



Complete matrix properties of $[001]_c$ and $[011]_c$ poled $0.33\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-0.38\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.29\text{PbTiO}_3$ single crystals

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ABSTRACT

The elastic, piezoelectric, and dielectric properties of $[001]_c$ and $[011]_c$ poled $0.33\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-0.38\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.29\text{PbTiO}_3$ single crystals have been fully characterized at room temperature, and the temperature and frequency dependence of the dielectric susceptibility ϵ_{33} were also measured. The depoling temperature of this crystal is more than 20 °C higher than that of the corresponding binary $0.71\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.29\text{PbTiO}_3$ system. From the measured P – E hysteresis loops, the coercive fields along $[001]_c$ and $[011]_c$ directions have been determined to be 6.0 kV/cm and 6.6 kV/cm, respectively, which indicate that these domain engineered ternary relaxor-based ferroelectric single crystals are excellent candidates for high-power applications.

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1. Introduction

Ternary relaxor-based ferroelectric single crystals $x\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-(1-x-y)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-y\text{PbTiO}_3$ (PIN–PMN–PT) with composition near the morphotropic phase boundary (MPB) have attracted much attention for their comparable electromechanical properties to that of binary $\text{Pb}(\text{B}_1\text{B}_2)\text{O}_3$ – PbTiO_3 ($\text{B}_1 = \text{Mg}^{2+}$, Zn^{2+} ; $\text{B}_2 = \text{Nb}^{5+}$) single crystals but with much higher coercive fields, mechanical quality factors, and phase transition temperatures [1–7].

It is well known that the $[001]_c$ poled domain engineered relaxor–PT single crystals in the rhombohedral crystal phase have superior longitudinal piezoelectric coefficient, d_{33} (>2000 pC/N) and very high electromechanical coupling factors, k_{33} (>90%) [8–10], while $[011]_c$ poled rhombohedral phase crystals show excellent shear and transverse piezoelectric coefficients, d_{15} and d_{32} , with very high electromechanical coupling factors k_{15} and k_{32} [11–13]. Hence, $[001]_c$ and $[011]_c$ poled multi-domain rhombohedral phase relaxor–PT single crystals are now being used to replace PZT ceramics in making superior longitudinal, transverse, and shear mode electromechanical devices.

In this work, we have fully investigated the elastic, piezoelectric, and dielectric properties of $[001]_c$ and $[011]_c$ poled multi-domain $0.33\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3-0.38\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.29\text{PbTiO}_3$

(0.33PIN–0.38PMN–0.29PT) ternary single crystals. The temperature and frequency dependence of dielectric susceptibility ϵ_{33} are also measured in order to gain some knowledge on temperature and frequency stabilities. The P – E hysteresis loops were measured to determine the coercive fields in both $[001]_c$ and $[011]_c$ directions. More importantly, two sets of full matrix material properties have been determined by combined resonance and ultrasonic methods. These self-consistent data sets are much needed for both fundamental studies as well as input for the design of electromechanical devices using finite element packages.

2. Experimental

The 0.33PIN–0.38PMN–0.29PT single crystals used in this work were supplied by H.C. Materials Corp. (Bolingbrook, IL). The crystal boule was grown by the modified Bridgman method and samples of desired geometries were cut from the same cross section slice of a crystal boule grown along $[011]_c$. The as-grown crystal was oriented by the Laue machine with an accuracy of $\pm 0.5^\circ$. Each sample was cut and polished into a parallelepiped with the orientations of $[100]_c \times [010]_c \times [001]_c$ for $[001]_c$ -poled crystals, and $[0\bar{1}1]_c \times [100]_c \times [011]_c$ for $[011]_c$ -poled crystals, respectively. Specimens were annealed at 600 °C for 10 h to fill in some of the oxygen vacancies and to reduce residual stress that was developed during crystal growth and mechanical processing. Then, the samples were sputtered with gold electrodes on $[001]_c$ and $[00\bar{1}]_c$ or $[011]_c$ and $[0\bar{1}\bar{1}]_c$ surfaces, and poled at a field of 10 kV/cm for 30 min in silicone oil at room temperature. Each sample was checked for poling completeness by using a ZJ-2 piezo d_{33} meter.

Dielectric properties were measured as a function of temperature at the frequency of 1 kHz for both $[001]_c$ and $[011]_c$ poled 0.33PIN–0.38PMN–0.29PT single crystals using an Agilent E4980A precision LCR meter. Each sample was heated from 25 °C to 250 °C at a rate of 2 °C/min during the dielectric measurements. The dielectric constant was calculated from the measured capacitance based on the parallel

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capacitance approximation. High field polarization measurement was performed on the $[001]_c$ and $[011]_c$ oriented plate samples at room temperature using a modified Sawyer–Tower circuit.

The combined resonance and ultrasonic method has proven effective for getting self-consistent matrix data sets [14,15]. The dimensions and geometries of samples in resonance measurements were specified by the IEEE standards on piezoelectricity [16]. The resonance and anti-resonance frequencies were obtained by an HP 4194A impedance-phase gain analyzer. Two 3 mm cubes with the orientations of $[100]_c \times [010]_c \times [001]_c$ and $[011]_c \times [100]_c \times [011]_c$ were used for the ultrasonic measurements. A 15 MHz longitudinal wave transducer (Ultran Laboratories, Inc.) and a 20 MHz shear wave transducer (Panametrics Com.) were used for the ultrasonic pulse-echo measurements. The transducers were excited by a 200 MHz pulser/receiver (Panametrics Com.) and the time of flight between echoes was measured using a Tektronix 460A digital oscilloscope. The phase velocities of the longitudinal and shear waves were used to calculate the elastic constants together with the density, which was measured by the Archimedes's principle.

3. Results and discussion

Fig. 1 shows the temperature dependence of the dielectric constant (ϵ_{33}/ϵ_0) of $[001]_c$ and $[011]_c$ poled 0.33PIN–0.38PMN–0.29PT single crystals at the frequency of 1 kHz. Each curve shows two peaks: $T_{r-t} \sim 113^\circ\text{C}$ (rhombohedral–tetragonal phase transition temperature) for $[001]_c$ poling and $T_{r-t} \sim 118^\circ\text{C}$ for $[011]_c$ poling, respectively, and $T_c \sim 172^\circ\text{C}$ (Curie temperature) for both cases. The higher depoling temperatures of $[001]_c$ and $[011]_c$ poled 0.33PIN–0.38PMN–0.29PT than that of PMN–0.29PT ($T_{r-t} = 93^\circ\text{C}$ and $T_c = 137^\circ\text{C}$) make the ternary system a much better candidate for making more temperature stable electromechanical devices [17].

Fig. 2 shows the frequency dependence of the dielectric constant (ϵ_{33}/ϵ_0) and dielectric loss factor $\tan\delta$ in the range of 0.1–10 kHz. The results indicated that both the $[001]_c$ and $[011]_c$ poled crystals have very good dielectric stability against frequency variation. The dielectric constant of $[001]_c$ poled crystal only decreased slightly from 4579 at 0.1 kHz to 4498 at 10 kHz. The dielectric loss $\tan\delta$ has certain fluctuations as the operating frequency changes, but basically keeps its value between 0.7% and 0.8%. These fluctuations are largely due to the influence of environmental noises. The dielectric constant of $[011]_c$ poled crystal is unchanged from 0.1 kHz to 10 kHz with a value of ~ 3400 , and its dielectric loss $\tan\delta$ is relatively lower with a value between 0.2% and 0.3%.

Fig. 3 shows the polarization hysteresis loops for $[001]_c$ and $[011]_c$ oriented 0.33PIN–0.38PMN–0.29PT single crystals. The coercive field, remnant polarization, and spontaneous polarization of $[001]_c$ oriented crystal are: 6.0 kV/cm, 25.8 $\mu\text{C}/\text{cm}^2$, and

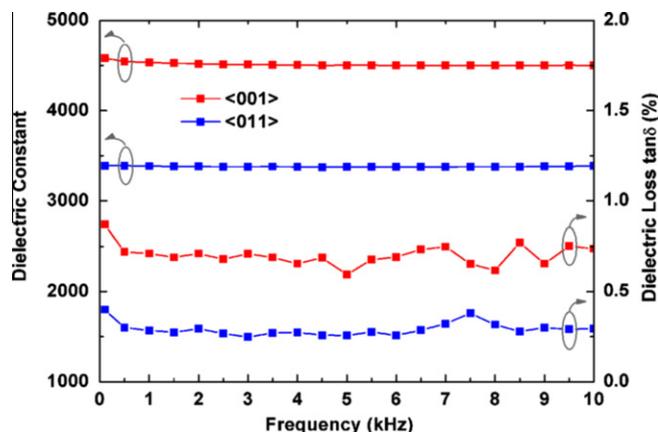


Fig. 2. Frequency dependence of dielectric constant ϵ_{33}/ϵ_0 and dielectric loss $\tan\delta$ for 0.33PIN–0.38PMN–0.29PT single crystals in (a) $[001]_c$ and (b) $[011]_c$ directions at room temperature.

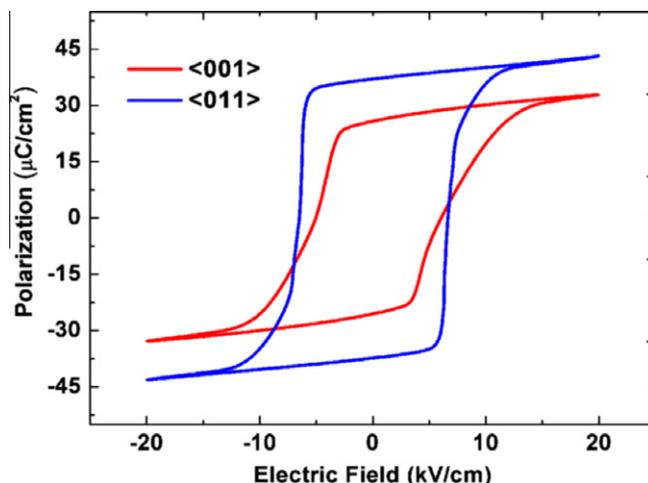


Fig. 3. Polarization hysteresis loops of $[001]_c$ - and $[011]_c$ -oriented 0.33PIN–0.38PMN–0.29PT single crystals at room temperature.

27.9 $\mu\text{C}/\text{cm}^2$, respectively, while for $[011]_c$ oriented crystal, they are: 6.6 kV/cm, 37.0 $\mu\text{C}/\text{cm}^2$, and 40.0 $\mu\text{C}/\text{cm}^2$, respectively. The coercive field is a little larger than that of 0.24PIN–0.46PMN–0.30PT (5.3 kV/cm) due to the higher content of PIN, but nearly triple that of the corresponding binary 0.71PMN–0.29PT (~ 2.2 kV/cm) single crystals [17].

For a multi-domain rhombohedral 0.33PIN–0.38PMN–0.29PT, the $[001]_c$ poled single crystal shows tetragonal $4m$ symmetry macroscopically, which has 11 independent material constants: 6 elastic, 3 piezoelectric, and 2 dielectric constants. But for $[011]_c$ poled single crystals, the macroscopic symmetry is orthorhombic $mm2$, which has 17 independent material constants: 9 elastic, 5 piezoelectric, and 3 dielectric constants. We have experimentally determined the complete sets of elastic, piezoelectric and dielectric constants for both $[001]_c$ and $[011]_c$ poled 0.33PIN–0.38PMN–0.29PT single crystals, and the results are given in Table 1. In comparison, the piezoelectric coefficients and electromechanical coupling factors of $[011]_c$ poled 0.33PIN–0.38PMN–0.29PT single crystal are much better than that of 0.26PIN–0.46PMN–0.28PT single crystal [12]. It can be seen that the 0.33PIN–0.38PMN–0.29PT single crystals with the PT composition only slightly away from the MPB on the rhombohedral phase side are the excellent candidates for high-power transducers for their better temperature stability and good electromechanical properties.

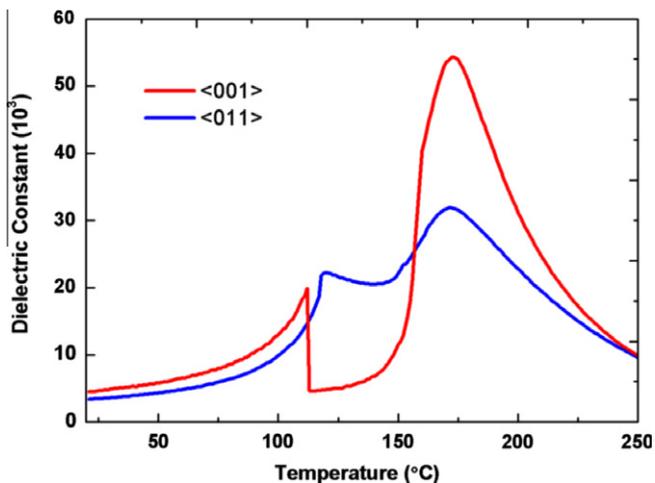


Fig. 1. Temperature dependence of the dielectric constant ϵ_{33}/ϵ_0 for 0.33PIN–0.38PMN–0.29PT single crystals in (a) $[001]_c$ and (b) $[011]_c$ directions at the frequency of 1 kHz.

Table 1

Measured and derived material constants of [001]_c and [011]_c poled 0.33PIN–0.38PMN–0.29PT multi-domain single crystals [directly measured constants are denoted by star (*)].

	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			
Elastic stiffness constants: c_{ij}^E and c_{ij}^D (10^{10} N/m ²)												
[001] _c	11.57	10.03	10.15	11.57	10.15	11.32	6.45	6.45	5.44			
[011] _c	20.41	14.01	8.55	16.21	13.61	15.07	6.79	0.71	4.88			
	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			
[001] _c	11.86	10.32	8.99	11.86	8.99	15.97	7.12	7.12	5.44			
[011] _c	21.14	13.59	10.35	16.46	12.57	19.48	7.20	4.44	4.88			
Elastic compliance constants: s_{ij}^E and s_{ij}^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			
[001] _c	47.18	−17.75	−26.39	47.18	−26.39	56.15	15.50	15.50	18.38			
[011] _c	18.29	−29.35	16.13	72.62	−48.93	41.68	14.73	140.85	20.49			
	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			
[001] _c	36.62	−28.32	−4.67	36.62	−4.67	11.52	14.04	14.04	18.38			
[011] _c	10.08	−8.35	0.04	18.91	−7.77	10.13	13.90	22.54	20.49			
Piezoelectric coefficients: e_{iz} (C/m ²), d_{iz} (10^{-12} C/N), g_{iz} (10^{-3} Vm/N), and h_{iz} (10^8 V/m)												
	e_{15}	e_{24}	e_{31}	e_{32}	e_{33}	d_{15}	d_{24}	d_{31}^*	d_{32}^*	d_{33}^*		
[001] _c	9.48	9.48	−4.81	−4.81	19.31	147	147	−651	−651	1338		
[011] _c	16.25	6.38	6.62	−3.83	16.26	2288	94	496	−1268	972		
	g_{15}	g_{24}	g_{31}	g_{32}	g_{33}	h_{15}	h_{24}	h_{31}	h_{32}	h_{33}		
[001] _c	9.97	9.97	−16.23	−16.23	33.36	7.10	7.10	−6.00	−6.00	24.10		
[011] _c	51.71	8.84	16.56	−42.35	32.45	22.94	6.36	11.04	−6.39	27.10		
Dielectric constants: $\epsilon_{ij}(\epsilon_0)$ and $\beta(10^{-4}/\epsilon_0)$												
	ϵ_{11}^*	ϵ_{22}^*	ϵ_{33}^*	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
[001] _c	1509	1509	905	1666	1666	4532	6.63	6.63	11.05	6.00	6.00	2.21
[011] _c	800	1133	678	5000	1201	3384	12.50	8.83	14.75	2.00	8.33	2.96
Electromechanical coupling factors k_{ij} and density												
	k_{15}	k_{24}	k_{31}^*	k_{32}^*	k_{33}^*	k_t^*	Density (kg/m ³)					
[001] _c	0.31	0.31	0.47	0.47	0.89	0.54	8141					
[011] _c	0.92	0.24	0.67	0.86	0.87	0.49	8141					

4. Summary and conclusions

The temperature and frequency dependence of dielectric constant showed that the 0.33PIN–0.38PMN–0.29PT single crystal has higher phase transition temperatures and good frequency stability compared to its binary counterpart. The crystals have coercive fields nearly three times as high that of the corresponding 0.71PMN–0.29PT single crystals in both [001]_c and [011]_c directions, so that this ternary single crystal is a much better candidate for high-power applications. In addition, we have experimentally determined the complete sets of elastic, piezoelectric, and dielectric constants for both [001]_c and [011]_c poled 0.33PIN–0.38PMN–0.29PT single crystals, which are very useful for the design of electromechanical devices as well as for theoretical studies on these relaxor-based multidomain single crystals.

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