

Memory effect in [001] poled $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ single crystals

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We have conducted dielectric and pyroelectric measurements in [001] poled rhombohedral phase $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ single crystals from room temperature to 250 °C. An interesting poling history dependence has been revealed from the experimental results. Compared with room-temperature poled samples, crystals poled via the field-cooling method have a much lower rhombohedral-to-tetragonal phase transition temperature and have enhanced spontaneous polarization while heating up to the tetragonal phase. Such phenomena may be explained by the memory effect of dipolar defect alignment in the sample poled by the field-cooling method. © 2005 American Institute of Physics. [DOI: 10.1063/1.1922575]

$(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN-PT) and $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PZN-PT) single crystals with compositions near the morphotropic phase boundary have been under intense investigation in recent years due to their extremely high electromechanical properties in the [001] direction poled multidomain state.^{1,2} Because of the nature of a solid solution between a relaxor and a ferroelectric, there are many interesting physical phenomena being discovered in these crystals. For example, dielectric investigations of poled and then thermally depoled samples have shown noticeable differences.³⁻⁵

Usually, the crystals are poled at room temperature using an electric field that is about three to four times greater than the coercive field. On the other hand, crystals can also be poled by cooling under a bias electric field at a temperature above the Curie point in the paraelectric phase. The bias field can be much smaller than the coercive field at room temperature (based on the principle of field biased phase transition). Granzow *et al.*⁶ have shown that applying an electric field at temperatures above the Curie temperature in a Ce-doped $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ relaxor crystal induced a preferred orientation for the polar vector, which is stable even after repeated heating and cooling through the phase transition. Their work indicated a memory effect in the relaxor system.

In this letter, we report an investigation of similar phenomena in the $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ (PZN-8%PT) crystals through measuring the temperature dependence of dielectric and pyroelectric coefficients for both room-temperature (RT) poled and field-cooling (FC) poled [001]-oriented crystals. Internal bias is clearly present in the FC poled PZN-8%PT sample, similar to the case of pure relaxor Ce-doped $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$. This internal bias field reflects the alignment of charged defects in the perovskite structure, which produces a significant enhancement of the polarization in the tetragonal phase, and lowers the transition temperature between the rhombohedral and tetragonal phases.

The PZN-8%PT crystals, provided by the JFE Mineral Company, Ltd., Japan, were grown by the flux method. They were transparent in light yellow color and had no observable defects under an optical microscope. The crystals were oriented, cut, and optically polished into a plate shape with the orientations of [100]/[010]/[001] based on the cubic coordinates and the dimensions of $4 \times 4 \times 1 \text{ mm}^3$. The dielectric and pyroelectric responses were measured using an HP4284A LCR meter and a HP4140B pA meter, respectively. The temperature was controlled by a computer-assisted Delta 9023 oven with a changing rate of 3 °C/min, and the temperature was measured by both a platinum resistance thermocouple and an Agilent 34970 Data Acquisition/Switch Unit. The thermocouple was mounted inside an aluminum plate, which supported the sample.

The samples were poled using two different procedures. One procedure was poling at RT by applying a 13 kV/cm electric field for 15 min, and the other was going through FC from 250 °C down to RT under an electric bias field of 2.5 kV/cm (RT tests showed the sample is fully poled as described below), which was slightly less than the RT coercive field of 2.7 kV/cm for this orientation. Before each poling process, the sample was annealed at 250 °C for 0.5 h, then cooled down slowly to room temperature to make sure that the sample started at a depoled and stress free state.

The dielectric and pyroelectric measurements were performed upon heating from RT up to 250 °C without electric field. Curves (a) and (b) in Fig. 1 are the changes of dielectric constant with temperature for the crystals poled by the two methods. Each thick curve actually contains three curves measured at frequencies of 100 Hz, 1 kHz, and 10 kHz, respectively. No noticeable dispersion with frequency was found. The sharp peaks at 171 °C are related to the tetragonal to cubic phase transition, and the two curves (a) and (b) are almost coincide in the temperature region near this transition. However, the rhombohedral-to-tetragonal transition temperatures for the two cases are significantly different. The sample poled at RT had a rhombohedral-to-tetragonal phase transition near 95 °C, which was very close to the corresponding transition temperature (near 93 °C) of the depoled sample, as

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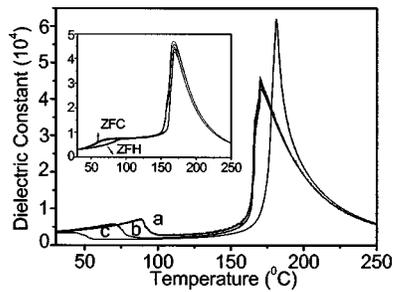


FIG. 1. Temperature dependence of the dielectric constant under different frequencies for (a) ZFH after RT poling, (b) ZFH heating after FC poling, and (c) FC with an electric field of 2.5 kV/cm. Each case was measured using three different frequencies: 100 Hz, 1 kHz, and 10 kHz, respectively, with the lower-frequency value slightly larger, but the difference is not significant. The inset is the temperature dependence of the dielectric constant for the cases of zero FC, and subsequent ZFH. Each case was also measured in three different frequencies.

shown in the inset picture of Fig. 1. Although the FC poled sample had a much lower transition temperature of about 75 °C, we noticed that this transition temperature was shifted further down to 52 °C during the FC process as shown in curve (c) of Fig. 1 because the external field along [001] stabilized the tetragonal phase.

Figures 2(a) and 2(b) show the pyroelectric current and spontaneous polarization as a function of temperature upon zero-field heating (ZFH) of samples poled using the two methods, respectively. Corresponding to the dielectric curves in Fig. 1, the broad current peaks centered near 165 °C represent the occurrence of the tetragonal-to-cubic phase transition. We found that the right-hand side edges of both broad peaks were at 171 °C, which coincided with the dielectric peaks. The multiple current peaks near the transition temperature indicated the nonuniform transition in the sample. In other words, there are microheterogeneities in the crystals. Based on the pyroelectric current measurements, the rhombohedral-to-tetragonal phase transition for the RT poled case happened between 90 and 100 °C and showed 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. Clearly, the phase transition temperature regions are consistent with those of the dielectric anomalies in both cases.

It is interesting to note that the FC poled sample possesses a much higher polarization than that of the RT poled sample in the tetragonal phase. At 120 °C, the spontaneous polarization for the FC poled sample is 25.6 $\mu\text{C}/\text{cm}^2$, while the polarization of the RT poled one is only 17.0 $\mu\text{C}/\text{cm}^2$. The polarization at 30 °C is near 29 $\mu\text{C}/\text{cm}^2$ for both cases, which is consistent with the value reported in fully poled [001]-oriented PZN-8%PT.⁷

In addition, we also checked the poling condition by varying the poling field level from 10 to 14 kV/cm for the RT poling case, and the bias level from 1 to 3 kV/cm for the FC poling case. No significant difference was found in the dielectric and pyroelectric measurements, indicating that the two poling procedures used above were sufficient to fully pole the samples.

Compared with the RT poled case, two main features can be found upon ZFH of the FC poled [001]-oriented PZN-8%PT crystal.

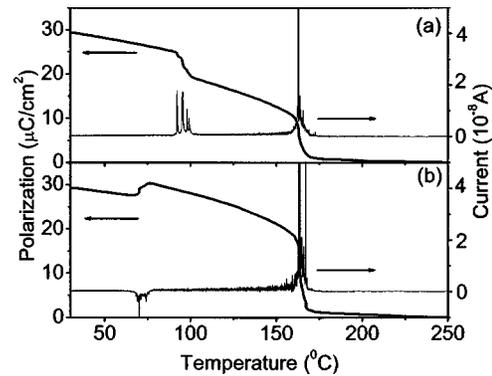


FIG. 2. Temperature dependence of the pyroelectric current and the corresponding spontaneous polarization for both cases: (a) RT poled sample and (b) FC poled sample.

- (1) The transition temperature from rhombohedral to tetragonal phase is significantly lower.
- (2) The spontaneous polarization is substantially enhanced in the tetragonal phase.

The implication is that the FC poled sample has an internal bias field that makes the tetragonal domain state with a polarization in [001] become more stable than domains with a polarization in other orientations. We believe that the FC process actually left a “memory” of dipolar defect alignment, which produced a preferred dipolar direction in the tetragonal phase. In other words, this alignment of dipolar defects in the crystal acted as an internal bias to make one of the tetragonal domains preferable. The process was similar to the one observed by Granzow *et al.* for a Ce-doped SBN relaxor crystal.^{6,8} At high temperatures, the charge defects in the crystal are easily movable, and will arrange themselves under fields. In a way, the process is similar to the thermal fixing of a holographic space-charge carrier grating in optical data storage.^{9,10} Upon heating the FC poled sample, this internal bias field would help the system transform into this preferred tetragonal phase at a lower transition temperature. In addition, the bias field along the [001] polar direction will enhance the polarization, leading to an increase of the remnant polarization in the tetragonal phase.

In conclusion, dielectric and pyroelectric measurements have been conducted on [001] poled 0.92Pb(Zn_{1/3}Nb_{2/3})O₃-0.08PbTiO₃ single crystals. Two different poling methods were used, i.e., RT poling and poling by FC from the cubic phase. Samples poled by the two methods were heated from RT without field (ZFH) through both the rhombohedral-to-tetragonal and tetragonal-to-cubic phase transitions. No difference was found in the tetragonal-to-cubic phase transition, but a significant difference was found in the rhombohedral-to-tetragonal phase transition. Compared to the RT poled case, the FC poled sample had a much lower phase transition temperature and the spontaneous polarization was also enhanced in the tetragonal phase. This feature was a clear demonstration of an internal bias field present in the FC poled sample. We propose that this phenomenon is due to the memory of the dipolar defect alignment that was formed during the FC process. Hence, defect dipoles are critical in controlling the properties of these PMN-PT and PZN-PT single crystals.

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