

Investigation of single and multidomain $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ crystals with $mm2$ symmetry

Shujun Zhang,^{1,a)} Fei Li,^{1,2} Jun Luo,³ Ru Xia,¹ Wesley Hackenberger,³ and Thomas R. Shrout¹

¹Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania 16802, USA

²Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

³TRS Technologies Inc., 2820 East College Avenue, State College, Pennsylvania 16801, USA

(Received 17 August 2010; accepted 8 September 2010; published online 27 September 2010)

The piezoelectric properties of $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ crystals with various engineered domain configurations were investigated. Rhombohedral and monoclinic/orthorhombic crystals poled along their crystallographic [011] directions were found to possess macroscopic $mm2$ symmetry, with “2R” and “1O” domain, respectively. Crystals with the “2R” domain configuration were found to exhibit high extensional piezoelectric coefficients d_{33} (~ 1300 pC/N) and d_{32} (~ -1680 pC/N), while crystals with the “1O” configuration possessed high shear coefficients d_{15} (~ 3500 pC/N) and d_{24} (~ 2070 pC/N), with relatively low extensional piezoelectric coefficients d_{33} (~ 340 pC/N) and d_{32} (~ -260 pC/N). The observed results were explained by “polarization rotation” model, as related to their respective domain configurations. © 2010 American Institute of Physics. [doi:10.1063/1.3494532]

The ultrahigh piezoelectric properties of [001] poled relaxor-based single crystals are realized through domain engineering, with engineered domain configuration “4R” (4R is one of the domain-engineered structures designated according to the crystal phase and poling direction^{1,2}). High electromechanical coupling factors ($k_{33s} > 0.9$) and piezoelectric coefficients ($d_{33s} > 1500$ pC/N) have been reported in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZNT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMNT) crystals.^{3,4} Additional stable engineered domain configurations, including “2R,” can be achieved in [011] poled relaxor-based crystals, with comparable piezoelectric properties to the [001] crystals, where electromechanical coupling k_{33s} and piezoelectric coefficients d_{33s} were found to be on the order of ~ 0.9 and > 1000 pC/N, respectively. Of particular interest are their ultrahigh transverse properties, with k_{32} coupling factors and piezoelectric d_{32} coefficients being on the order of ~ 0.9 and $-1100 \sim -1600$ pC/N, respectively.⁵⁻⁷ Furthermore, the mechanical quality factor Q_s of [011] poled crystals have been found to be significantly higher, when compared to their [001] poled counterparts (> 500 versus ~ 100), due to the reduced domain wall mobility. The high Q values, with their yet high piezoelectric properties, indicate [011] oriented crystals promising for high power applications.⁸

Recently, theoretical and practical studies have been carried out on various [011] poled relaxor-PT crystal systems, including PZNT, PMNT, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbZrO}_3\text{-PbTiO}_3$ (PMN-PZT), $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) crystals.⁹⁻¹⁶ To date, most of investigations have been carried out on [011] poled rhombohedral crystals with the engineered domain configuration “2R,” focusing on the high transverse piezoelectric d_{32} , with limited reports on the single domain “1O” properties, due to the narrow monoclinic/orthorhombic compositional region.

In this work, both rhombohedral and orthorhombic PIN-PMN-PT single crystals were poled along the [011] direction, resulting in “2R” and “1O” engineered domain configurations. The longitudinal, transverse, and shear electromechanical properties were explored. Large property variations and strong anisotropic behavior in “2R” and “1O” domain states were analyzed using the “polarization rotation” model, as related to two types of engineered domain configuration.

Ternary $x\text{PIN}-(1-x-y)\text{PMN}-y\text{PT}$ ($x=0.25-0.35$ and $y=0.30-0.32$) single crystals were grown using the modified Bridgman technique with [001] oriented seeds. The obtained as-grown crystals were 75 mm in diameter and 100 mm in length. The compositions investigated in this research were selected near the rhombohedral to monoclinic/orthorhombic morphotropic phase boundaries (MPB). The crystals were oriented using real-time Laue x-ray and the samples were cut into different vibration resonators, according to the IEEE standard on piezoelectricity.¹⁷ Prior to property measurements, the samples were sputtered with gold electrodes on the parallel (011) surfaces. The samples were poled at room temperature using 15 kV/cm dc field. For transverse 31- and 32-vibration modes, the vibration direction is along [0-11] and [100] orientations, respectively. For shear 15- and 24-vibration modes, the electrodes were subsequently removed from the (011) faces and re-electroded on the (0-11) and (100) faces. The dielectric permittivity of the various samples was determined at 1 kHz, using an HP4284A multifrequency inductance-capacitance-resistance (LCR) meter. The resonance and antiresonance frequencies were measured using an HP4294A impedance-phase gain analyzer. The electromechanical coupling factors (k_{ij} s) and elastic constants (s_{ij}/c_{ij}) were calculated from the measured resonance and antiresonance frequencies.

Figure 1 shows the dielectric permittivity as function of temperature for [011] poled PIN-PMN-PT crystal samples with compositions close to the R-O MPB. The Curie tem-

^{a)}Author to whom correspondence should be addressed. Electronic mail: soz1@psu.edu.

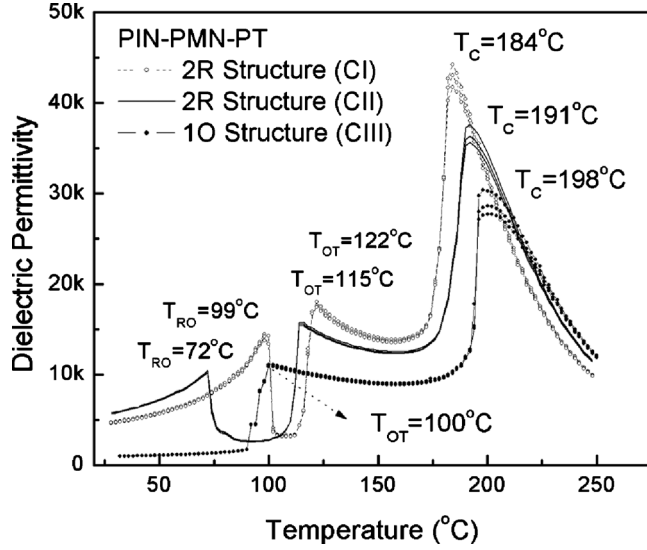


FIG. 1. Dielectric permittivity as function of temperature for PIN-PMN-PT with “1O” and “2R” engineered domain configurations.

perature (T_C) for various crystal samples, crystal I (abbreviated as CI)—crystal III (CIII), were found to be 184 °C, 191 °C, and 198 °C, respectively, indicating that the PT content increased from CI to CIII, according to the phase diagram.¹⁸ Two ferroelectric-ferroelectric (F-F) phase transitions are evident prior to T_C for CI and CII, corresponding to rhombohedral-orthorhombic (T_{RO}) and orthorhombic-tetragonal (T_{OT}) phase transitions, respectively. T_{RO} and T_{OT} were found to be 99 and 122 °C for CI, being 72 and 115 °C for CII, due to the curved MPB.¹⁸ As shown in Fig. 1, permittivity values in the intermediate temperature range (T_{RO} – T_{OT}) for CI and CII were low, indicating the existence of an “1O” metastable single domain state, which was bounded by a low temperature, domain engineered “2R” state and engineered domain configuration “2T” at high temperature. For the CIII composition with the monoclinic/orthorhombic phase, however, only one F-F transition was observed prior to T_C , corresponding to the O-T phase transition, being on the order of 100 °C. The dielectric permittivity of CIII at room temperature was significantly lower than both CI and CII, suggesting that a pseudosingle domain state “1O” was achieved in [011] poled monoclinic PIN-PMN-PT crystals. It should be noted that both crystals with “1O” and “2R” domain states possess macroscopic $mm2$ symmetry.

Table I list the elastic constants (s_{ij}/c_{ij}), electromechanical couplings (k_{ij}), piezoelectric coefficients (d_{ij}) and dielectric permittivities (ϵ_{ii}/ϵ_0) for PIN-PMN-PT single crystals with “1O” (CIII) and “2R” (CI) domain states. The elastic compliances of the extensional vibration modes in “2R” engineering domain state were higher when compared to the values in “1O” single domain, while the shear elastic compliances show higher values in “1O” domain state. The high value of elastic compliance s_{55}^E was found in PIN-PMN-PT with “1O” single domain, being on the order of 288 pm^2/N , corresponding to an ultralow frequency constant of ~ 330 Hz m. Electromechanical coupling factors k_{32} , k_{33} , and k_{15} were found to be 0.901, 0.919, and 0.935, respectively, for crystals with “2R” domain state. The corresponding piezoelectric coefficients d_{32} , d_{33} , and d_{15} were on the order of -1680 , 1300, and 2900 pC/N. For the single domain state “1O,” however, extensional mode electromechani-

TABLE I. Piezoelectric properties of PIN-PMN-PT single crystals with single domain “1O” and multidomain “2R” configurations ($s_{ij}^E: \times 10^{-12} \text{ m}^2/\text{N}$; $c_{33}^D: \times 10^{10} \text{ N/m}^2$; $d_{ij}: \text{pC/N}$).

PIN-PMN-PT	s_{11}^E	s_{22}^E	s_{33}^E	s_{44}^E	s_{55}^E	c_{33}^D
1O (CIII)	17.6	18.1	22.1	45.9	288	23.2
2R (CI)	24.8	89.9	52.1	16.1	160	18.7
PIN-PMN-PT	k_{31}	k_{32}	k_{33}	k_{24}	k_{15}	k_t
1O (CIII)	0.670	0.654	0.820	0.827	0.944	0.412
2R (CI)	0.750	0.901	0.919	0.427	0.935	0.500
PIN-PMN-PT	d_{31}	d_{32}	d_{33}	d_{24}	d_{15}	
1O (CIII)	260	-260	340	2070	3490	
2R (CI)	730	-1680	1300	200	2900	
PIN-PMN-PT	$\epsilon_{11}^T/\epsilon_0$	$\epsilon_{22}^T/\epsilon_0$	$\epsilon_{33}^T/\epsilon_0$	T_C (°C)	T_{FF} (°C)	E_C (kV/cm)
1O (CIII)	5360	15 500	900	198	100	6.3
2R (CI)	6810	1480	4360	184	122/99	6.1

cal coupling factors and piezoelectric coefficients decreased significantly when compared to the values in multi domain “2R” state, while the properties of shear vibration modes (24- and 15 modes) increased greatly.

In order to elucidate the large variations in piezoelectric coefficients for “2R” and “1O” domain states, the “polarization rotation” model is considered. There are eight possible degenerate domain variants in the rhombohedral state, two of which will be energetically favored upon the application of an electric field along the $[011]_C$ direction, being equally inclined to the poling direction at an angle of 35.5°, thus, only 71° domain walls remain. However, for crystals with the O phase, the spontaneous polar vectors are along the $[011]_C$ crystallographic directions, thus a single domain “1O” state can be realized as a result of applying an electric field along the $[011]_C$. According to the IEEE standard, the orthorhombic principle axes are notated as $[001]_O$, $[010]_O$, and $[100]_O$, being equal to $[011]_C$, $[0-11]_C$, and $[100]_C$ cubic axes, respectively, via a simple coordinate transform.

Due to the facilitated polarization rotation process in relaxor-PT based crystals,⁵ high transverse dielectric (ϵ_{11} and ϵ_{22}) and shear piezoelectric properties (d_{15} and d_{24}) are expected in “1O” single domain crystals, as shown in Fig. 2 and evident in Table I. For “2R” domain engineered crystals, however, it is interesting to note that the level of the d_{24} coefficient is only ~ 200 pC/N, much lower than that of d_{15} (~ 2900 pC/N), though the crystals show the same macro-

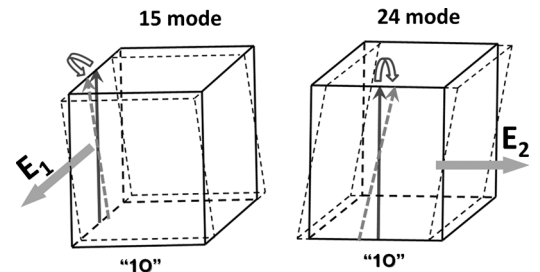


FIG. 2. Two independent shear piezoelectric responses (15- and 24-mode) and related polarization rotation paths in crystals with “1O” pseudosingle domain state.

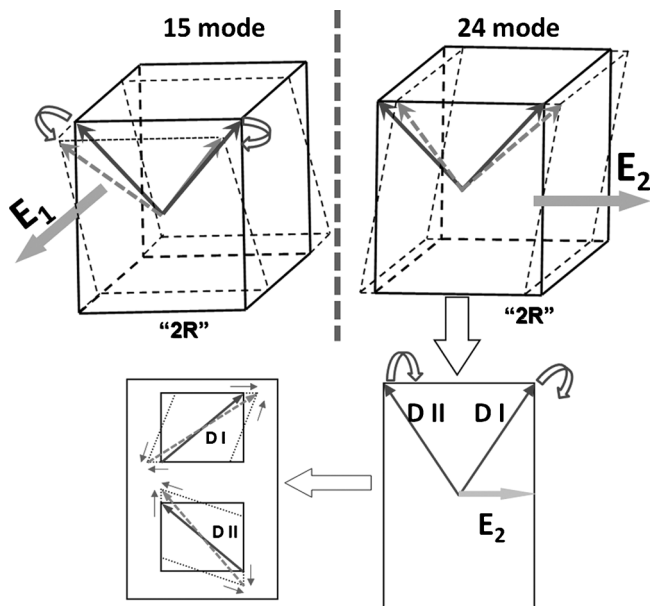


FIG. 3. Two independent shear piezoelectric responses (15- and 24-mode) and related polarization rotation paths in crystals with “2R” engineered domain state, where the shear deformations were contributed by polarization rotation of domain I (DI) and domain II (DII).

scopic $mm2$ symmetry as “1O” domain state. As shown in Fig. 3, upon application of the electric field E_1 , polarization rotation of domains I and II will contribute to the shear piezoelectric deformation S_5 , leading to high piezoelectric coefficients (d_{15}). If an electric field E_2 applied, however, contributions to the shear deformation S_4 through polarization rotations of domains I and II are opposed, negating one another. As a consequence, the apparent piezoelectric coefficient d_{24} is minimized. Analogous to the above analysis, the small shear piezoelectric coefficients observed for [001] poled “4R” domain engineered crystals (~ 100 – 200 pC/N) (Refs. 19 and 20) are the results of the negated shear deformations.

As observed in crystals with the “4R” engineered domain configuration,^{1–3} [011] poled “2R” crystals exhibit relatively high extensional d_{31} , d_{32} , and d_{33} values, due to the facilitated polarization rotation (high level of shear piezoelectric coefficient in single domain state “1R”), by the application of electric field E_3 , as shown in Fig. 4. It should be noted that the extensional piezoelectric coefficients of “2R” crystals increased as the composition approaching R-O phase boundary, due to the flattening of free energy,⁵ where the d_{33} s were on the order of 1300 pC/N and 1500 pC/N for CI and CII, respectively. However, these extensional piezoelectric coefficients are small in “1O” single domain crystals, due to the electric field E_3 coincides with the spontaneous polarization direction, where no “polarization rotation” occurs and the collinear piezoelectric effect dominates.⁵

In summary, [011] poled PIN-PMN-PT single crystals with “2R” and “1O” domain states were investigated. High extensional piezoelectric coefficients d_{33}/d_{32} were observed in engineered multi domain “2R” crystals, as a result of the facilitated polarization rotation. Of particular interest is the high shear piezoelectric coefficient d_{24} found in

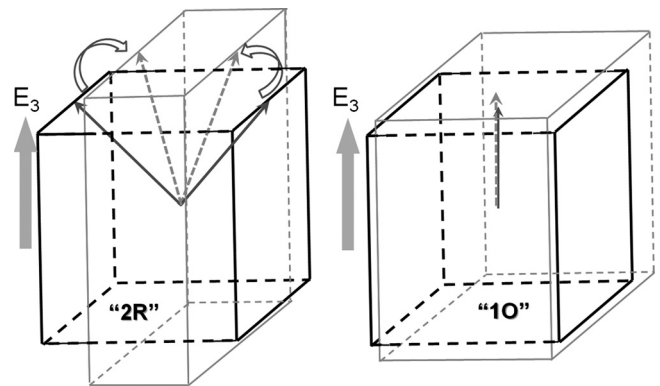


FIG. 4. Extensional piezoelectric response and related polarization rotation paths in crystals with “1O” and “2R” domain states.

crystals with the “1O” domain state (~ 2070 pC/N), when compared to the value of “2R” multidomain configuration (~ 200 pC/N), owing to the negated shear deformation S_4 in “2R” domain engineered structure.

The work was supported by NIH under Grant No. P41-EB21820 and ONR. The author F. Li (XJTU) acknowledged the National Basic Research Program of China (973 Program) under Grant No. 2009CB623306, International Science & Technology Cooperation Program of China under Grant No. 2010DFR50480, and the National Nature Science Foundation of China (Grant Nos. 10976022 and 50632030).

- ¹M. Davis, D. Damjanovic, D. Hayem, and N. Setter, *J. Appl. Phys.* **98**, 014102 (2005).
- ²M. Davis, D. Damjanovic, and N. Setter, *Appl. Phys. Lett.* **87**, 102904 (2005).
- ³S.-E. Park and T. R. ShROUT, *J. Appl. Phys.* **82**, 1804 (1997).
- ⁴S. J. Zhang, J. Luo, R. Xia, P. W. Rehrig, C. A. Randall, and T. R. ShROUT, *Solid State Commun.* **137**, 16 (2006).
- ⁵M. Davis, M. Budimir, D. Damjanovic, and N. Setter, *J. Appl. Phys.* **101**, 054112 (2007).
- ⁶S. J. Zhang, C. A. Randall, and T. R. ShROUT, *Jpn. J. Appl. Phys., Part 2* **42**, L1152 (2003).
- ⁷R. Zhang, B. Jiang, W. Jiang, and W. Cao, *Appl. Phys. Lett.* **89**, 242908 (2006).
- ⁸S. Zhang, N. Sherlock, R. Meyer, Jr., and T. ShROUT, *Appl. Phys. Lett.* **94**, 162906 (2009).
- ⁹Y. Lu, D. Y. Jeong, Z. Y. Cheng, Q. M. Zhang, H. S. Luo, Z. W. Yin, and D. Viehland, *Appl. Phys. Lett.* **78**, 3109 (2001).
- ¹⁰J. Peng, H. S. Luo, D. Lin, H. Xu, T. He, and W. Jin, *Appl. Phys. Lett.* **85**, 6221 (2004).
- ¹¹D. Viehland and J. F. Li, *J. Appl. Phys.* **92**, 7690 (2002).
- ¹²R. Zhang, B. Jiang, and W. Cao, *J. Phys. Chem. Solids* **65**, 1083 (2004).
- ¹³K. K. Rajan, J. Jin, W. S. Chang, and L. C. Lim, *Jpn. J. Appl. Phys.* **46**, 681 (2007).
- ¹⁴E. Sun, S. Zhang, J. Luo, T. ShROUT, and W. Cao, *Appl. Phys. Lett.* **97**, 032902 (2010).
- ¹⁵S. Zhang, S. Lee, D. Kim, H. Lee, and T. ShROUT, *J. Am. Ceram. Soc.* **90**, 3859 (2007).
- ¹⁶S. J. Zhang, J. Luo, W. Hackenberger, N. P. Sherlock, R. J. Meyer, Jr., and T. R. ShROUT, *J. Appl. Phys.* **105**, 104506 (2009).
- ¹⁷IEEE Standard on Piezoelectricity, 1987.
- ¹⁸S. J. Zhang and T. R. ShROUT, Relaxor-PT Single crystals: Observations and Developments, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **57**, 2138 (2010).
- ¹⁹S. J. Zhang, J. Luo, W. Hackenberger, and T. R. ShROUT, *J. Appl. Phys.* **104**, 064106 (2008).
- ²⁰X. Liu, S. Zhang, J. Luo, T. ShROUT, and W. Cao, *J. Appl. Phys.* **106**, 074112 (2009).