



# Temperature dependence of electric-field-induced domain switching in $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.3\text{PbTiO}_3$ single crystal

Zhu Wang<sup>a</sup>, Rui Zhang<sup>a,\*</sup>, Enwei Sun<sup>a</sup>, Wenwu Cao<sup>a,b</sup>

<sup>a</sup> Center for Condensed Matter Science and Technology, Department of Physics, Harbin Institute of Technology, Harbin, Heilongjiang 150080, China

<sup>b</sup> Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

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## ABSTRACT

The influence of temperature on electric-field-induced domain switching of  $[001]_c$  oriented  $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.3\text{PbTiO}_3$  (PMN-0.3PT) single crystal has been studied. The piezoelectric properties of PMN-0.3PT single crystal change drastically at one critical field at  $30^\circ\text{C}$  and two critical fields at  $90^\circ\text{C}$  corresponding to electric-field-induced domain switching. The domain structures were studied by polarizing light microscopy on the  $[100]_c$  surface under the electric field applied along  $[001]_c$  direction. The PMN-0.3PT single crystal exhibits a rapid increase in piezoresponse at  $100\text{V/mm}$ , which is related to  $\text{R}-\text{M}_A$  phase transformation. At  $90^\circ\text{C}$ , the  $\text{M}$  and  $\text{T}_{001}$  phases coexist at  $100\text{V/mm}$ , while  $\text{T}_{001}$  mono-domain appears at  $300\text{V/mm}$ . The domain switching process here can be identified as  $(\text{T}_{100}$  or  $\text{T}_{010}) \rightarrow \text{M} \rightarrow \text{T}_{001}$ . The experimental results show that the phase state and domain structures of the crystal are closely related to the piezoelectric behaviors.

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## 1. Introduction

Relaxor-based ferroelectric single crystals, such as  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PMN- $x$ PT) and  $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PZN- $x$ PT), have been extensively studied due to their very large longitudinal piezoelectric coefficient  $d_{33}$  ( $>2000\text{pC/N}$ ) and ultra-high electromechanical coupling coefficient  $k_{33}$  ( $>0.90$ ) in the  $[001]_c$  poled crystals [1–3]. They are also interesting subjects of fundamental studies, particularly for the morphotropic phase boundary (MPB) composition in which different phases can coexist [4,5]. The multiphase state is due to flattened Gibbs free energy profile [6,7]. The intermediate phase monoclinic (M) and orthorhombic (O) may be induced by electric field to form a multiphase state. Thus, it is important to investigate possible intermediate phases in the crystals in order to understand the origin of the high piezoelectric properties of relaxor-based ferroelectric single crystals.

The intermediate phase and polarization rotation path of the PMN-PT and PZN-PT single crystals have been extensively investigated both theoretically and experimentally [8,9]. It was suggested that the intermediate monoclinic (M) phase can be induced to bridge the rhombohedral (R)-tetragonal (T) transformation

[10]. Upon the application of an electric field along the  $[001]_c$  direction, the polarization rotation path of  $\text{R}-\text{M}-\text{T}$  was identified by some *in situ* experiments [11,12]. The  $\text{M}_C$  phase was observed by high-resolution synchrotron X-ray and neutron diffraction [13,14]. Recently, the volume average of R and T twin domains was evidenced directly by transmission electron microscopy [15]. All these results indicate that different phases can coexist in the crystals and they could transform from one to another under external electric field [16–18].

In this study, the influence of temperature on electric-field-induced domain switching of  $[001]_c$  oriented  $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.3\text{PbTiO}_3$  (PMN-0.3PT) single crystal was studied. The piezoelectric properties of  $[001]_c$  oriented PMN-0.3PT single crystal were measured as a function of electric field at both  $30^\circ\text{C}$  and  $90^\circ\text{C}$ , aiming to confirm the range of electric field in which the intermediate phase can present. Domain structures were also studied based on extinction angle observed along  $[100]_c$  direction, and the correlation between the electromechanical properties and domain structures has been investigated.

## 2. Experimental details

The  $[001]_c$ -oriented PMN-0.3PT single crystal used in this work was grown by the modified Bridgman technique [19,20], which was purchased from the Shanghai Institute of Ceramics, Chinese Academy of Sciences. The sample was oriented, cut and polished into a  $k_{31}$  resonator with dimensions of  $9.65\text{mm}/[100]_c^L \times 1.20\text{mm}/[010]_c^W \times 0.35\text{mm}/[001]_c^T$ . In our experiment, the sample was first

\* Corresponding author. Tel.: +86 0451 86402797; fax: +86 0451 86402797.

E-mail addresses: [ruizhang\\_ccmst@hit.edu.cn](mailto:ruizhang_ccmst@hit.edu.cn), [ruizhang\\_ccmst@yahoo.com.cn](mailto:ruizhang_ccmst@yahoo.com.cn) (R. Zhang).

annealed at 300 °C for 2 h to depole, then cooled down slowly without electric field to release the internal stresses. Afterwards, the piezoelectric properties were measured by an Agilent 4294A Precision Impedance Analyzer following the IEEE standard [21], which was done under electric field applied along  $[001]_c$  direction. In order to achieve a quasi-static condition, the whole measurement took about 5 h to complete. The remnant polarization  $P_r$  and coercive field  $E_c$  were obtained from hysteresis loops by Precision Premier II (Radiant Technologies). The sample with sizes  $1.10\text{ mm}/[100]_c^L \times 5.20\text{ mm}/[010]_c^W \times 2.10\text{ mm}/[001]_c^T$  was used to observe the domain structures on the  $[100]_c$  surface under the electric field applied along  $[001]_c$  direction. Domain structures were observed by a polarizing light microscopy (Zessi Axioskop40) with a DC source and a heating-cooling optical stage (Linkam Thmse600).

When observing the  $[100]_c$  surface of  $[001]_c$  poled crystal between a crossed P/A pair, the extinction angle is related to the angle between one of the polarizer/analyzer (P/A) pair axes and the  $[001]_c$  direction. The extinction angle of T phase is 0° or 90°, and R phase is 45°, respectively. The M phase can be observed based on extinction angle of 10° [10], which is obviously different from that of R and T phases. Thus, the R, M, T phases can be distinguished with the corresponding extinction angles and domain wall orientations.

### 3. Results and discussion

Fig. 1 shows the dependence of piezoelectric properties of rhombohedral PMN–0.3PT single crystal on the poling field at 30 °C. Resonance peaks appear in the admittance spectra at 45 V/mm, indicating that some domains begin to switch, producing non-zero polarization. The piezoelectric constant  $d_{31}$  increases drastically at 100 V/mm, afterwards,  $d_{31}$  changes slightly with

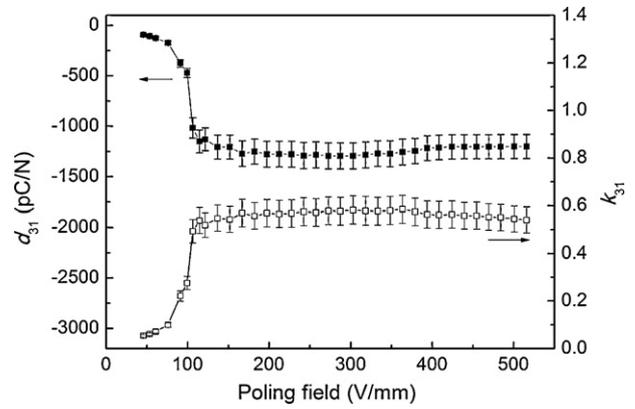


Fig. 1. The piezoelectric properties of PMN–0.3PT measured as a function of poling field under an electric field along  $[001]_c$  at 30 °C.

electric field. The electromechanical coupling coefficient  $k_{31}$  also changes drastically at 100 V/mm. The  $d_{31}$  and  $k_{31}$  reach –1200 pC/N and 0.54 at 500 V/mm, respectively.

To understand what caused the drastic change in piezoreponse at 100 V/mm, the domain structures were observed at 30 °C. As shown in Fig. 2(a) and (b), most parts of the crystal

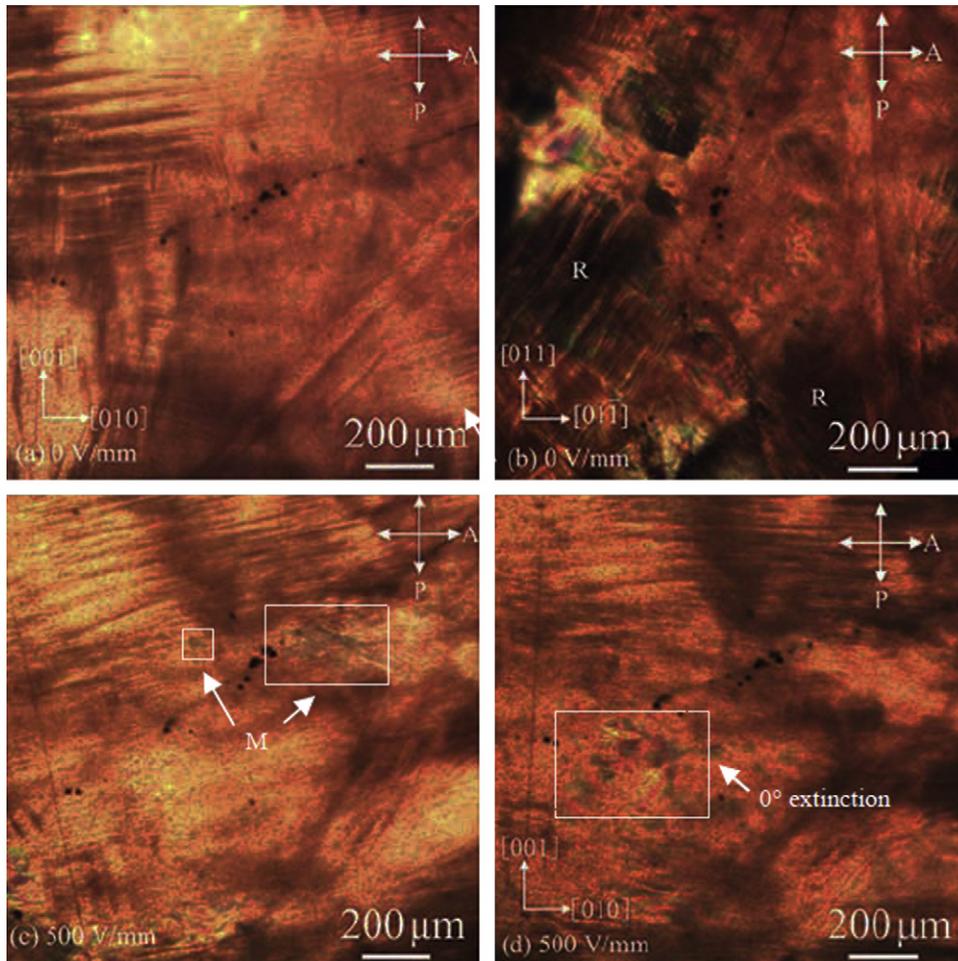


Fig. 2. Domain structures observed in  $[100]_c$ -oriented PMN–0.3PT crystal under an electric field along  $[001]_c$  at 30 °C. (a) and (b) 0 V/mm, (c) and (d) 500 V/mm.

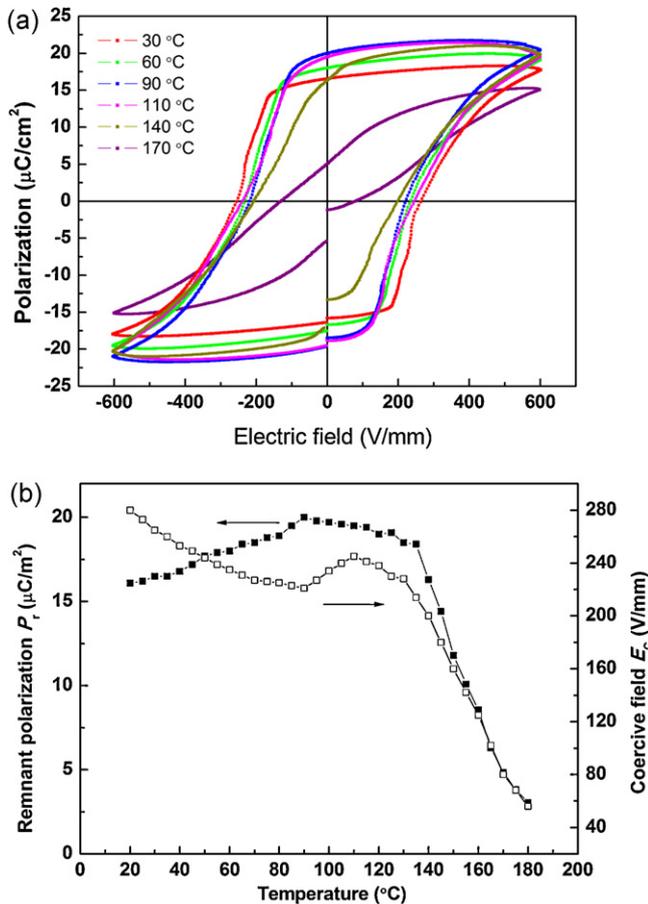


Fig. 3. Temperature dependence of (a) hysteresis loops and (b) remnant polarization ( $P_r$ ) and coercive field ( $E_c$ ).

reveals 45° extinction at 0 V/mm, the T phase (with 0° extinction angle) does not appear at this temperature, indicating a majority R phase. As the electric field increases, the M phase with 10° extinction appears and can be stabilized at 500 V/mm as shown in Fig. 2(c). Only a portion of the crystal reveals 0° extinction without drastic changes in piezoresponse (Fig. 2(d)), which exhibits irregular shaped micro-domain distributed randomly in the crystal.

The [001]<sub>c</sub>-oriented rhombohedral PMN-0.3PT crystal can be poled effectively by a relatively low electric field (~200 V/mm) which is much smaller than the critical field of M<sub>C</sub> phase [22]. The origin of the rapid increase in piezoresponse is related to R-M<sub>A</sub> phase transformation, which is consistent with the first-principles calculations [8]. The R-M<sub>A</sub> phase transformation is predicted to be the minimum energy path of polarization rotation. The irregular shaped micro-domains are possibly caused by rotating microdomains or nanocluster polarizations into alignment, which play an important role in PMN-PT single crystals because they can accommodate the spontaneous lattice distortion and minimize the elastic strain energy [23,24].

Fig. 3(a) shows the temperature dependent hysteresis loops, and Fig. 3(b) shows the remnant polarization ( $P_r$ ) and coercive field ( $E_c$ ) vs temperature. As shown in Fig. 3(b), the remnant polarization  $P_r$  exhibits a peak at 90 °C corresponding to the ferroelectric phase transition from rhombohedral to tetragonal phase, which has been previously confirmed experimentally [16], while the abrupt change at 140 °C indicates the phase transition from tetragonal

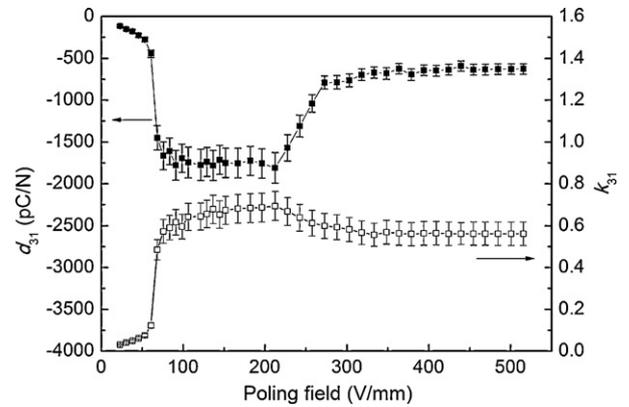


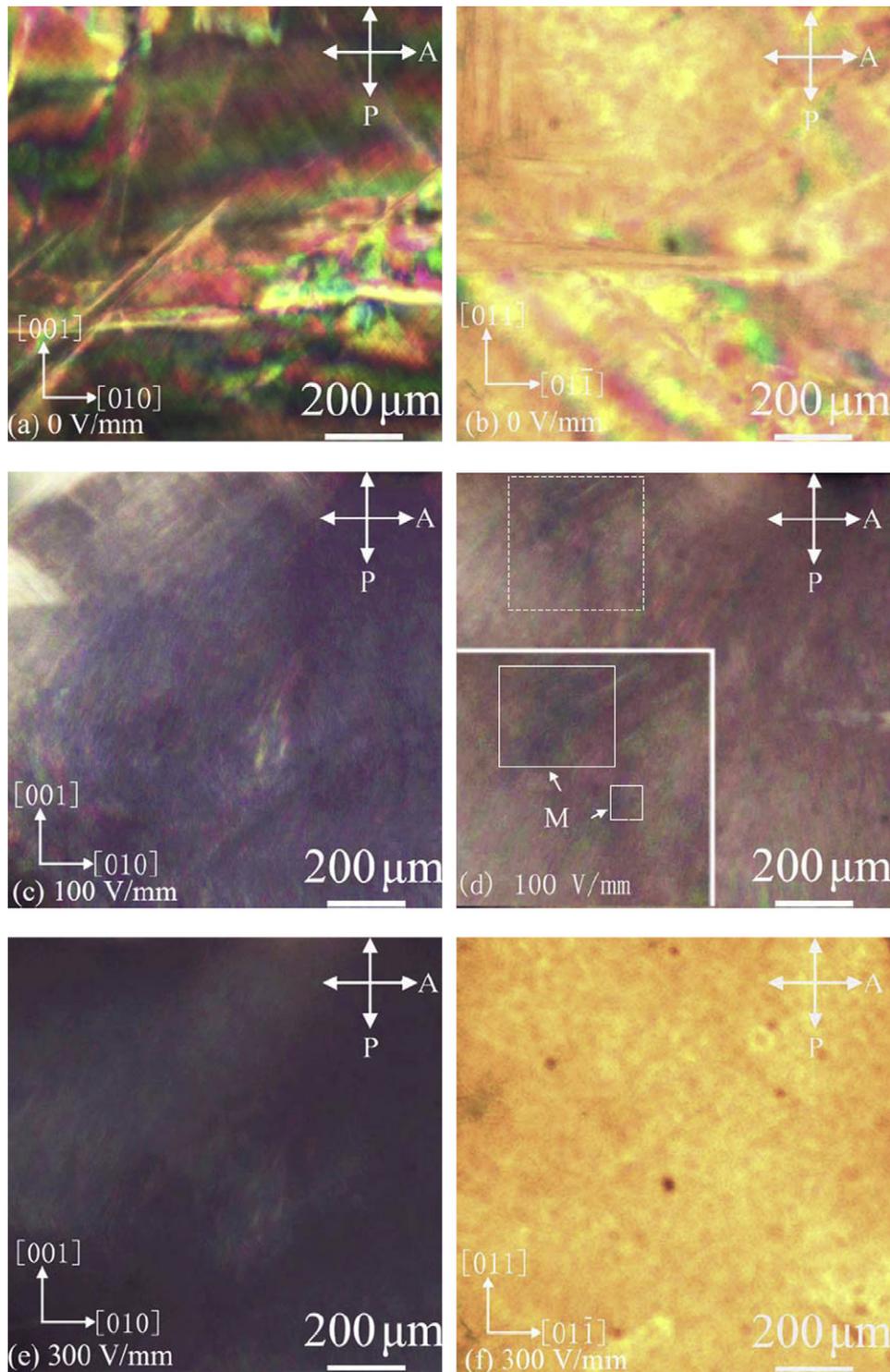
Fig. 4. The piezoelectric properties of PMN-0.3PT measured as a function of poling field under an electric field along [001] at 90 °C.

ferroelectric phase to cubic paraelectric phase. The coercive field  $E_c$  also changes drastically near 90 °C and 140 °C.

Fig. 4 shows the dependence of piezoelectric properties of tetragonal PMN-0.3PT single crystal on the poling field at 90 °C. The resonance peaks appear in the admittance spectra at 20 V/mm,  $d_{31}$  and  $k_{31}$  are -113 pC/N and 0.03, respectively. Upon further increase of the electric field,  $d_{31}$  increases drastically at 60 V/mm, and then decreases at 210 V/mm. The electromechanical coupling coefficient  $k_{31}$  also changes drastically near the two critical fields, which indicates the presence of an intermediate phase.

In order to explain this phenomenon, the domain structures of PMN-0.3PT single crystal were observed at 90 °C. As shown in Fig. 5(a) and (b), the T phase is dominant in the crystal without electric field at 90 °C, but no complete extinction direction was observed because of the reflection of light from dense domain walls [25]. As shown in Fig. 5(c), most parts of the crystal reveals 0° extinction at 100 V/mm, which indicates the [001] tetragonal phase, as indicated by  $T_{001}$ , is induced under this condition. In Fig. 5(d), the laminar domains with 10° extinction are observed which can be confirmed to be M phase. As shown in Fig. 5(e) and (f), the image indicates  $T_{001}$  mono-domain structure at 300 V/mm. At 90 °C, [001]<sub>c</sub> direction is one of the polar axes of the tetragonal PMN-0.3PT single crystal. Mono-domain state can be obtained when the poling field is sufficiently large along one of the polar axes, the domain switching process here can be identified as ( $T_{100}$  or  $T_{010}$ ) → M →  $T_{001}$ , i.e., a monoclinic phase serves as an intermediate phase. Similar phenomenon was also observed in PMN-0.4PT and PZN-0.09PT single crystals [26,27].

Considering the excellent piezoelectric properties obtained in poling process, the domain wall contribution should be considered. There are two types of domains: the 180° and non-180° ferroelectric domains. The strain tensors are the same for the two domains connected by a 180° domain wall, so that this kind of domain walls only contribute to the polarization and dielectric properties. The non-180° domain walls refer to walls between domains of different strain tensors. In general, both 180° and non-180° domains form to reduce the effects of depolarization field, whereas only non-180° domains contribute to the minimization of the elastic energy [28]. The non-180° domain wall contribution is strongly dependent on the microstructure and crystal structure, which is significantly large in the crystal that contains multi-phases [29,30].



**Fig. 5.** Domain structures observed in  $[100]_c$ -oriented PMN-0.3PT crystal under an electric field along  $[001]$  at  $90^\circ\text{C}$ . (a) and (b) 0 V/mm, (c) and (d) 100 V/mm, (e) and (f) 300 V/mm. In Fig. 3(d), the dashed area is magnified at the left corner.

#### 4. Conclusions

In this study, the influence of temperature on electric-field-induced domain switching was investigated. The piezoelectric properties and domain structures of PMN-0.3PT single crystal for different poling fields were characterized at  $30^\circ\text{C}$  and  $90^\circ\text{C}$ . The PMN-0.3PT single crystal exhibits a rapid increase in piezoresponse at one critical field (100 V/mm) at  $30^\circ\text{C}$ , which is related to  $R-M_A$  phase transformation. A portion of the crystal reveals  $0^\circ$

extinction at 500 V/mm, which is related to rotating microdomains or nanocluster polarizations into alignment. At  $90^\circ\text{C}$ , the piezoelectric properties of PMN-0.3PT single crystal change drastically at two critical fields (60 V/mm and 210 V/mm), the M and  $T_{001}$  phases coexist at 100 V/mm, while  $T_{001}$  mono-domain appears at 300 V/mm. Based on the fact that overpoling phenomenon observed at  $90^\circ\text{C}$ , we conclude that non- $180^\circ$  domain switching is the primary route to accomplish the poling. Our results clearly show that the phase state and the domain structure of the

crystal are closely related to the extraordinary high piezoelectric behaviors.

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