

# Optimization of piezoelectric properties for $[001]_c$ poled $0.94\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.06\text{PbTiO}_3$ single crystals

Yang Xiang,<sup>1</sup> Rui Zhang,<sup>1,a)</sup> and Wenwu Cao<sup>1,2,b)</sup>

<sup>1</sup>Department of Physics, Harbin Institute of Technology, Harbin, Heilongjiang 150080, People's Republic of China

<sup>2</sup>Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

(Received 2 December 2009; accepted 21 January 2010; published online 1 March 2010)

The piezoelectric properties of  $[001]_c$  poled  $0.94\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.06\text{PbTiO}_3$  single crystals were greatly enhanced by controlling their domain configurations. Contrary to the interpretation of charged domain walls being the main contributor to the piezoelectric enhancement, we found that smaller domain size and more neutral domain walls were the main contributors for the piezoelectric enhancement of these multidomain crystals. The properties of  $109^\circ$  neutral domain walls in  $0.94\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.06\text{PbTiO}_3$  single crystals were extracted by using a piezoelectric domain wall model. © 2010 American Institute of Physics. [doi:10.1063/1.3314285]

Domain engineering is an important technique developed in recent years for obtaining enhanced piezoelectric properties in ferroelectric materials. 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 exhibit ultrahigh piezoelectric properties, which are ideal for many electromechanical applications such as high-sensitivity sensors, broadband transducers, and large displacement actuators.<sup>1,2</sup>

However, the macroscopic properties for crystals with the same chemical composition vary significantly according to different research groups. For instance, the piezoelectric coefficients  $d_{33}$  of PZN-7%PT crystals showed deviations up to 23% from the average value,<sup>3-5</sup> which produced difficulties for practical applications and theoretical investigations. Such a property discrepancy was always attributed to the solute segregation during the crystal growth process.<sup>6</sup> It should be noted that the properties of ferroelectric single crystals are sensitive to the poling conditions.<sup>7,8</sup> In order to gain a comprehensive understanding on the effect of poling conditions, in this work we adopted different poling procedures for PZN-6%PT single crystals and simulated the property enhancement using a piezoelectric domain wall model.

PZN-6%PT single crystals used in this work were supplied by Microfine Materials Technologies P/L (Singapore). One  $k_{33}$  resonator was prepared with the dimensions of  $1\text{ mm}/[100]^L \times 1\text{ mm}/[010]^W \times 6\text{ mm}/[001]^T$  and the 3 pairs of parallel surfaces were fine-polished. The sample was poled at various fields near  $T_c \sim 165^\circ\text{C}$ . The  $k_{33}$  resonator was heated to  $T_1=160^\circ\text{C}$  at  $2^\circ\text{C}/\text{min}$ , and maintained at  $T_1$  for 1 h. Then, at  $T_1$ , an  $E$ -field was slowly increased to  $E_1=180\text{ V/mm}$  and held for 25 min; with the crystal being cooled down to  $T_2=100^\circ\text{C}$  at  $1^\circ\text{C}/\text{min}$ , the  $E$ -field was slowly reduced to  $E_2=80\text{ V/mm}$  and held for 25 min. After that, the crystal was cooled down to  $T_3=50^\circ\text{C}$  at  $1^\circ\text{C}/\text{min}$  and the  $E$ -field was slowly reduced to  $E_3=40\text{ V/mm}$ ; after maintaining at  $E_3$  and  $T_3$  for 25 min, the crystal was finally cooled down to room temperature and the  $E$ -field was completely removed. This poling procedure (a)

was summarized in Table I. Other three similar poling procedures (b), (c), and (d) were also performed on the  $k_{33}$  resonator, as detailed in Table I. Before each repoling, the sample was annealed at  $400^\circ\text{C}$  for 3 h to completely depole the sample and release the internal stresses. The electromechanical coupling factor  $k_{33}$  and elastic compliance constant  $s_{33}^E$  were determined from the impedance spectrum measured by an impedance analyzer, and  $d_{33}$  was measured by a Berlincourt-type meter.  $k_{33}$ ,  $s_{33}^E$ , and  $d_{33}$  measured in PZN-6%PT crystal poled by those four poling procedures were listed in Table II. In procedures (c) and (d), both  $d_{33}$  and  $k_{33}$  have notable enhancement compared to the values of  $d_{33} \sim 2400\text{ pC/N}$  and  $k_{33} \sim 0.93$  of PZN-6%PT crystal reported by Park *et al.*<sup>9</sup>

Permissible orientations of domain walls in  $[001]_c$  poled rhombohedral crystals had been discussed by Yin and Cao.<sup>10</sup> Neutral walls in piezoelectric crystals are energetically favored to minimize the electrostatic energy.<sup>11</sup> In addition, multilayer structure is typical in the domain engineered crystals.<sup>12</sup> Based on these analyses, a schematic diagram of the domain patterns in a  $[001]_c$  poled PZN-6%PT crystal is depicted in Fig. 1. There are two twin structures, the first one contains two domains with polarizations  $\text{P}^{\text{II}}[111]_c$  and  $\text{P}^{\text{III}}[\bar{1}\bar{1}\bar{1}]_c$  and a  $109^\circ$  neutral domain wall, and the second one is composed of two domains with polarizations  $\text{P}^{\text{II}}[\bar{1}\bar{1}\bar{1}]_c$  and  $\text{P}^{\text{IV}}[1\bar{1}\bar{1}]_c$  as well as a  $109^\circ$  neutral wall. These two twin structures are alternately layered along  $[100]_c$  with a charged layer interface oriented in  $[100]_c$ .

Using a polarized optical microscope, domain configurations were observed for the  $k_{33}$  resonator. Figures 2(a)–2(d)

TABLE I. Poling procedures for PZN-6%PT single crystals.

Poling procedure	$T_1$ (°C)	$T_2$ (°C)	$T_3$ (°C)	$E_1$ (V/mm)	$E_2$ (V/mm)	$E_3$ (V/mm)
(a)	160	100	50	180	80	40
(b)	170	100	50	90	65	35
(c)	168	130	50	110	60	50
(d)	166	130	50	100	60	45

<sup>a)</sup>Electronic mail: rui Zhang\_ccmst@hit.edu.cn.

<sup>b)</sup>Electronic mail: dzk@psu.edu.

TABLE II. Measured and calculated properties of PZN-6%PT single crystal.

Poling procedure	Measurement results				Calculations		
	Domain size ( $\mu\text{m}$ )	$d_{33}$ (pC/N)	$k_{33}$ (%)	$s_{33}^E$ ( $\text{pm}^2/\text{N}$ )	$v^{(w)}$ (%)	$d_{33}$ (pC/N)	$s_{33}^E$ ( $\text{pm}^2/\text{N}$ )
(a)	20	2180	92.7	132.4	2.44	2218	128.9
(b)	16	2550	93.8	140.1	3.03	2438	132.8
(c)	11	2890	94.7	146.2	4.35	2918	141.3
(d)	8	3425	95.6	152.7	5.88	3494	151.6

are the domain structures on the (100) surface of the same sample poled by the (a), (b), (c), and (d) procedures, respectively. The width of stripe domains was statistically averaged by Micro-image Analysis & Process software and defined as the domain size in this paper. The domain sizes in Figs. 2(a)–2(d) were given in Table II. Upon decreasing the domain size from about 20  $\mu\text{m}$  to 8  $\mu\text{m}$ ,  $d_{33}$  increases rapidly from 2180 to 3425 pC/N and  $k_{33}$  increases from 92.7% to 95.6%, while  $s_{33}^E$  increases relatively slowly from 132.4 to 152.7  $\text{pm}^2/\text{N}$ . The results indicate that the domain walls contribute significantly to the piezoelectricity of PZN-6%PT crystal because smaller domain size means more domain walls.

By focusing the microscope at different depth along  $[100]_c$  of the same surface area, multilayered structures with stripes along  $[010]_c$  were observed. The netlike domains on (010) surface and stripe domains on (001) surface shown in Figs. 3(a) and 3(b), respectively, as well as the stripe domains on (100) surface of PZN-6%PT crystal in Fig. 2 are consistent with the patterns depicted in Fig. 1. These results indicate that the dominant domain walls in the  $[001]_c$  poled PZN-6%PT crystal are  $109^\circ$  neutral walls rather than the  $71^\circ$  charged walls assumed previously.<sup>2</sup>

A piezoelectric domain wall model can be used to study the effective property of a twin structure.<sup>13</sup> For a poled PZN-6%PT crystal, the internal continuity conditions for the first or the second twin structure are taken the same as that for BaTiO<sub>3</sub> crystal in Ref. 13, so that the Eq. (9) in Ref. 13 can be applied to calculate the effective properties of each twin structure, viz.,

$$\bar{M} = \left[ \sum_{n=1,2,w_{12}} v^{(n)} M^{(n)} [b^{(n)}]^{-1} \right] \times \left[ \sum_{n=1,2,w_{12}} v^{(n)} [b^{(n)}]^{-1} \right]^{-1}, \quad (1)$$

where  $v^{(1)}$ ,  $v^{(2)}$ , and  $v^{(w_{12})}$  are the volume fractions of domain 1, domain 2, and a  $109^\circ$  neutral domain wall in between,

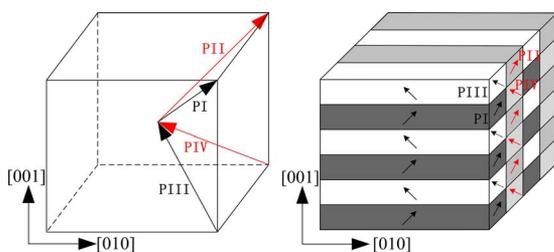
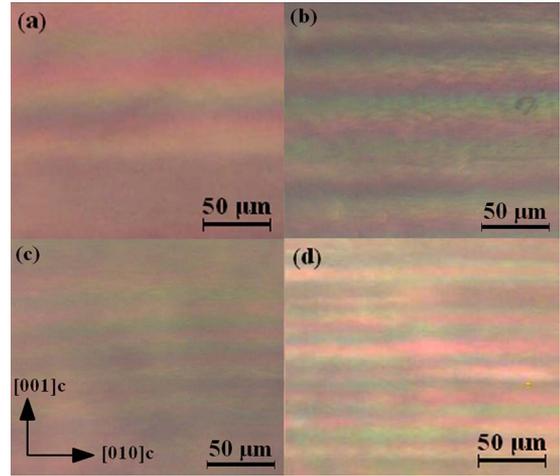
FIG. 1. (Color online) Illustration of domain patterns formed in  $[001]_c$  poled PZN-6%PT single crystal.

FIG. 2. (Color online) Domain structures observed on (100) surface of PZN-6%PT single crystal poled by the procedures (a), (b), (c), and (d).

respectively, with  $v^{(1)} + v^{(2)} + v^{(w_{12})} = 1$ ;  $b^{(n)}$  and  $M^{(n)}$  are  $12 \times 12$  matrices for the first and the second twin structures.<sup>13</sup>

Equation (1) is applied again to calculate the properties of the whole system using the properties of the two twin structures. It should be mentioned that besides those boundary conditions used for the first or the second twin structure, the electric displacement component  $D_2^{(n)}$  is also continuous across the interface between the first and the second twin structures, so that  $b^{(n)}$  and  $M^{(n)}$  become  $13 \times 13$  matrices while calculating the properties of the whole system. The properties used as input of the four domains in  $[001]_c$  poled PZN-6%PT crystal were calculated from the experimental values given in Ref. 14 through coordinate transformation.

For simplicity, we only calculated the effective properties of  $109^\circ$  neutral walls, while the interface between the two twins was neglected to reduce the number of variables. In reality, the domain wall is a transition region between two adjacent domains.<sup>15</sup> Based on the AFM measurements, the domain wall width for LiNbO<sub>3</sub> crystals was found to be about 0.15  $\mu\text{m}$ .<sup>16</sup> While for PZN-6%PT crystal, it has considerably higher spontaneous polarization, which will make the transition region wider. Using different domain wall widths to fit the experimental data, we found that the wall widths from 0.25 to 0.5  $\mu\text{m}$  result in reasonable values. Here we use 0.5  $\mu\text{m}$  as the wall width in our calculations, which results in good agreement with the experimental data.

The fitting procedure and the definition of weighting factors  $a_{ij}$ ,  $b_{ij}$ , and  $c_{ij}$  for elastic compliance, piezoelectric, and dielectric properties of the domain wall can be found in Ref. 13. Based on the experimental data in this work and from Ref. 5, a set of  $a_{ij}$ ,  $b_{ij}$ , and  $c_{ij}$  factors has been determined by the rules defined in Ref. 13

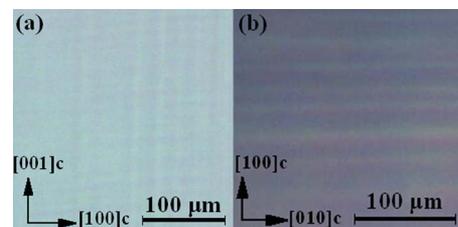


FIG. 3. (Color online) Domain structures observed on (010) and (001) surfaces of PZN-6%PT single crystal poled by the procedure (b).

$$a_{ij} = \begin{cases} 1.2, & i=1, j=1 \\ 1.4, & i=1, j=3, \text{ or } i=2, j=3 \text{ or } i=3, j=1, 2 \\ 1.8, & i=j=5, 6 \\ 1.0, & \text{else,} \end{cases}, \quad (2)$$

$$b_{ij} = \begin{cases} 0.9, & i=2, j=1 \\ 2.0, & i=j=2 \\ 2.25, & i=2, j=3 \\ 1.6, & \text{else} \end{cases}, \quad (3)$$

$$c_{ij} = \begin{cases} 0.6, & i=j=1,2 \\ 1.8, & \text{else} \end{cases}. \quad (4)$$

This set of factors shows that there is much stronger anisotropy in the  $109^\circ$  domain wall region than that in the  $90^\circ$  wall,<sup>13</sup> which might be used to enhance functional properties of PZN-6%PT crystals through rotation. The properties of PZN-6%PT crystals with different volume fractions of  $109^\circ$  walls were given in Table II. From the theoretical calculations, the electromechanical properties of PZN-6%PT crystal are being enhanced progressively with increasing the volume fraction of  $109^\circ$  domain wall (i.e., decreasing the domain size), which is consistent with our experimental results.

In summary, various domain sizes were introduced in PZN-6%PT crystal by adopting different poling procedures. We found that the majority of the domain walls in  $[001]_c$  poled PZN-6%PT crystals are the  $109^\circ$  neutral domain walls rather than the  $71^\circ$  charged walls as assumed by many researchers. Based on the experimental values, we have extracted the effective properties of  $109^\circ$  neutral walls by the piezoelectric domain wall model. Our experimental and the-

oretical results demonstrated that smaller domain size and more neutral domain walls can provide stronger enhancement to the piezoelectricity of domain engineered single crystals. Such domain size dependence of the effective macroscopic properties also provides a reasonable explanation to crystal property variations reported by different groups.

This research was supported by the NSFC Grants Nos. 50602009 and 50972034, PSRDFHP Grant Nos. LBH-Q06068 and NCET-06-0345, and SRF for ROCS, SEM and the NIH Grant No. P41-EB21820.

<sup>1</sup>J. Kuwata, K. Uchino, and S. Nomura, *Ferroelectrics* **37**, 579 (1981).

<sup>2</sup>S.-E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).

<sup>3</sup>K. Harada, Y. Hosono, T. Kobayashi, Y. Yamashita, S. Wada, and T. Tsurumi, *J. Cryst. Growth* **237-239**, 848 (2002).

<sup>4</sup>Y. Hosono, K. Harada, T. Kobayashi, K. Itsumi, M. Izumi, Y. Yamashita, and N. Ichinose, *Jpn. J. Appl. Phys., Part 1* **41**, 7084 (2002).

<sup>5</sup>R. Zhang, B. Jiang, W. W. Cao, and A. Amin, *J. Mater. Sci. Lett.* **21**, 1877 (2002).

<sup>6</sup>T. Karaki, M. Adachi, Y. Hosono, and Y. Yamashita, *Jpn. J. Appl. Phys., Part 2* **41**, L402 (2002).

<sup>7</sup>K. K. Rajan, Y. S. Ng, J. Zhang, and L. C. Lim, *Appl. Phys. Lett.* **85**, 4136 (2004).

<sup>8</sup>M. Shanthi, K. H. Hoe, C. Y. H. Lim, and L. C. Lim, *Appl. Phys. Lett.* **86**, 262908 (2005).

<sup>9</sup>S.-E. Park and T. R. Shrout, *Proceedings of Eighth US-Japan Seminar on Dielectric and Piezoelectric Ceramic Thin Films* (Eighth US-Japan Seminar on Dielectric and Piezoelectric Ceramic Thin Films, Plymouth, MA, 1997), Vol. 235.

<sup>10</sup>J. H. Yin and W. W. Cao, *J. Appl. Phys.* **87**, 7438 (2000).

<sup>11</sup>A. A. Bokov and Z.-G. Ye, *J. Appl. Phys.* **95**, 6347 (2004).

<sup>12</sup>J. P. Han and W. W. Cao, *Appl. Phys. Lett.* **83**, 2040 (2003).

<sup>13</sup>Y. Xiang, R. Zhang, and W. Cao, *J. Appl. Phys.* **106**, 064102 (2009).

<sup>14</sup>J. Jin, K. K. Rajan, and L. C. Lim, *Jpn. J. Appl. Phys., Part 1* **45**, 8744 (2006).

<sup>15</sup>W. Cao and L. E. Cross, *Phys. Rev. B* **44**, 5 (1991).

<sup>16</sup>J. Wittborn, C. Canalias, K. V. Rao, R. Clemens, H. Karlsson, and F. Laurell, *Appl. Phys. Lett.* **80**, 1622 (2002).