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## Pyroelectric Study on Dipolar Alignment in 0.69Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.31PbTiO<sub>3</sub> Single Crystals

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Pyroelectric measurements are conducted during zero-field heating in [001], [110] and [111] poled 0.69Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.31PbTiO<sub>3</sub> single crystals. Compared to the room-temperature-poled samples, the crystals poled by using the field cooling method show broad but well recognizable pyroelectric current peaks near 190°C, which is much higher than the Curie point (126°C) of the crystal. We propose that this peak of the crystals poled by field-cooling above the Curie point is ascribed to the order-disorder transition of the dipoles in polar nano-regions formed at the Burns temperature.

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Single crystals of Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>PbTiO<sub>3</sub> (PMN-PT) and Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>PbTiO<sub>3</sub> (PZN-PT) with compositions near the morphotropic phase boundary have been under intense investigation in recent years because of their extraordinary piezoelectric and dielectric properties that may induce revolutionary change in sensors, transducers, actuators and other electromechanical devices.<sup>[1–4]</sup> In fact, PMN-PT crystals have already been used in medical imaging transducers to produce much better resolutions. Also, many interesting physical phenomena have been discovered in these crystals owing to the nature of the relaxorferroelectric solid solution systems. In particular, history poling dependence of polarization was observed in PZN-PT and Ce-doped Sr<sub>0.61</sub>Ba<sub>0.39</sub>Nb<sub>2</sub>O<sub>6</sub> crystals.<sup>[5–8]</sup>

The origin of the high electromechanical performance of PMN-PT crystals is closely related to the micro-inhomogeneity of the PMN.<sup>[9,10]</sup> The difference in valence (5<sup>+</sup>-2<sup>+</sup>) and ionic radii (0.64–0.72 Å, CN6) between the Nb<sup>5+</sup> and Mg<sup>2+</sup> ions on the B site of the ABO<sub>3</sub> perovskite structure results in local symmetry breaking compositional and/or structural disorder in nanometer scale. One manifestation of this local disorder is the formation of localized dipolar nano-regions, leading to randomly oriented polarization at a temperature much higher than the ferroelectric transition temperature  $T_C$ . For PMN, the formation temperature of local disordered nano-regions is about 340°C, the so-called Burns temperature  $T_B$ .<sup>[11]</sup> Upon cooling from  $T_B$ , the appearance of the polar nano-regions (PNRs) can not be considered as a regular structural phase transition because it is not accompanied by the change of crystal structure in the unit cell scale. These PNRs dramatically affect the behavior of the crystal, giving rise to the unique ultra-high piezoelectric properties in relaxor-based solid solution systems.<sup>[12,13]</sup>

In spite of years of experimental and theoretical investigations, very little is known about the nature

of these PNRs. One fundamental problem is: whether the randomly oriented polarization in PNRs can be further oriented after poling, i.e., achieving full alignment like in a normal ferroelectric system. In this Letter, we report pyroelectric measurements in [001], [110] and [111] poled 0.67PMN-0.31PT single crystals. Our results reveal some interesting facts that may shed some light on this intriguing question.

Compared to room-temperature (RT) poled samples, crystals poled by using the field cooling (FC) method from 250°C to RT show clear peaks of pyroelectric current near 190°C, which are much higher than the Curie point ( $T_C \sim 126^\circ\text{C}$ ). Such peaks were ascribed to an order-disorder transition of dipoles in the PNRs in the sample poled by the FC method.

The 0.69PMN-0.31PT crystal grown by the high temperature flux method was oriented, cut and optically polished into a plate shape with three pairs of mutually perpendicular surfaces with orientations given by [100]/[010]/[001], [110]/[001]/[110] and [111]/[110]/[112], respectively, based on the cubic coordinates. The dimensions of the plate are 3.0 × 3.0 × 1.0 mm<sup>3</sup>. All the crystals are poled along the thickness direction (the 1 mm direction) using gold electrodes, i.e., [001], [110] and [111], respectively. The dielectric and pyroelectric responses were measured using an HP4284A LCR meter and an HP4140B pA meter. The temperature was controlled by a computer-assisted Delta 9023 oven at a rate of 3°C/min using a platinum resistance thermocouple and an Agilent 34970 data acquisition/switch unit. The thermocouple was mounted inside an aluminum plate, which supports the sample. The pyroelectric constant  $p$  was calculated by

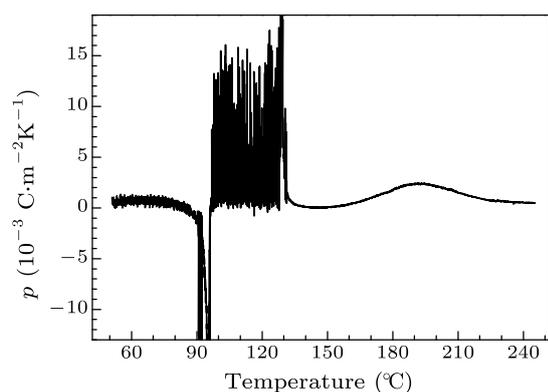
$$p = \frac{I}{A} \frac{dT}{dt},$$

where  $I$  is the measured pyroelectric current,  $A$  the electrode area, and  $dT/dt$  the heating rate.

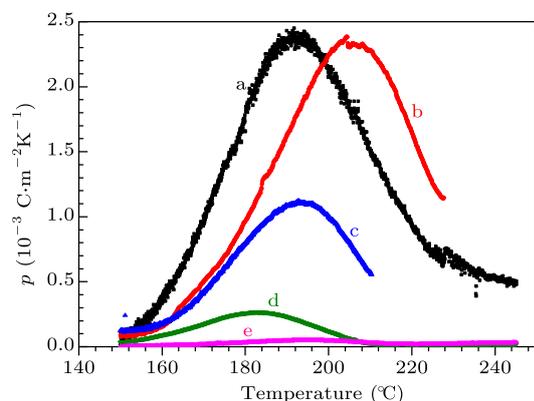
The sample was poled using two different proce-

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dures. One is poling at RT by applying a 12 kV/cm electric field for 15 min, and the other is going through FC from a temperature above  $T_C$  down to RT under an electric field of only 1.0 kV/cm. Before each poling process, the sample was annealed at 250°C for half an hour and cooled slowly to RT to make sure that all the samples started at the same depoled state. The pyroelectric and dielectric measurements were performed on heating from room temperature up to 250°C without an electric field.



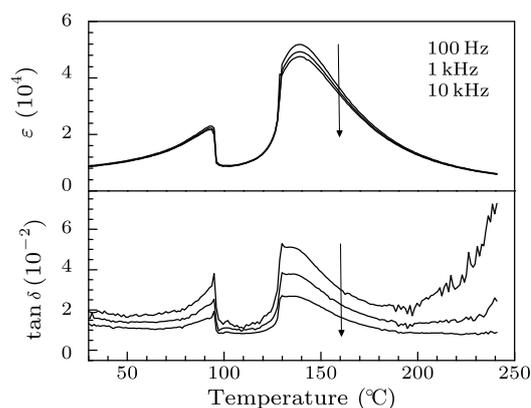
**Fig. 1.** Temperature dependence of the pyroelectric coefficient during ZFH for the [001] PMN-PT crystal poled through FC from 250°C to RT.



**Fig. 2.** Enlarged pyroelectric coefficient peaks above  $T_C$ . a: [001] PMN-PT crystal FC poled from 250°C. c: [001] PMN-PT crystal FC poled from 150°C. e: [001] PMN-PT crystal poled at RT. b and d curves are related to the [111] and [110] oriented crystals, respectively; both are FC poled from 250°C.

Figure 1 shows the pyroelectric current as a function of temperature upon zero-field heating (ZFH) for the [001] oriented crystal poled through FC from 250°C down to RT. Two sharp current peaks have been observed. One is at 95°C, corresponding to the rhombohedral-to-tetragonal phase transition. The other is at 126°C, representing the tetragonal-to-cubic phase transition, i.e., the Curie point  $T_C$ . Compared with other regions, it seems that there is much noise in the temperature range 95–126°C. Such a result indicates a nonuniform transition in the sample. In other words, the domains in this temperature range are more

heterogeneous in the crystals.<sup>[14]</sup> It is interesting to note one more current peak in Fig. 1, which is broad and centered at about 195°C. Figure 2 presents the enlarged section (black curve), along with the results for the same sample poled at RT (cyan curve) and for the sample poled through FC from 150°C (blue curve). The pyroelectric current peak for the FC poling from 250°C is obviously higher than the one from FC poling from 150°C. In addition, the broad peak for the FC poling from 150°C moves to a lower temperature of about 185°C. It is important to point out that the sample poled at RT exhibits only a negligible current peak, indicating that the broad peak above  $T_C$  is induced by the high temperature FC poling. Similar results are found in [110] and [111] oriented crystals, as shown in Fig. 2, where the data for the FC poling from 250°C are presented. The [111] oriented crystal has nearly the same intensity of current peak as that of the [001] oriented sample, but the peak position moves to 206°C. However, the [110] exhibits a much weaker intensity of this current peak.



**Fig. 3.** Temperature dependence of the dielectric constant and loss for the sample corresponding to Fig. 1.

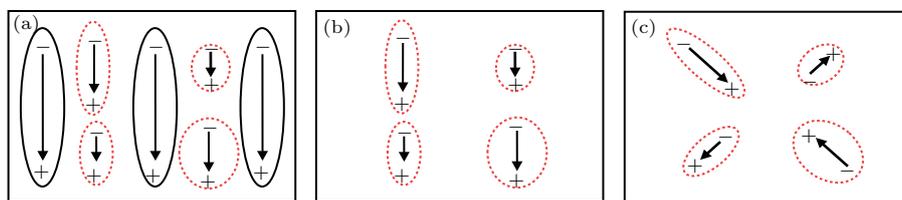
Figure 3 plots the changes of dielectric constant and loss with temperature for the [001] oriented crystal poled through FC from 250°C. Corresponding to the pyroelectric curve in Fig. 1, the anomalies at 95°C and 126°C represent the rhombohedral-to-tetragonal and tetragonal-to-cubic phase transitions, respectively. We can not find any anomalies near 195°C from the dielectric constant curves. However, there are valleys at about 170°C in the loss curves. On the right of the valley, the dielectric loss increases with the increase of temperature, indicating the increase of mobile charges in the crystal. Thus, the appearance of the broad pyroelectric peak above  $T_C$  coincides with the increase of the mobile charges in the crystals.

For a normal ferroelectric, pyroelectric current comes from the change of polarization with temperature. Structural phase transition will dramatically modify the magnitude and/or orientation of the polarization, leading to a sharp and intensive pyroelectric current peak at  $T_C$ , or at the phase transition temperature from rhombohedral to tetragonal during

ZFH shown in Fig. 1. Another way to produce the pyroelectric current peak is the order-disorder transition of the polarization driven by temperature change, because this process also leads to quick change of the surface charges. We propose that the observed broad pyroelectric peak above  $T_C$  originates from the polarization order-disorder transition of the PNRs in these crystals.

As proved by Burns and Dacol through optical measurement, PNRs exist in relaxors, starting at a temperature  $T_d$ , which is far above  $T_C$ .<sup>[11]</sup> For PMN,  $T_d$  is about 343°C. Thus, we may propose that there exist PNRs in PMN-PT crystals at temperature above  $T_C$ . Upon FC poling, most of the PNRs rearrange themselves along the external electric field direction. Below  $T_C$ , normal ferroelectric polarizations appears,

reflecting the nature of PT. Thus two sets of ordered polarizations are formed in the crystals, one from ordering of PNRs and the other from the onset of ferroelectric phase transition. This picture is schematically drawn in Fig. 4(a). When ZFH the sample to  $T_C$ , normal polarizations disappear, however the ordering of PNRs remains until the temperature reaches  $T_p$  (about 190°C). Near  $T_p$ , the PNRs become dynamic, as indicated by the loss curves, leading to the order-disorder transition of the polarization in PNRs. The process is illustrated in Figs. 4(b) and 4(c). When the samples are poled at RT, normal ferroelectric polarizations can be ordered, however the ones in PNRs are not dynamic enough to follow the external electric field. Consequently, the polarizations in PNRs are not ordered in the RT poled samples.



**Fig. 4.** Schematic representation of the polarization state for the PMNPT crystals at different temperature stages during ZFH after FC poling. (a)  $T < T_C$ ; (b)  $T_C < T < T_p$ ; (c)  $T_p < T < T_d$ . The black ellipses represent the normal ferroelectric polarization, while the red (dotted line) ones are the polarization of the PNRs.

Currently, models for the cause of the formation of PNRs can be subdivided into two categories.<sup>[12]</sup> The first category considers the PNRs to be a result of local “phase transitions” or phase fluctuations so that nano-sized polar islands are embedded in a cubic matrix. The second category assumes the transition to occur in all regions of the crystal and the crystal consists of low-symmetry nanodomains separated by domain walls but not by regions of cubic symmetry matrix. Both categories of models indicate that the PNRs are non-uniform regions of different sizes in the crystal. Thus, the order-disorder transitions of the PNRs at  $T_p$  do not appear at the same temperature. This can explain why the measured pyroelectric current peaks at  $T_p$  are broadened. In addition, the non-uniformity of the PNRs may also be orientation dependent, leading to the shifting of the current peaks and the change of peak intensity for crystals with different orientations.

In summary, pyroelectric measurements have been conducted on [001], [110] and [111] oriented 0.69PMN-031PT single crystals upon ZFH. It is found that the crystals poled using the FC method show broad pyroelectric current peaks near 190°C, which is much higher than  $T_C$ , while the samples poled at RT exhibit negligible current peaks in the same temperature region. We propose that these peaks originate from the order-disorder transition of the dipolar alignment in

PNRs, which exists in FC poled relaxor crystals. A physical picture is proposed to explain the experimental results. Our study indicates that the randomly oriented polarization in PNRs can be oriented after FC poling in the PMN-PT relaxor crystals but cannot be aligned at RT poling.

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