectric and electromechanical properties.²

In contrast to ferroelectric (FE) crystals, such as PT, PZN is a typical relaxor ferroelectric material, which exhibits a broad phase transition and a frequency dependent dielectric response. It has Nb^{5+} and Zn^{2+} randomly distributed on the *B* sites of the perovskite (ABO_3) structure. The differences in valence ($5+$ vs $2+$) and ionic radii (0.64 \AA vs 0.74 \AA) between the Nb^{5+} and Zn^{2+} ions on the *B* site of the ABO_3 perovskite structure prevent long range order so that local polar clusters or nanodomains are formed. These clusters, resulting from short range correlated ionic displacements, are dispersed as islands in the host lattice, which produces unusual relaxor behavior in PZN crystals.³⁻⁶ In addition, neither Nb^{5+} nor Zn^{2+} fit well at the $4+$ site in the perovskite structure, which produces charge imbalance for ordering and some electrical charge carriers in relaxor.^{7,8} The charged defects can influence the poling process in typical relaxors, such as $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ (SBN) crystal.⁹

Poling is a critical step in making ferroelectric materials piezoelectric. Most ferroelectric crystals are usually poled at room temperature using an electric field about three to four times of the coercive field. On the other hand, crystals can also be poled by cooling under a bias electric field from a temperature above the Curie point using a field level much smaller than the coercive field at room temperature. In order to obtain the best poling results, it is very important to know which poling procedure is better for the PZN-*x*PT crystals.

Granzow *et al.*^{10,11} have shown that electric field applied at temperatures above the Curie temperature in Ce-doped SBN crystal will induce a preferred direction in the crystal, which is stable and can make the polarization aligned again below the Curie point (repoling effect) even after repeated heating and cooling through the phase transition without external bias. It was found that the temperature dependence of dielectric and pyroelectric properties in [001] oriented PZN-8%PT crystal poled by field cooling (FC) are significantly different from those of the same crystal poled at room temperature (RT).¹² This intrigued us to further the poling study on PZN-8%PT and PZN-4.5%PT with both [001] and [111] orientations. In this paper, we report the poling effect on the piezoelectric, pyroelectric, and dielectric properties of PZN-*x*PT single crystals and analyze the physical mechanism behind different electric behaviors caused by different poling processes in PZN-*x*PT crystals.

II. EXPERIMENTAL DETAILS

The PZN-8%PT and PZN-4.5%PT crystals grown by the flux method are transparent in light yellow color and have no observable defects under an optical microscope. The crystals were oriented, cut, and optically polished into a plate shape with three pairs of mutually perpendicular surfaces of

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TABLE I. The piezoelectric constants d_{33} of the PZN-xPT crystals with different orientations.

Crystals		[001]	[001]	[111]	[111]
		PZN-8%PT	PZN-4.5%PT	PZN-8%PT	PZN-4.5%PT
d_{33} (pC/N)	RT poling	2082±25	1742±28	149±13	143±10
	FC poling	2344±20	1992±32	152±12	143±12

[100]/[010]/[001] and [111]/ $[\bar{1}\bar{1}0]$ / $[\bar{1}\bar{1}2]$, respectively, based on the cubic coordinates (note: the crystal symmetry is rhombohedral). The dimensions of the plate are $4 \times 4 \times 1 \text{ mm}^3$ and the thickness direction for the samples is either [001] or [111]. All crystals are poled along the thickness direction using gold electrodes.

Each sample was poled using two different methods. One is regular poling at RT by applying a 13 kV/cm electric field for 15 min, and the other is going through FC from 250 °C down to room temperature under an electric field of only 2.5 kV/cm. We have checked the effect of different poling fields from 10 to 14 kV/cm for RT poling case and from 1 to 3 kV/cm for the FC poling case, but no significant difference was found for the piezoelectric, dielectric, and pyroelectric properties, indicating that the two poling procedures were sufficient to fully pole these samples. Before each poling process, the sample was annealed at 250 °C for half an hour and then cooled slowly to room temperature to make sure that the samples all start at the same depoled state.

The dielectric and pyroelectric response were measured using an HP4284A LCR meter and a HP4140B pA meter. The temperature was controlled by a computer assisted Delta 9023 oven at a cooling/heating rate of 3 °C/min and the temperature was measured using a platinum resistance thermocouple. All physical property data were recorded by an Agilent 34970 data acquisition/switch unit. The piezoelectric constants (d_{33}) were obtained by a quasistatic method, using a Radiant Precision materials analyzer which has a piezo-D meter attached.

III. RESULTS AND DISCUSSIONS

The piezoelectric constants d_{33} were measured directly through applying a stress in the thickness direction of the samples and the results are shown in Table I. It must be noted that the piezoelectric constants obtained by the static method are usually different from those obtained by dynamic ones owing to the fact that the boundary conditions in the two methods are different.¹³ In our measurements, each d_{33} value was averaged ten times and the standard deviation is also given in Table I. From Table I, we can see that the FC poled [001] oriented PZN-8%PT and PZN-4.5%PT crystals have much higher (exceed to 10%) piezoelectric constants than those of the RT poled samples at room temperature. However, the corresponding [111] oriented samples show almost the same d_{33} values, whether poled through FC or RT methods.

Figures 1(a)–1(d) show the pyroelectric current and the spontaneous polarization as a function of temperature from RT up to 250 °C without electric field. Note that the occurrence of multiple current peaks near the transition temperature indicates that the transformation does not happen uni-

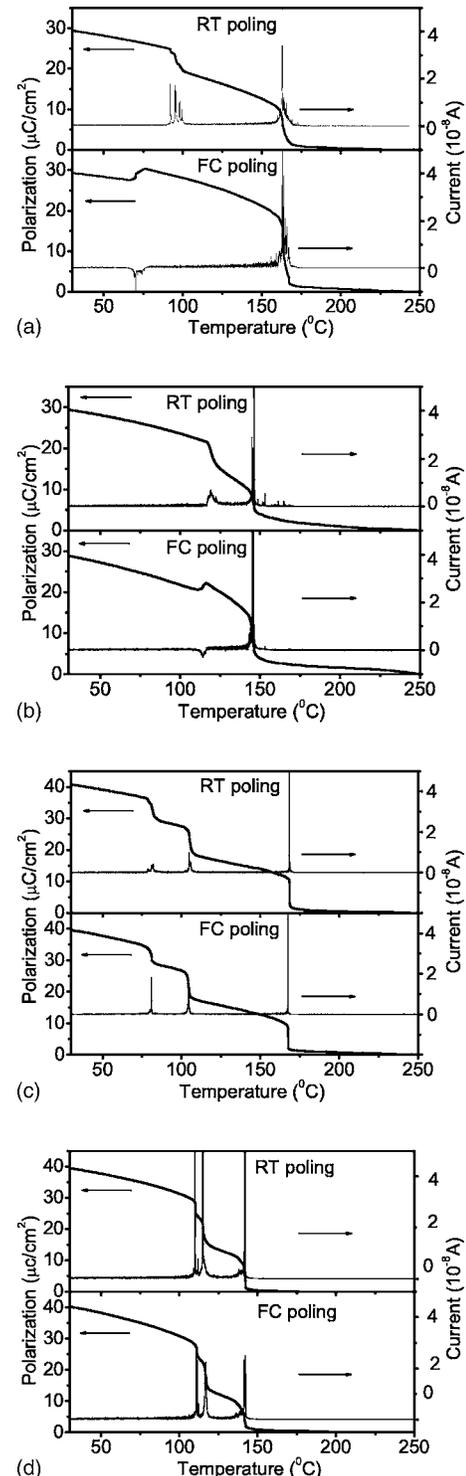


FIG. 1. Temperature dependence of the pyroelectric current and the corresponding spontaneous polarization for the samples corresponding to Table I. (a) [001] oriented PZN-8%PT; (b) [001] oriented PZN-4.5%PT; (c) [111] oriented PZN-8%PT; and (d) [111] oriented PZN-4.5%PT.

formly throughout the crystal. There are microheterogeneities in the crystals.¹⁴ For [001] poled PZN-8%PT crystal, broad current peaks centered near 165 °C were found in Fig. 1(a), which represent the tetragonal to cubic phase transition. The position of the peak is the same for both the FC and RT poled samples. However, the transition temperatures of the rhombohedral to tetragonal phase are significantly different for the two cases. The phase transition for the RT poled sample happened between 90 and 100 °C and shows positive discharge current peaks in this temperature region; while for the FC poled case, the transition happened between 68 and 78 °C with negative current peaks. In other words, the phase transition temperature is significantly lowered when the sample is poled through FC process. In addition, it is interesting to note that the FC poled sample possesses much higher polarization than that of the RT poled sample in the tetragonal phase region, although they have almost the same remnant polarization in the rhombohedral phase. For example, at 120 °C, the spontaneous polarization for the FC poled sample is 25.6 $\mu\text{C}/\text{cm}^2$, while that for the RT poled one is only 17.0 $\mu\text{C}/\text{cm}^2$. Similar results can be obtained in the FC poled [001] oriented PZN-4.5%PT crystal as shown in Fig. 1(b). At 125 °C, the spontaneous polarization for the FC poled PZN-4.5%PT sample is 20.1 $\mu\text{C}/\text{cm}^2$, while that for the RT poled one is only 14.6 $\mu\text{C}/\text{cm}^2$.

On the other hand, such phenomena are not observed in PZN-8%PT and PZN-4.5%PT crystals poled along [111], as shown in Figs. 1(c) and 1(d). There are three transitions for each samples observed, corresponding to the rhombohedral to orthorhombic, orthorhombic to tetragonal, and tetragonal to cubic transitions, respectively. The transition temperatures for the FC and RT poled cases are almost the same, they are near 81, 104, and 168 °C, for PZN-8%PT, and 111, 115, and 142 °C, for PZN-4.5%PT, respectively. Note that the existence of an orthorhombic phase as an intermediate region between rhombohedral and tetragonal phases is essential to accommodate the strain generated by the deformation of the crystal structure from $3m$ to $4mm$ symmetries.¹⁴ It can be seen from Figs. 1(c) and 1(d) that the pyroelectric current peaks in [111] oriented crystals are much sharper than those in [001] oriented ones. Since the symmetry of the low temperature phase is rhombohedral, the application of an electrical field along the polar [111] direction will help the alignment of the dipoles so that the amplitude of the polarization is larger than that of the [001] poled samples. The larger polarization change during zero field heating will naturally produce sharper pyroelectric current peaks at the phase transition.

The dielectric measurements were also performed on heating from room temperature up to 250 °C without field and the results are given in Fig. 2. Each curve actually contains three curves measured at frequencies of 100 Hz, 1 kHz, and 10 kHz. Clearly, the dielectric anomalies found in the dielectric measurement for all the cases are consistent with the pyroelectric measurements in Fig. 1. For example, the sharp peaks in Fig. 2(a) at 171 °C are related to the tetragonal to cubic phase transition, which are very close to the right edges of the corresponding pyroelectric peak shown in

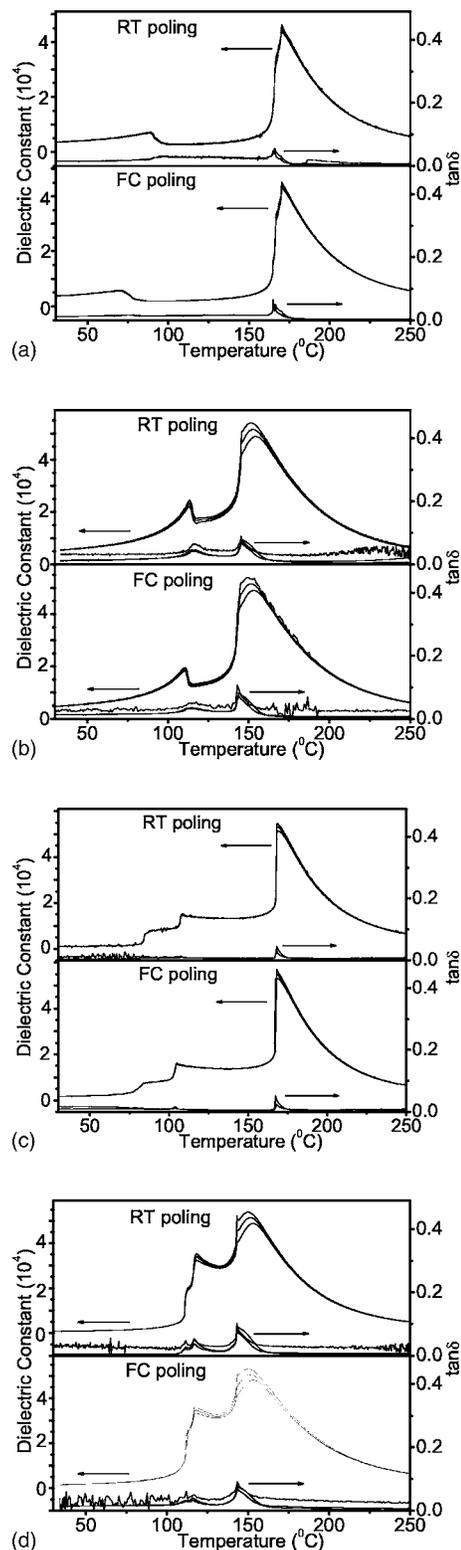


FIG. 2. Temperature dependence of the dielectric constant and loss corresponding to Fig. 1. Each case was measured using three different frequencies: 100 Hz, 1 kHz, and 10 kHz, respectively.

Fig. 1(a). In the [001] oriented samples, the dielectric constants in the tetragonal region for the FC case is lower than those of the RT poled case. For example, at 125 °C and 10 kHz, the dielectric constants of the PZN-8%PT for the FC poled sample is 2512, while that for the RT poled one is 3101. The corresponding values of the PZN-4.5%PT are

13 866 and 17 137, respectively. On the other hand, no significant difference between the FC and RT cases was found in the dielectric properties of the [111] oriented crystals, as shown in Figs. 2(c) and 2(d).

Through the measurements of piezoelectric, pyroelectric, and dielectric properties of PZN-8%PT and PZN-4.5%PT crystals, four main features have been found in the FC poled [001] oriented crystals upon zero field heating: (1) d_{33} values are enhanced at room temperature compared to the RT poled sample; (2) the transition temperature from rhombohedral to tetragonal phase is significantly lowered; (3) the spontaneous polarization in the tetragonal phase becomes larger; and (4) the dielectric constant in the tetragonal phase is decreased.

For the [001] oriented crystals, it was found that the phase transition temperature from tetragonal to rhombohedral phase is lowered and the dielectric constants are decreased in the tetragonal phase when cooling under a bias electric field along [001].¹² Based on this fact, we believe that the FC process induced an internal bias in the [001] oriented crystal, resulting from the alignment of dipolar defects. Such internal bias had been studied before and had been utilized to stabilize preferred domains in some relaxors, such as SBN crystals.⁹⁻¹¹ However, for PZN- x PT crystals, the effect of the internal bias on the stabilization of domains seems to have strong dependence on the crystal orientation since the four features were only found in [001] oriented samples and not in the [111] oriented ones. The difference between the two situations reveals an important fact, i.e., the charged defects are actually formed defect dipoles and these defect dipoles are formed between the B site cations and the oxygen vacancies in the perovskite structure. In other words, all dipolar defects are oriented in the $\langle 001 \rangle$ directions. Charged defects are usually present in relaxor ferroelectrics due to the existence of compositional and/or structural disorder, which plays a decisive role in frequency dependent phase-transition behavior.⁷ We also found that the so called repoling effect presented in Ce-doped SBN crystals is not observed in PZN- x PT crystals. Thus, in the PZN- x PT crystals, the aligned defect dipoles become disordered again when the temperature is increased above the Curie point.

It is a known fact that the mobility of oxygen vacancies increases with temperature; therefore, in the high temperature cubic phase, oxygen vacancies can rearrange to make the defect dipoles aligned with the external field along [001] for the [001] oriented sample during the FC process. These aligned dipoles will join the spontaneous polarization produced at the cubic to tetragonal phase transition to form a well ordered single domain state in favor of the applied field direction. When the sample is cooled to the second transition point, the dipolar direction will change to one of the four possible $\langle 111 \rangle$ directions under bias so that multidomain state is formed. However, the defect dipoles are still aligned in the field direction of [001]. They can produce an internal bias electric field along $\langle 001 \rangle$ even after the external electric field is removed. Upon zero field heating, this internal bias electric field produced by the aligned defect dipoles will assist the system to transform into the preferred tetragonal phase at a much lower transition temperature. The perfect alignment of all dipoles (regular and defect dipoles) makes the remnant

polarization bigger and the dielectric constant smaller for the tetragonal phase. Because most properties become larger closer to a phase transition temperature, it is understandable that a higher piezoelectric constant has been observed in the FC poled sample, which has its phase transition temperature closer to room temperature.

On the other hand, for [111] oriented samples, the external field cannot fully align the defect dipoles so that no single preferred tetragonal orientation exists to provide an additional polarization component for the tetragonal phase to help lower the rhombohedral-tetragonal phase transition. Therefore, the phenomena observed in the [001] oriented sample do not occur in the [111] oriented sample. On average, there might also be a small level bias field produced by the partial alignment of defect dipoles along [111] but it does not seem to be sufficient to produce enough strength to produce a noticeable increase of the rhombohedral to tetragonal phase transition.

IV. SUMMARY AND CONCLUSIONS

In summary, we have conducted systematic measurements on the piezoelectric, pyroelectric, and dielectric constants on [001] and [111] oriented PZN-8%PT and PZN-4.5%PT single crystals that were poled using two different poling methods. One method is poling at room temperature by applying a field three to four times of the coercive field, while the other is cooling through the Curie point under a bias field that is smaller than the RT coercive field. Four very interesting features were found in the [001] FC poled sample when heating it from room temperature all the way to 250 °C: enhanced RT piezoelectric properties, lower rhombohedral to tetragonal phase transition temperature, increased polarization, and decreased dielectric constant in the tetragonal phase region. Such phenomena did not occur in the [111] oriented sample. Based on the experimental fact we can make two very important conclusions:

- (1) There is a “memory effect” produced by the alignment of dipolar defects in the FC poling process.
- (2) Dipolar defects are formed between B and O sites in the ABO_3 perovskite structure so that their orientation is along $\langle 001 \rangle$.

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