

Single-domain properties of $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ single crystals under electric field bias

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We report a complete set of material properties of single-domain, relaxor-based $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ [PMN-33%PT] single crystals. Because the single-domain state is unstable in natural conditions, a bias electric field of 0.2 MV/m was applied along the dipole direction of the rhombohedral phase during the measurements. It was found that the electromechanical coupling coefficient k_{33} and the piezoelectric constant d_{33} for single-domain PMN-33%PT are 69% and 190 pC/N, respectively. Both of them are much smaller than those of multidomain PMN-33%PT poled along [001] direction. However, the shear piezoelectric constant d_{15} of single-domain PMN-33%PT reaches 4100 pC/N, which is much higher than that of multidomain PMN-33%PT. © 2003 American Institute of Physics. [DOI: 10.1063/1.1541937]

Multidomain $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ (PMN-33%PT) single crystals show extraordinarily large electromechanical coupling coefficient, $k_{33} > 94\%$, and piezoelectric constant, $d_{33} > 2500$ pC/N at room temperature, which are even more pronounced than that of the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ single crystals.¹⁻³ The discovery of these extraordinary properties in domain engineered single crystals has opened up many new possibilities to make large displacement actuators, single-element and phased-array medical ultrasonic transducers, and other electromechanical devices.³⁻⁵ However, the fundamental question remains: Why do these multidomain crystals have such extraordinary properties? In order to extend the methodology of domain engineering to other systems, one must understand the mechanism. There have been some attempts on this issue, but they could not provide quantitative results due to the lack of single-domain, single-crystal data.⁶⁻¹⁴

At room temperature, PMN-33%PT system has rhombohedral ferroelectric phase with 3m symmetry. There are eight possible dipole orientations along the body diagonal directions, or along the $\langle 111 \rangle$ family in the cubic coordinate systems. When an electric poling field is applied to the crystals along [001] of the cubic axes, a multidomain configuration can be produced consisting of four degenerate states and charged domain walls. Since the macroscopic material properties of a multidomain ferroelectric system are the collective average of individual domains,¹⁵⁻¹⁸ a complete set of elastic, dielectric, and piezoelectric coefficients for single-domain PMN-33%PT single crystals is urgently needed for theoretical studies.

In this letter, we report a complete set of elastic, piezoelectric, and dielectric constants for single domain PMN-33%PT single crystals under a bias electric field. A hybrid method combining the advantages of ultrasonic and resonance techniques was employed, and an improved characterization scheme was followed to minimize the propagation of

measurement errors and improve the consistency of the complete data set.

There are, all together, 12 independent constants for a piezoelectric material with 3m symmetry: six elastic, four piezoelectric, and two dielectric constants. Theoretically, all independent elastic, piezoelectric, and dielectric constants for any piezoelectric materials can be determined by either a resonance method or an ultrasonic method, as long as sufficient numbers of differently oriented samples are available.^{19,20} In reality, however, the resonance measurement becomes complicated for materials with low symmetry, since more samples must be prepared, and some large aspect ratio resonators are difficult to fabricate. For example, it has been demonstrated that a clean thickness-shear mode may be obtained in a shear piezoelectric vibrator only when the aspect ratio is larger than 20.²¹

On the other hand, since the ultrasonic technique can only measure certain elastic constants through the measurements of phase velocities, large errors could be introduced for the derived material constants that are not related to pure

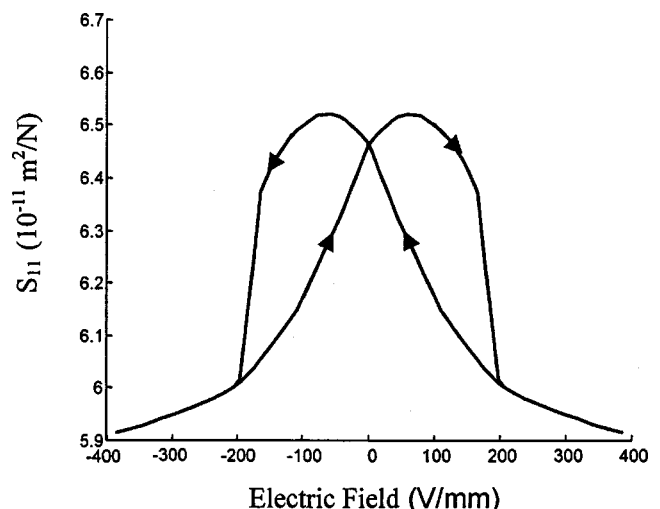


FIG. 1. Variation of elastic compliance constant s_{11} with a bias field along [111] of cubic axis for PMN-33%PT single crystals.

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TABLE I. Measured phase velocities (m/s) of ultrasonic waves in single-domain PMN–33%PT single crystals, and the relationships between phase velocities and elastic constants.

Propagation direction	[111]	[$\bar{1}\bar{1}\bar{1}$]	[$1\bar{1}0$]	[$\bar{1}\bar{1}0$]	[$1\bar{1}0$]	[112]	[$1\bar{1}\bar{2}$]	[$1\bar{1}\bar{2}$]
	v_l	v_s	v_l	$v_{s\parallel}$	$v_{s\perp}$	v_l	$v_{s\parallel}$	$v_{s\perp}$
ρv^2	c_{33}^D	c_{44}^E	c_{11}^E	c_1	c_2	c_3	c_{66}^E	c_4
v (m/s)	5220	1896	4996	3491	1689	5118	2813	2408

modes. High acoustic attenuation of certain modes may also damp the propagation of ultrasonic waves in certain directions, so that a complete set of material constants for low symmetry systems is difficult to obtain using the ultrasonic method alone. We therefore used a hybrid of the two methods for the task.

The consistency of the complete data can be improved greatly using the hybrid method because the property of PMN–PT single crystals can vary dramatically from sample to sample, particularly with the composition near the morphotopic phase boundary (MPB).

The crystals were first oriented using the Laue machine with an accuracy of $\pm 0.5^\circ$. Each sample was then cut and polished into a rectangular shape with three pairs of parallel surfaces along [111], [$1\bar{1}0$], and [$1\bar{1}\bar{2}$], respectively. Gold electrodes were sputtered onto the [111] and [$\bar{1}\bar{1}\bar{1}$] faces of each sample. An external electric field of 0.3–0.5 MV/m was applied to pole the sample at room temperature into a single domain state. It was found that the single-domain state was unstable for this system in natural conditions. Therefore, during the ultrasonic and resonance measurements, a bias electric field was applied along the [111] of each sample to maintain the single-domain state. One must note that the application of a bias electric field will cause some property variations. To evaluate the field influence, we have measured the elastic compliance constant s_{11} variation with a bias electric field, as shown in Fig. 1. The compliance s_{11} increases about 10% when the bias field is removed. In order to maintain the single-domain state of PMN–33%PT crystal system, a bias field of 0.2 MV/m, which is a little higher than the coercive field of 0.18 MV/m, was employed along [111] direction of all samples. All of our single-domain data were measured under this bias electric field.

In order to simplify the characterization procedure, only those resonance samples with exciting field in [111] were used. The final dimensions of the samples used for the ultrasonic measurements were about 4 mm \times 4 mm \times 2 mm. For the length and thickness extensional resonance measurements, the aspect ratios of samples exceeded 5:1 in order to yield nearly pure resonance modes.²⁰

A 15-MHz longitudinal wave transducer (Ultran Laboratories, Inc.) and a 20-MHz shear wave transducer (Panametrics) were used for the pulse-echo measurements. The electric pulses used to excite the transducer were generated by a Panametrics 200-MHz pulser/receiver, and the time of flight between echoes was measured using a Tektronix™ 460A digital oscilloscope.

For the length and thickness extensional resonance measurements, an HP 4194A impedance/gain phase analyzer was

employed. The dielectric measurements were carried out on an HP 4194A at a frequency far away from the fundamental resonance.

The capacitances along [$1\bar{1}0$] and [$1\bar{1}\bar{2}$] were first measured with the bias electric field holding in [111] at a frequency much higher than their fundamental frequencies, from which the dielectric constant ϵ_{11}^S was calculated. The relationship between the measured phase velocities and related elastic constants could be derived from the Christoffel wave equations and are listed in Table I.²² The measured phase velocities of longitudinal and shear waves propagating along different crystal orientations of the single-domain PMN–33%PT single crystals are also listed in Table I, where v_l , $v_{s\parallel}$, and $v_{s\perp}$ denote the ultrasonic wave velocities of longitudinal wave, and shear waves with displacement parallel and perpendicular to the poling direction, respectively. The constants c_1 , c_2 , c_3 , c_4 are defined below:

$$c_1 = \frac{c_{44}^D + c_{66}^D + \sqrt{(c_{44}^D + c_{66}^D)^2 - 4[c_{44}^D c_{66}^D - (c_{14}^D)^2]}}{2}, \quad (1)$$

$$c_2 = \frac{c_{44}^D + c_{66}^D - \sqrt{(c_{44}^D + c_{66}^D)^2 - 4[c_{44}^D c_{66}^D - (c_{14}^D)^2]}}{2}, \quad (2)$$

TABLE II. Measured and derived material properties of single-domain PMN–33%PT single crystals.

Elastic stiffness constants: c_{ij}^E (10^{10} N/m ²)							
c_{11}^{Ea}	c_{12}^{Ea}	c_{13}^E	c_{14}^{Ea}	c_{33}^E	c_{44}^{Ea}	c_{66}^{Ea}	
20.12	7.36	11.50	4.15	17.12	2.90	6.38	
Elastic stiffness constants: c_{ij}^D (10^{10} N/m ²)							
c_{11}^D	c_{12}^D	c_{13}^D	c_{14}^{Da}	c_{33}^{Da}	c_{44}^{Da}	c_{66}^{Da}	
20.43	7.62	10.32	3.87	21.94	5.63	6.50	
Elastic compliance constants: s_{ij}^E (10^{-12} m ² /N)							
s_{11}^{Ea}	s_{12}^E	s_{13}^E	s_{14}^E	s_{33}^E	s_{44}^E	s_{66}^E	
62.16	–53.85	–5.58	–166.24	13.34	510.98	232.02	
Elastic compliance constants: s_{ij}^D (10^{-12} m ² /N)							
s_{11}^D	s_{12}^D	s_{13}^D	s_{14}^D	s_{33}^{Da}	s_{44}^{Da}	s_{66}^D	
9.39	–3.94	–2.57	–9.15	6.97	30.33	26.65	
Piezoelectric constants: $e_{i\lambda}$ (C/m ²) and $d_{i\lambda}$ (10^{-12} C/N)							
e_{15}^{a}	e_{22}^{a}	e_{31}	e_{33}	d_{15}	d_{22}	d_{31}^{a}	d_{33}^{a}
7.52	0.78	–2.88	11.83	4100	1340	–90	190
Piezoelectric constants: $g_{i\lambda}$ (10^{-2} Vm/N) and $h_{i\lambda}$ (10^8 V/m)							
g_{15}	g_{22}	g_{31}	g_{33}	h_{15}	h_{22}	h_{31}	h_{33}
11.72	3.83	–1.59	3.35	36.38	3.78	–9.94	40.78
Dielectric constants: $\epsilon(\epsilon_0)$ and $\beta(10^{-4}/\epsilon_0)$							
ϵ_{11}^{Sa}	ϵ_{33}^S	ϵ_{11}^T	ϵ_{33}^{Ta}	β_{11}^S	β_{33}^S	β_{11}^T	β_{33}^T
233	328	3950	640	42.84	30.53	2.53	15.63
Electromechanical coupling constants and density							
k_{15}	k_{31}^{a}	k_{33}^{a}	k_t^{a}	ρ (kg/m ³)			
0.70	0.15	0.69	0.47	8060			

^aMeasured properties.

$$c_3 = \frac{c_{44}^D + c_{11}^F + \sqrt{(c_{44}^D + c_{11}^F)^2 - 4[c_{44}^D c_{11}^F - (c_{14}^D)^2]}}{2}, \quad (3)$$

$$c_4 = \frac{c_{44}^D + c_{11}^F - \sqrt{(c_{44}^D + c_{11}^F)^2 - 4[c_{44}^D c_{11}^F - (c_{14}^D)^2]}}{2}, \quad (4)$$

where

$$c_{11}^F = c_{11}^E + \frac{e_{22}^2}{\epsilon_{11}^S}. \quad (5)$$

From two length and one thickness extensional resonators, electromechanical coupling coefficients k_{31} , k_{33} , and k_t , elastic compliance s_{11}^E and s_{33}^D , dielectric constant ϵ_{33}^T , and piezoelectric coefficients d_{31} and d_{33} are determined. Since we obtained more than 20 measured values for 12 independent constants, there are several self-consistency checks.

Finally, a complete set of elastic, piezoelectric, and dielectric constants of single-domain PMN–33%PT single crystals under bias were derived and listed in Table II. The independent material constants marked with ^a in Table II were obtained through direct measurements, while the other constants in Table II were derived using the constitutive relations.

We found that the electromechanical coupling coefficient k_{33} and the piezoelectric constant d_{33} for single-domain PMN–33%PT single crystals are 69% and 190 pC/N, respectively. These values are much smaller than those of domain engineered PMN–33%PT single crystals. However, the shear piezoelectric constant d_{15} of single-domain PMN–33%PT single crystals reaches 4100 pC/N, which is much larger than that of multidomain PMN–33%PT single crystals.

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