

Characterization of single domain $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ crystals with monoclinic phase

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(Received 11 July 2011; accepted 14 August 2011; published online 22 September 2011)

Ternary single crystals $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ with monoclinic phase poled along [011] direction show single domain state (1O state) with macroscopic $mm2$ symmetry. The complete set of material constants was determined using the combination of impedance and ultrasonic methods. The thickness shear vibrations in the single domain state give the highest piezoelectric coefficients, with values being on the order of $d_{15} = 4550$ pC/N and $d_{24} = 4100$ pC/N. The rotated value of d_{33}^* along [001], calculated using the single domain data, is in good agreement with the [001] poled multidomain crystal, being 1790 pC/N versus 2010 pC/N, exhibiting the high longitudinal piezoelectric in multidomain comes from the high shear properties in single domain state, with the extrinsic contribution about $\sim 11\%$, induced by the phase boundary motion. © 2011 American Institute of Physics. [doi:10.1063/1.3639316]

I. INTRODUCTION

Relaxor based ferroelectric single crystals, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMNT) and $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT), have been extensively studied in last two decades due to their ultrahigh piezoelectric and electromechanical properties in domain engineered configurations.¹⁻⁷ For example, piezoelectric d_{33} and electromechanical coupling k_{33} were found to be on the order of > 2000 pC/N and $> 90\%$, respectively, when the rhombohedral crystals were poled along nonpolar crystallographic direction [001], with the engineered domain configuration “4R”. For the as-grown PMNT or PIN-PMN-PT single crystals by modified Bridgman approach, large composition variations were observed along the growth direction due to the Ti segregation. Thus, the crystals are in rhombohedral (R), monoclinic (or orthorhombic M/O), and tetragonal (T) phases, depending on the PT content. The monoclinic phase (recognized as pseudo-orthorhombic phase, designed as O phase hereafter) can be readily distinguished from R or T phase by the dielectric-temperature and strain-electric field measurements. In the PMNT system, the crystals are in the O phase with PT in the range of 0.31~0.35.⁶ Until now, however, most research was focused on the high piezoelectric properties in R phase relaxor-PT single crystals, although lot of studies have been carried out on the monoclinic phase in relaxor-PT crystals, which were thought to play roles in the high piezoelectric properties of domain engineered crystals;⁸⁻¹⁰ there are limited references on the properties of “1O” single domain state.¹¹ It was reported that the piezoelectric d_{33} and electromechanical coupling k_{33} were ~ 2000 pC/N and $> 90\%$, for [001] poled O phase single crystals with engineered domain configuration “4O”, comparable to those values obtained from domain engineered rhombohedral

crystals.^{6,7} Analogous to [001] poled domain engineered “4R” crystals, the origin of the large piezoelectric coefficients in [001] poled “4O” crystals were associated with a strong crystalline anisotropy: i.e., an intrinsically large variation of the piezoelectric coefficient in space,¹²⁻²⁰ where the large piezoelectric d_{33} in engineered domain configuration “4R” is attributed to the monodomain “1R” piezoelectric shear coefficient d_{15} (polarization rotation).¹²⁻¹⁸ Nevertheless, there is no report on the complete material constant matrix on the single domain state “1O” in PIN-PMN-PT crystal system, which is desirable for the evaluation of the intrinsic and extrinsic contributions to the high d_{33} in “4O” domain state.

The aim of this research is to determine the full matrix material constants for [011] poled PIN-PMN-PT single crystals with “1O” monodomain configuration. The measured piezoelectric d_{33} of [001] poled crystals with “4O” domain configuration was compared to the value calculated by using the single domain data. In addition, the temperature dependent properties were tested to show the advantage of the “O” phase crystals from viewpoint of applications.

II. EXPERIMENTAL

The PIN-PMN-PT single crystals with starting compositions of (0.25~0.35)PIN-PMN-(0.30~0.32)PT were grown using the modified Bridgman technique.⁵ The as-grown crystals are 3 in. in diameter and 5 in. in length, the crystals with “O” composition (about 0.27PIN-0.40PMN-0.33PT) were selected based on the dielectric and strain measurements. The crystals were oriented by real-time Laue x-ray, along the crystallographic directions [001] and [011]. Vacuum sputtered gold was applied to the polished (011) surfaces as the electrodes and poled at 10 kV/cm electric field at room temperature. The macroscopic symmetry of [011] poled crystals is $mm2$, thus, there are total 17 independent material constants to be determined, including nine elastic, five piezoelectric, and

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TABLE I. Relationship between the phase velocity and elastic constants for crystals with mm2 symmetry and the measured phase velocities for 0.27PIN-0.40PMN-0.33PT with “1O” single domain state.

Propagation direction	[011]	[011]	[011]	[0 $\bar{1}$ 1]	[0 $\bar{1}$ 1]	[0 $\bar{1}$ 1]	[100]	[100]	[100]
Velocity	v_1	v_{s1}	v_{s2}	v_1	$v_{s\parallel}$	$v_{s\perp}$	v_1	$v_{s\parallel}$	$v_{s\perp}$
m/s	4820	629	1257	4579	2155	2820	4140	2887	2820
ρv^2	c_{33}^D	c_{55}^E	c_{44}^E	c_{11}^E	c_{55}^D	c_{66}^E	c_{22}^E	c_{44}^D	c_{66}^E

three dielectric constants.¹⁹ The combination of resonance and ultrasonic methods were employed to determine the material constants to mitigate the effect of inhomogeneous composition and improve the self-consistency. In this study, [011] is poling direction and deemed as z axis, according to IEEE standard on piezoelectricity,²¹ The x axis is parallel to the smaller nonpolar axes, thus [0 $\bar{1}$ 1] is selected as x axis, [100] is selected to be y axis to form the right-hand orthogonal coordinate. Table I lists the phase velocities of longitudinal and shear waves propagating along different crystal orientations and the related elastic stiffness constants, measured by ultrasonic method, where v_1 , $v_{s\parallel}$, and $v_{s\perp}$ refer to the phase velocities of longitudinal wave, shear waves with displacement parallel and perpendicular to the poling direction, while v_{s1} and v_{s2} are shear waves with displacements parallel to [0 $\bar{1}$ 1] and [100] directions, respectively.²²

To confirm the composition, the dielectric temperature behavior was investigated on all the studied samples. Figure 1 shows the dielectric permittivity K_{11}^T , K_{22}^T , and K_{33}^T as a function of temperature for [011] poled “O” phase PIN-PMN-PT single crystals, where the Curie temperatures (T_C) were found to be on the order of 189–191°C, with monoclinic to tetragonal phase transition temperatures (T_{MT}) of 98–102°C, indicating that the samples used in this study are with the same composition, guaranteeing the self-consistency of the full matrix material constants.

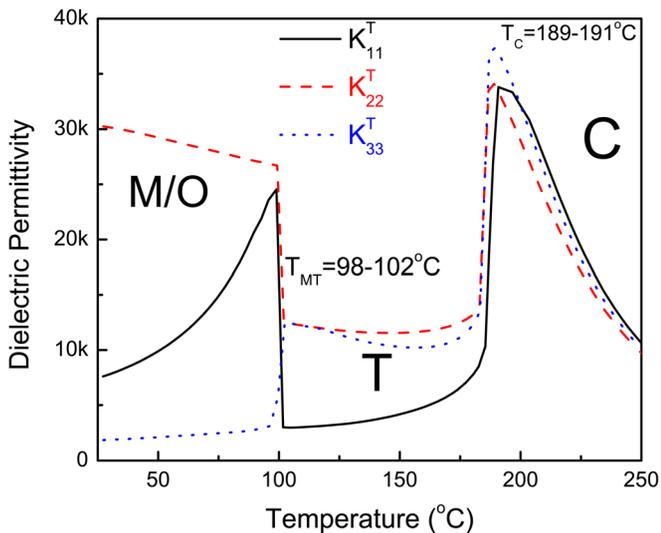


FIG. 1. (Color online) Temperature dependent dielectric permittivity for [011] poled PIN-PMN-PT single crystals with monoclinic phase.

III. RESULTS AND DISCUSSIONS

A. Complete set of material constants for 0.27PIN-0.40PMN-0.33PT with “1O” single domain state, compared to “2R” engineered domain state

The measured and derived elastic, piezoelectric and dielectric material constants of the single domain PIN-PMN-PT crystals are listed in Table II. Compared to [011] poled rhombohedral single crystals with engineered domain “2R”, (Ref. 19) as shown in Table III, the extensional piezoelectric coefficients (d_{31} , d_{32} , and d_{33}) and electromechanical couplings (k_{31} , k_{32} , and k_{33}) were found to be much smaller due to the fact that no “polarization rotations” occur when applied field coincides with the spontaneous polarization in “1O” single domain state, while the shear piezoelectric properties were found to increase due to the facilitated “polarization rotation” when applied field is vertical to spontaneous polarization, as observed in other single domain states.²³ Of particular interest is that the shear piezoelectric d_{24} , being on the order of 4100 pC/N at room temperature, > 25 times higher than the value obtained from “2R” domain engineered crystals,^{19,24} owing to the negated shear deformation s_4 in “2R” engineered domain configuration.²⁴ It should be noted that the measured shear piezoelectric coefficients are higher than those values in Ref. 24 due to the fact that the orthorhombic composition selected in this study is at the proximity of rhombohedral to orthorhombic morphotropic phase boundary (MPB), induce easier polarization rotation and improve the shear piezoelectric properties.

B. Intrinsic and extrinsic contributions of high piezoelectric coefficient along non-polar directions

Based on the single domain data given in Table II, the intrinsic piezoelectric coefficient d_{33}^* in [001] poled PIN-PMN-PT crystals with “4O” multidomain state 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 φ and θ are the Euler angles, describing the rotation angles around z and x' axes, which are 90° and 45° for [001] direction. Thus, the preceding equation can be simplified as:

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

The intrinsic piezoelectric d_{33}^* was calculated to be 1790 pC/N, attributes to the high d_{15} value. In addition, the piezoelectric d_{33} for the [001] poled PIN-PMN-PT crystal with the same “O” composition was measured by impedance method using longitudinal bars, and found to be on the order of 2010 pC/N, slightly higher than the value obtained by single domain data, with discrepancy about ~11%. This is related to the extrinsic contribution from the R-O phase boundary motion, in good agreement with that analyzed by Rayleigh approach.^{6,7}

For comparison, the intrinsic contribution of the large piezoelectric coefficient d_{33} along the nonpolar directions in R and T phases was also evaluated. Table III listed the

TABLE II. Measured and derived material constants for [011] poled 0.27PIN-0.40PMN-0.33PT crystal with “1O” single domain state.

Elastic stiffness: c^E, c^D (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			
17.0	6.76	0.07	13.9	9.59	14.1	1.28	0.32	6.44			
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			
17.1	6.55	0.89	14.2	8.40	18.8	6.75	3.76	6.44			
Elastic compliance: s^E, s^D (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			
9.20	-8.38	5.64	21.2	-14.4	16.8	78.1	316	15.5			
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			
7.44	-4.39	1.61	12.2	-5.23	7.57	14.8	26.6	15.5			
Piezoelectric: d (10^{-12} C/N), e (C/m ²), g (10^{-3} Vm/N), h (10^8 V/m)											
d_{15}	d_{24}	d_{31}	d_{32}	d_{33}	e_{15}	e_{24}	e_{31}	e_{32}	e_{33}		
4550	4100	153	-346	350	14.4	52.5	3.18	-4.12	16.4		
g_{15}	g_{24}	g_{31}	g_{32}	g_{33}	h_{15}	h_{24}	h_{31}	h_{32}	h_{33}		
63.7	15.5	11.5	-26.1	27.1	24.0	10.4	5.01	-7.30	28.8		
Dielectric $\varepsilon(\varepsilon_0)$; $\beta(\times 10^{-4}/\varepsilon_0)$											
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
678	5687	643	8070	30000	1500	14.8	1.76	15.6	1.24	0.33	6.67
Electromechanical coupling: k and density											
k_{15}	k_{24}	k_{31}	k_{32}	k_{33}	k_t	ρ (kg/m ³)					
96%	90%	44%	65%	74%	50%	8100					

piezoelectric coefficients for PIN-PMN-PT crystals with various single domain states, large piezoelectric anisotropic factors (d_{15}/d_{33}) were observed for all single domain states, thus, high longitudinal piezoelectric response along nonpolar axes are expected, taking the advantage of the domain engineering. Similar to the calculation of d_{33}^* along the [001] nonpolar axis in O phase crystals, in R phase, when polarization rotate from spontaneous polarization direction [111] to nonpolar direction [001], engineered domain configuration “4R” formed, the following equation is used to calculate d_{33}^* :

$$d_{33}^* = \frac{1}{3\sqrt{3}} [2d_{31} - 2\sqrt{2}d_{22} + 2d_{15} + d_{33}] \quad (3)$$

The intrinsic piezoelectric d_{33}^* was found to be 1122 pC/N, while the experimental measurement of the longitudinal piezoelectric d_{33} for [001] poled PIN-PMN-PT with the same R composition was found to be 1160 pC/N, being only ~3% higher than the calculation, showing minimum extrinsic contribution. The low extrinsic contribution is due to the fact that the studied R composition is far away from the R-M phase boundary, in good agreement with the Rayleigh analysis.⁷ In addition, for PIN-PMN-PT with T phase composition, when polarization rotate from spontaneous polarization direction [001] to nonpolar direction [011], engineered domain configuration

TABLE III. Piezoelectric coefficients (pC/N) of PIN-PMN-PT crystals with “1O” single domain state and “2R” engineered domain configuration, showing macroscopic mm2 symmetry.

Domain State	d_{15}	d_{24}	d_{31}	d_{32}	d_{33}
1O (mm2)*	4550	4100	153	-346	350
1O (mm2) ¹⁹	3354	162	744	-1781	1363

*This work.

“2T” formed, and the same Eq. (2) was used to calculate the intrinsic piezoelectric d_{33}^* , being on the order of 940 pC/N, slightly lower than the measured longitudinal d_{33} for the same T phase composition, being around 1050 pC/N (Ref. 25) with extrinsic contribution being on the order of 11%, induced by the O-T phase boundary movement.

C. Properties as a function of temperature

The temperature dependent dielectric and piezoelectric properties of “1O” single domain state were also studied. Figure 2 presents the dielectric permittivity variation as a function of temperature, where it was observed that the dielectric permittivity K_{11}^T exhibited the highest variation in

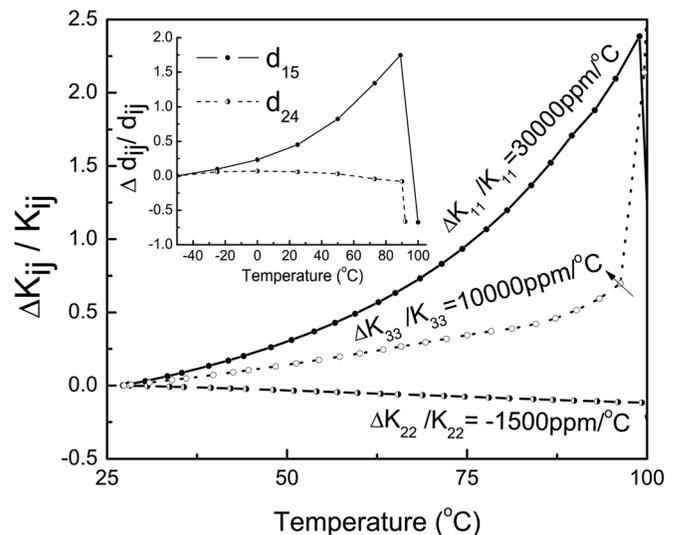


FIG. 2. Dielectric permittivity variation as a function of temperature for [011] poled single domain PIN-PMN-PT crystals, the small inset shows the shear piezoelectric variation as a function of temperature.

TABLE IV. Piezoelectric coefficients (pC/N) of PIN-PMN-PT crystals with various single domain states.

Domain State	d_{15}	d_{22}	d_{24}	d_{31}	d_{32}	d_{33}	d_{15}/d_{33}
1R (3 m) ²²	2190	-511	2190	-34	-34	74	30
1O (mm2)*	4550	0	4100	153	-346	350	13
1T (4 mm) ²⁰	2350	0	2350	-200	-200	530	4.4

* This work.

the studied temperature range of $25^\circ\text{C} \sim T_{\text{MT}}$, with temperature coefficient of permittivity ($\text{TC}\epsilon$) being on the order of $30\,000\text{ ppm}/^\circ\text{C}$, of particular significance is that the dielectric permittivity K_{22}^T , with value being $30\,000$ at room temperature, showing minimum temperature dependent behavior, ($\text{TC}\epsilon \sim -1500\text{ ppm}/^\circ\text{C}$), due to the vertical R-O morphotropic phase boundary.²⁶ The variations of shear piezoelectric coefficients as a function of temperature in the range of $-50 \sim 100^\circ\text{C}$ are given in the small inset. The piezoelectric d_{15} was found to possess high temperature variation, being on the order of 180% , while the piezoelectric d_{24} was only -6% in the same temperature range, related to the temperature stability of permittivity, demonstrating the great potential for applications where the temperature stability is required.

IV. SUMMARY

In summary, complete set of material constants were determined by combined impedance and ultrasonic measurements, on [011] poled PIN-PMN-PT crystals with single domain “1O” state. The ultrahigh shear piezoelectric properties are related to the facilitated “polarization rotation”, where the large d_{15} contribute to the intrinsic piezoelectric d_{33}^* in engineered domain configuration “4O” when poled along nonpolar [001] direction. The discrepancy of $\sim 11\%$ between the measured and calculated d_{33} is due to the extrinsic contribution, induced by the R-O phase boundary motion. Furthermore, the temperature dependent dielectric and piezoelectric behaviors were studied. The temperature independent large d_{24} is important for applications, where the temperature stability is desired.

ACKNOWLEDGMENTS

This work supported by the Office of Naval Research.

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