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Elastic, dielectric and piezoelectric characterization of single domain PIN-PMN-PT: Mn crystals

Xiaoqing Huo,[1,2] Shujun Zhang,[2,a)] Gang Liu,[2] Rui Zhang,[1,b)] Jun Luo,[3] Raffi Sahul,[2,3] Wenwu Cao,[1,2] and Thomas R. Shrout[2]
[1]*Condensed Matter Science and Technology Institute, Harbin Institute of Technology, Harbin 150001, China*
[2]*Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, USA*
[3]*TRS Technologies, Inc., 2820 E. College Ave., State College, Pennsylvania 16801, USA*

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Mn modified $0.26Pb(In_{1/2}Nb_{1/2})O_3-0.42Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$ (PIN-PMN-PT:Mn) single crystals with orthorhombic perovskite crystal structure were polarized along [011] direction, resulting in the single domain state "1O." The complete set of material constants was determined using the combined resonance and ultrasonic methods. The thickness shear piezoelectric coefficient d_{15} and electromechanical coupling factor k_{15} were found to be on the order of 3100 pC/N and 94%, respectively, much higher than longitudinal $d_{33} \sim 270$ pC/N and $k_{33} \sim 70\%$. Using the single domain data, the rotated value of d_{33}* along [001] direction was found to be 1230 pC/N, in agreement with the experimentally determined d_{33} value of 1370 pC/N, conferring extrinsic contributions being about 10%, which was also confirmed using the Rayleigh analysis. In addition, the mechanical quality factors Q_m were evaluated for different "1O" vibration modes, where the longitudinal Q_m was found to be ∼1200, much higher than the value for "4O" crystals, ∼300. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4772617]

I. INTRODUCTION

Relaxor-$PbTiO_3$ (PT) based single crystals have been extensively studied in the past two decades owing to their excellent piezoelectric and electromechanical properties.[1–8] Relaxor-PT single crystals possess rhombohedral (R), monoclinic/orthorhombic (M/O), and tetragonal (T) phases depending on the PT level. For [001] poled R phase binary $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) and ternary $Pb(In_{1/2}Nb_{1/2})O_3$-$Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PIN-PMN-PT) single crystals, longitudinal piezoelectric coefficients d_{33} and electromechanical coupling factors k_{33} are on the order of $\geq$1500 pC/N and $>$90%, respectively. In addition to the longitudinal properties, thickness shear piezoelectric coefficients d_{15} and electromechanical coupling factors k_{15} were reported for [111] poled crystals with "1R" single domain state.[9–12] For orthorhombic crystals, there are twelve spontaneous polarization exist along crystallographic directions {011}, as shown in Figure 1, "1O" single domain state will be induced when poled along its spontaneous polarization direction [011], with macroscopic *mm*2 symmetry, while exhibiting "4O" engineered domain configuration when poled along [001] direction, with macroscopic 4*mm* symmetry.[6] Analogous to R phase crystals, the piezoelectric coefficient d_{33} and electromechanical coupling factor k_{33} for "1O" single domain crystals were found to be smaller than the values of "4O" domain engineered crystals, but with much higher shear properties.[13] Recently, manganese modified PIN-PMN-PT crystals have been studied, exhibiting enhanced mechanical quality factor Q_m and increased field stability, potential for high power transducer applications.[14,15] To date, however, there are no reports on the complete material constant matrix for [011] poled PIN-PMN-PT:Mn crystals, which is the target of this research.

Full material constants matrix of [011] poled PIN-PMN-PT:Mn single crystals with the "1O" single domain state were determined. The mechanical quality factors Q_m were evaluated for various vibration modes and compared to crystals with "4O" engineered domain configuration. The piezoelectric coefficient d_{33} of "4O" crystals was experimentally determined and compared to the calculated d_{33}* using the single domain data. In addition, the intrinsic and extrinsic contributions to the longitudinal piezoelectric response were evaluated using the Rayleigh analysis.

II. EXPERIMENTAL

The Mn modified PIN-PMN-PT single crystals, with nominal composition 0.26PIN-0.42PMN-0.32PT, were grown using the modified Bridgman technique. The level of Mn doping was in the range of 1–5 mol. %. Associate with the Bridgman growth of the solid solution, various phases occurred along the growth direction due to the Ti segregation, where the studied single crystal section was in the O phase. In this work, orthorhombic samples were oriented by real-time Laue x-ray along [001] and [011] crystallographic directions and designed with aspect ratios according to the IEEE standards.[16,17] All samples were sputtered with gold electrodes on the desired surfaces and poled by field cooling method, in which the samples were poled under a 3 kV/cm dc electric field at 230 °C and then slowly cooled down to room temperature with electric field at the rate of 4 °C/min. There are 17 independent material constants: 9 elastic, 5 piezoelectric, and 3 dielectric permittivity. Here, $[0\bar{1}1]$ is defined as the X axis, and [100], [011] are selected as the Y and Z axes, respectively.

[a)] Electronic mail: soz1@psu.edu.

[b)] Electronic mail: ruizhang_ccmst@hit.edu.cn.

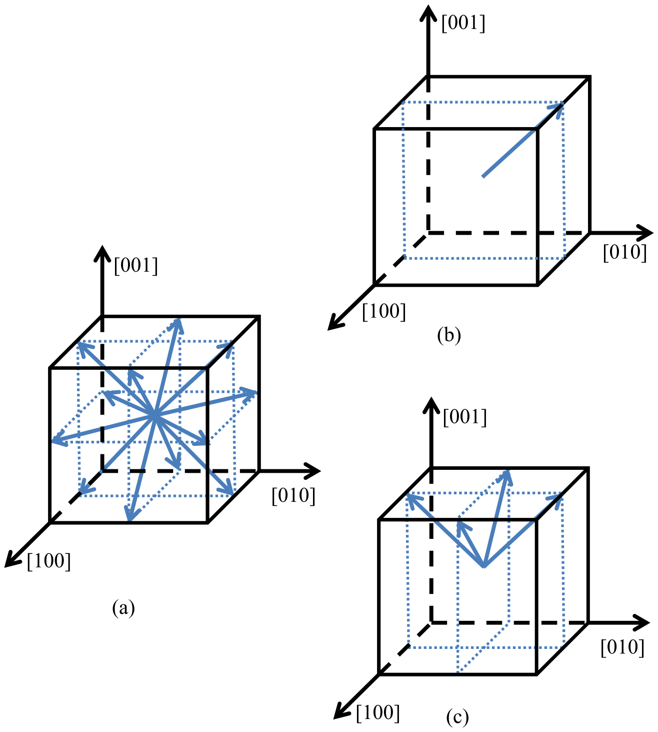

FIG. 1. (a) Spontaneous polarization directions in orthorhombic crystals; (b) "1O" single domain state showing polarization along [011] direction; (c) "4O" engineered domain configuration after poling along crystallographic [001] direction.

Combined resonance and ultrasonic methods were used to measure these independent materials constants, in order to mitigate the effect of inhomogeneous composition and improve the self-consistency of the full matrix.[5] For the resonance method, the resonance and anti-resonance frequencies were measured using an HP4194A impedance-phase gain analyzer, from which, corresponding electromechanical coupling factors k_{ij}s, piezoelectric coefficients d_{ij}s and elastic constants s_{ij}/c_{ij}s could be calculated. For the ultrasonic measurements, longitudinal and shear wave transducers were used to measure the phase velocities on cubic samples with dimension of $5.0 \times 5.0 \times 5.0$ mm^3. For these measurement, the eight elastic stiffness constants: c^E_{11}, c^E_{22}, c^D_{33}, c^E_{44}, c^D_{44}, c^E_{55}, c^D_{55}, and c^E_{66} could be calculated from the phase velocities. High field polarization measurements were performed on plate samples at room temperature using a modified Sawyer-Tower circuit. The electric-field-induced strain was measured on d_{33} bars using a linear variable differential transducer (LVDT) driven by a lock-in amplifier. The dielectric properties as a function of temperature were measured at 1 kHz using HP4284A precision *LCR* meter connected to a computer controlled furnace.

III. RESULTS AND DISCUSSION

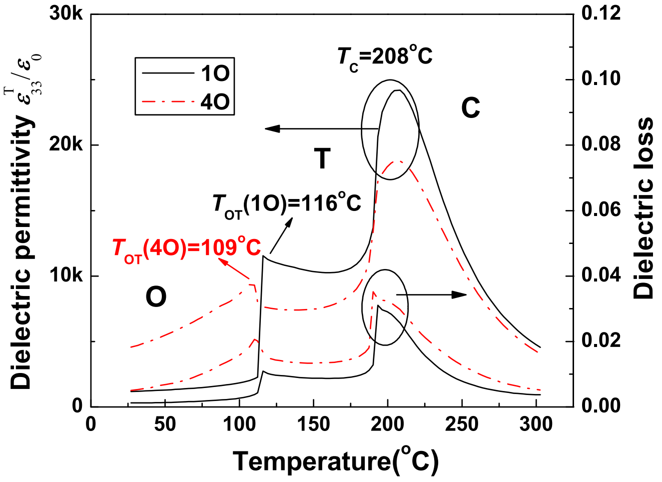

FIG. 2. Temperature dependence of dielectric permittivity and dielectric loss for PIN-PMN-PT:Mn single crystals with "1O" and "4O" domain configurations at 1 kHz.

Fig. 2 shows the dielectric permittivity and dielectric loss as a function of temperature for [011] and [001] poled O phase PIN-PMN-PT:Mn single crystals measured at 1 kHz. As shown, the orthorhombic to tetragonal phase transition temperatures T_{OT} were 116 °C for "1O" crystals and 109 °C for "4O" crystals, respectively, with the Curie temperatures (T_C) being on the order of 208 °C, demonstrating that the studied samples possess similar compositions. This is due to the fact that Curie temperature of relaxor-PT crystals is closely associated with the composition. At room temperature, the dielectric permittivity $\varepsilon^T_{33}/\varepsilon_0$ for PIN-PMN-PT:Mn single crystals with "1O" single domain state was found to be 1240, while the value with "4O" engineered domain crystals was 4570. The dielectric permittivity for "1O" crystals exhibited a flat dielectric behavior in the temperature range of 30–110 °C and increased sharply at the O-T phase transition temperature, above which, the crystals were in temperature induced tetragonal phase and possess "2T" engineered domain configuration, account for the enhanced permittivity. Meanwhile, the dielectric loss for crystals with "1O" single domain state was found to be on the order of 0.1% at room temperature, being lower than that of crystals with "4O" engineered domain configuration.

Fig. 3 shows polarization hysteresis loops for PIN-PMN-PT:Mn single crystals with "1O" and "4O" domain

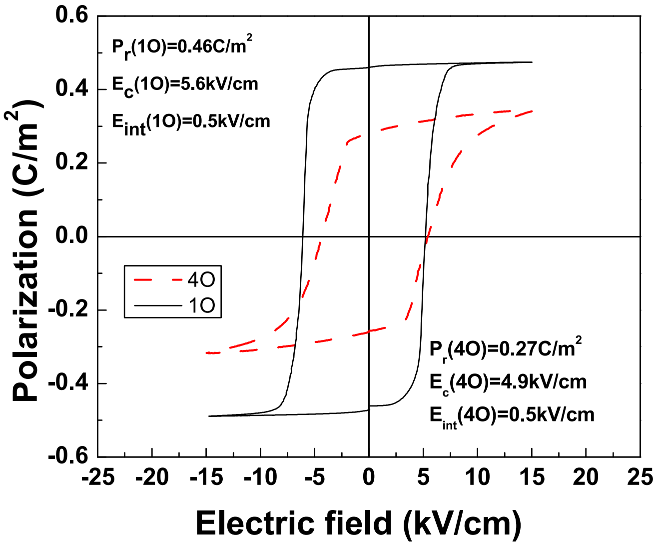

FIG. 3. Polarization hysteresis loops for PIN-PMN-PT:Mn single crystals with "1O" and "4O" domain configurations.

TABLE I. Measured and derived material constants of orthorhombic PIN-PMN-PT:Mn single crystals poled along [011] direction with "1O" single domain state.

Elastic stiffness constants: c_{ij}^E, $c_{\rm ij}^E$(10^{10} N/m^2)

c_{11}^E	c_{12}^E	c_{13}^E	c_{22}^E	c_{23}^E	c_{33}^E	c_{44}^E	c_{55}^E	c_{66}^E
20.0	10.6	4.64	14.9	10.2	15.0	1.84	0.49	7.14
c_{11}^D	c_{12}^D	c_{13}^D	c_{22}^D	c_{23}^D	c_{33}^D	c_{44}^D	c_{55}^D	c_{66}^D
20.1	10.3	5.34	15.7	8.34	19.2	6.69	4.33	7.14

Elastic compliance constants: $s_{\rm ij}^E$, $s_{\rm ij}^E$(10^{-12} m^2/N)

s_{11}^E	s_{12}^E	s_{13}^E	s_{22}^E	s_{23}^E	s_{33}^E	s_{44}^E	s_{55}^E	s_{66}^E
8.59	−7.99	2.75	19.9	−11.0	13.3	54.3	204	14.0
s_{11}^D	s_{12}^D	s_{13}^D	s_{22}^D	s_{23}^D	s_{33}^D	s_{44}^D	s_{55}^D	s_{66}^D
7.49	−4.96	0.07	11.6	−3.64	6.76	14.9	23.1	14.0

Piezoelectric coefficients: d_{ij}(10^{-12} C/N), e_{ij}(C/m^2), $g_{\rm ij}$(10^{-3} Vm/N), h_{ij}(10^8 V/m)

d_{15}	d_{24}	d_{31}	d_{32}	d_{33}	e_{15}	e_{24}	e_{31}	e_{32}	e_{33}
3100	2435	110	−302	267	15.2	44.8	2.38	−6.23	14.5
g_{15}	g_{24}	g_{31}	g_{32}	g_{33}	h_{15}	h_{24}	h_{31}	h_{32}	h_{33}
58.4	16.2	10.0	−27.5	24.3	25.3	10.8	4.80	−12.5	29.2

Dielectric permittivity: $\varepsilon_{\rm ij}/\varepsilon_0$, β_{ij}($10^{-4}/\varepsilon_0$)

ε_{11}^S	ε_{22}^S	ε_{33}^S	ε_{11}^T	ε_{22}^T	ε_{33}^T	β_{11}^S	β_{22}^S	β_{33}^S	β_{11}^T	β_{22}^T	β_{33}^T
679	4672	561	6000	17000	1240	14.7	2.14	17.8	1.67	0.59	8.06

Electromechanical coupling factors: k_{ij} and mechanical quality factors $Q_{\rm m}$

k_{15}	k_{24}	k_{31}	k_{32}	k_{33}	k_t
94%	85%	36%	65%	70%	47%
Q_{15}	Q_{24}	Q_{31}	Q_{32}	Q_{33}	$Q_{\rm t}$
70	30	490	390	1230	220

configurations. The coercive field $E_{\rm c}$ for the single domain "1O" crystals was found to be 5.6 kV/cm, with an internal bias being on the order of 0.5 kV/cm, while the coercive field $E_{\rm c}$ and internal bias for the crystals with "4O" engineered domain configuration were 4.9 kV/cm and 0.5 kV/cm, respectively. Modifying the PIN-PMN-PT single crystals with acceptor dopants $\rm Mn^{3+,2+}$ results in acceptor-oxygen defect dipoles, which occupy energetically preferred sites in the crystal lattice, forming anisotropic centers locally within a domain. The defect dipoles realign themselves along a preferential direction of the spontaneous polarization, giving rise to the internal bias, which is expected to clamp the domain wall motion and restrict the polarization rotation.[14,18]

Table I presents the elastic constants, piezoelectric coefficients and dielectric permittivities of the "1O" single domain crystals. High thickness shear piezoelectric properties and low mechanical $Q_{\rm m}$, with $d_{15} > 3000$ pC/N, $d_{24} > 2400$ pC/N, and $Q_{\rm m} < 100$, were obtained due to the fact that the applied field is perpendicular to the spontaneous polarization direction in the single domain state and leads to the facilitated "polarization rotation."[1,19–21] The overall piezoelectric properties of PIN-PMN-PT:Mn were found to be lower than those values of undoped counterpart, because accepter dopants $\rm Mn^{3+,2+}$ induce internal bias, which stabilize the domain wall and hinder the "polarization rotation." Table II gives the longitudinal property comparison of PIN-PMN-PT:Mn crystals with single domain state "1O" and engineered domain configuration "4O," where the d_{33} and k_{33} of the single domain crystals were found to be on the order of 267 pC/N and 70%, respectively, much smaller than those values of multidomain crystals, due to the fact that only longitudinal "extension" effect exists in single domain crystals, while the longitudinal piezoelectric properties of domain engineered crystals are dominated by "polarization rotation" effect.[19,20] Furthermore, low dielectric loss and high mechanical Q_{33} were observed in "1O" PIN-PMN-PT:Mn single domain crystals, with values being on the order of 0.1% and 1230, respectively, significantly increased when compared to multidomain "4O" crystals, owing to the lack of domain wall and polarization rotation. The properties of PIN-PMN-PT:Mn, PIN-PMN-PT and PMN-PT crystals had been compared in Table III. As shown, for all the single domain crystals, the shear piezoelectric coefficients d_{15} were much higher than the longitudinal piezoelectric coefficients d_{33}. Compared with PMN-PT crystals, PIN-PMN-PT:Mn and PIN-PMN-PT crystals offer increased temperature and field stability, due to their enhanced T_{OT} and E_C. In addition, the internal bias observed in Mn modified PIN-PMN-PT crystals accounts for higher field stability and improved mechanical Q.

The intrinsic piezoelectric coefficient d_{33}* of [001] poled PIN-PMN-PT:Mn crystals can be calculated based on the following formula:

$$d_{33}{}^* = \cos^3\theta\, d_{33} + \cos\theta \sin^2\theta[\sin^2\varphi(d_{31}+d_{15}) + \cos^2\varphi(d_{32}+d_{24})], \quad (1)$$

where d_{31}, d_{15}, d_{33} are single domain data and given in Table I. φ and θ are the Euler angles, which are 90° and 45°, related to the angles between [100] and [011]. Thus the preceding Eq. (1) can be simplified as

$$d_{33}{}^* = \frac{1}{2\sqrt{2}}(d_{31}+d_{15}+d_{33}). \quad (2)$$

Furthermore, the piezoelectric coefficient d_{33} for crystals poled along [001] direction (with "4O" engineered domain configuration) was determined using resonance method and

TABLE II. Dielectric permittivity $\varepsilon_{33}^{\rm T}/\varepsilon_0$, Dielectric loss, electromechanical coupling factor k_{33}, piezoelectric coefficient d_{33}(10^{-12} C/N), elastic compliance constant s_{33}^E(10^{-12} m^2/N), and mechanical quality factor Q_{33} for PIN-PMN-PT:Mn single crystals poled along different orientations.

Material	Domain engineered structure	$\varepsilon_{33}^T/\varepsilon_0$	Dielectric loss (%) at 1 kHz	k_{33}	d_{33} (10^{-12} C/N)	s_{33}^E (10^{-12} m^2/N)	Q_{33}
PIN-PMN-PT:Mn poled along [011]	1O	1240	0.1	0.70	267	13.3	1230
PIN-PMN-PT:Mn poled along [001]	4O	4280	0.4	0.91	1370	60.4	300

TABLE III. Property comparison of single domain PIN-PMN-PT:Mn, PIN-PMN-PT and PMN-PT crystals.

Material (domain state)	T_{FF} (°C)	T_C (°C)	E_C (kV/cm)	E_{int} (kV/cm)	d_{15} pC/N	d_{24} pC/N	d_{33} pC/N	d_{15}/d_{33}
PIN-PMN-PT:Mn(1O)[a]	116	208	5.6	0.5	3100	2435	267	12
PIN-PMN-PT(1O)[b]	98	189	5.5	…	4550	4100	355	13
PIN-PMN-PT(1R)[c]	123	167	4.5	…	2190	2190	74	30
PMN-PT(1R)[d]	65	155	2.5	…	4100	4100	190	22

[a] In this work.
[b] Refs. 13 and 15.
[c] Refs. 1 and 12.
[d] Refs. 1 and 9.

found to be 1370 pC/N, slightly higher than the calculated value ~1230 pC/N. The discrepancy was found to be ~10%, which is associated with the extrinsic contributions. In order to further delineate the intrinsic and extrinsic contributions to the piezoelectric response in [001] poled domain engineered PIN-PMN-PT:Mn crystals, Rayleigh analysis was performed on the [001] oriented crystals.

Fig. 4 shows the ac electric field dependent piezoelectric coefficient $d_{33}(E_0)$ for [001] poled PIN-PMN-PT:Mn single crystals at 1 Hz, where the inset presents a comparison between measured and calculated strain-electric field loop. The piezoelectric coefficient d_{33} was calculated from the peak to peak strain measured using small amplitude of electric field. It is shown that the electric field dependence of the piezoelectric coefficient d_{33} exhibited a linear behavior which can be descried using the Rayleigh formula,[22]

$$d(E_0) = d_{init} + \alpha E_0 \text{pm/V}, \tag{3}$$

where E_0 is the amplitude of electric filed. The d_{init} is considered to arise from the intrinsic contribution and αE_0 represents the extrinsic contribution to the total piezoelectric response. The value of d_{init} and α were found to be 1250 pm/V and 155 (cm/kV)^2, respectively, demonstrating that the extrinsic contribution to the piezoelectric response was ~11% at $E_0 = 1$ kV/cm, which is in good agreement with the value obtained by comparison of the calculated d_{33}* in "1O" single domain state and the measured d_{33} in "4O" domain engineered configuration.

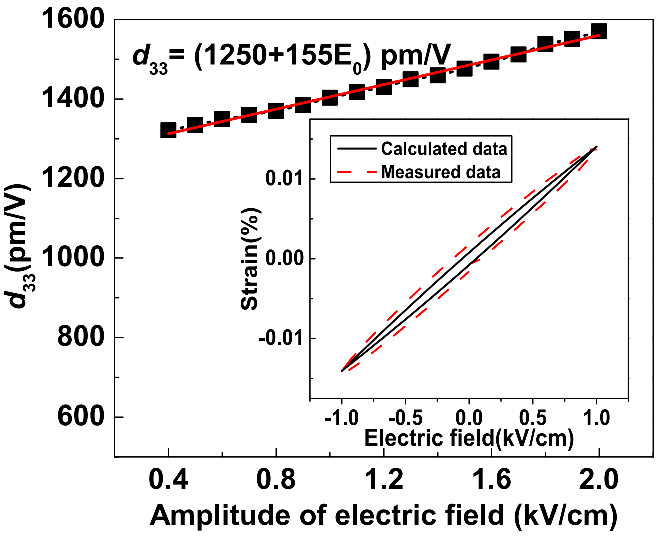

FIG. 4. Ac electric field dependent piezoelectric coefficient d_{33} for PIN-PMN-PT:Mn single crystals at 1 Hz, the comparison between the measured and calculated strain-electric field loops is given in the small inset.

IV. SUMMARY

The complete set of materials constants for "1O" single domain PIN-PMN-PT:Mn was determined using combined resonance and ultrasonic measurements. The mechanical Q_ms for crystals with "1O" single domain state were found to be more than 4 times higher than that of crystals with "4O" engineered domain configuration, because of the lack of "polarization rotation." Internal bias was observed in the polarization hysteresis loop for Mn modified PIN-PMN-PT crystals, being on the order of 0.5 kV/cm, further increase the mechanical Q_m when compared to their pure counterparts. The measured d_{33} for crystals with "4O" engineered domain configuration was found to be 1370 pC/N, slightly higher than the calculated $d_{33}{}^* \sim 1230$ pC/N, with discrepancy of ~11%, which was associated with the extrinsic contributions and was confirmed by Rayleigh's analysis.

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