

Complete set of elastic, dielectric, and piezoelectric coefficients of $0.93\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.07\text{PbTiO}_3$ single crystal poled along [011]

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The authors report a complete set of elastic, dielectric, and piezoelectric coefficients of rhombohedral phase $0.93\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.07\text{PbTiO}_3$ single crystal poled along [011] measured at room temperature. It was found that the electromechanical coupling coefficients k_{32} and k_{33} of this domain engineered single crystal can reach 0.86 and 0.87, respectively, and the piezoelectric coefficients d_{32} and d_{15} are -1460 and 1823 pC/N, respectively. This complete set of data can meet the urgent need of device designers using these super piezoelectric crystals and also provide important information for fundamental studies on domain engineering. © 2006 American Institute of Physics.

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It has been demonstrated that relaxor based $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PZN-PT) and $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ (PMN-PT) ferroelectric single crystal systems with composition near the morphotropic phase boundary (MPB) exhibit superior electromechanical properties at room temperature when being poled along the [001] of cubic coordinates.¹⁻⁵

For theoretical studies and for device designs, knowing the complete set of material properties is crucial. By using a hybrid technique that combines ultrasonic and resonance methods,⁶ we were able to measure several complete sets of material constants of [001] poled PMN-PT and PZN-PT single crystals with composition near the MPB.⁷⁻¹¹ These data have greatly facilitated the use of these super piezoelectric crystals and provided important input data for the fundamental studies of the domain engineering method.

The small d_{33} and k_{33} values of single-domain $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.33\text{PbTiO}_3$ (PMN-33%PT) crystals but large effective d_{33} and k_{33} values of multidomain PMN-33%PT crystals poled along [001] demonstrated that functional properties can be drastically improved through the orientation effect.¹² For single-domain crystals poled along the polar direction of [111], the d_{15} value is as high as 4100 pC/N even under electrical bias. Part of this large d_{15} is converted to the effective d_{33} in the [001] poled crystal. It is possible to obtain other effective piezoelectric coefficients if the crystals are being poled along other directions. In fact, in recent years, trying to improve specific material properties using domain engineering methodology has become a new trend in functional materials research.¹³⁻²⁴

Different poling directions can produce different domain patterns that will define the macroscopic symmetry of the multidomain system. Experimental results showed that the [011] direction is another promising poling direction to engineer better multidomain piezoelectric materials, which can produce very large $|d_{32}|$. In order to facilitate engineers to use such large d_{32} values and provide more information to study the domain orientation principle, we report here a

complete set of elastic, dielectric, and piezoelectric coefficients of a [011] poled $0.93\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.07\text{PbTiO}_3$ (PZN-7%PT) single crystal.

At room temperature, the PZN-7%PT crystal is in the rhombohedral phase with $3m$ crystal symmetry, and the dipoles in each unit cell is pointing along one of the eight $\langle 111 \rangle$ directions of the cubic phase [Fig. 1(a)]. There are two remaining energetic degenerate dipole orientations after poling along [011] [Fig. 1(b)]. Statistically, the remaining two types of domains have equal possibilities to form, so that the macroscopic symmetry is orthorhombic $mm2$.^{24,25} We take the poling direction as the x_3 direction, which is along [011] of the cubic coordinates, and the $[0\bar{1}1]$ and $[100]$ are defined as the x_1 and x_2 axes, respectively, for defining the macroscopic property matrices.

The single crystals used in this work were grown by a modified Bridgman method using a Pt crucible supported at its bottom by a conical insulator stand.¹⁴ The crystals were

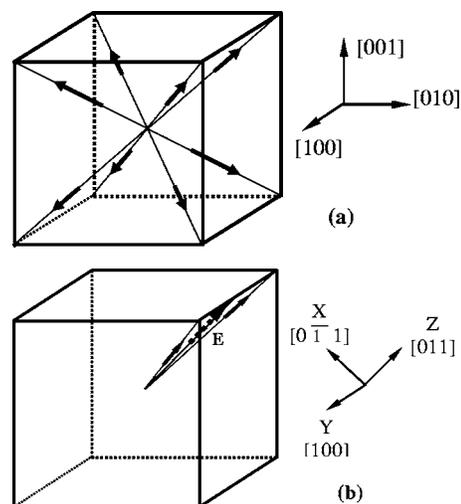


FIG. 1. (a) Eight polarization directions in PZN-7%PT single crystals before poling. (b) Two remaining polarization directions after being poled along [011].

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TABLE I. Complete set of electromechanical coefficients of PZN-7%PT single crystal poled along [011]. Density: $\rho=8038.4$ kg/m³.

Elastic stiffness coefficients: $c_{\lambda\mu}^E$ and $c_{\lambda\mu}^D$ (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
14.5000	15.3160	12.6660	18.0240	15.0000	14.1000	6.4720	0.3430	7.1000
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
17.3987	21.1639	11.4275	29.8217	12.5014	14.6292	6.5360	0.4065	7.1000
Elastic compliance coefficients: $s_{\lambda\mu}^E$ and $s_{\lambda\mu}^D$ (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
67.5153	-60.1637	3.3551	102.0024	-54.4683	62.0233	15.4512	291.5452	14.0845
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
59.4003	-35.3773	-16.1684	26.2949	5.1644	15.0523	15.2998	245.9933	14.0845
Piezoelectric coefficients: $e_{i\lambda}$, (C/m^2), $d_{i\lambda}$ ($10^{-12}C/N$), $g_{i\lambda}$ ($10^{-3}V m/N$), and $h_{i\lambda}$ ($10^8 V/m$)								
e_{15}	e_{24}	e_{31}	e_{32}	e_{33}				
6.2529	3.2360	-8.6446	-17.4399	3.6935				
d_{15}	d_{24}	d_{31}	d_{32}	d_{33}				
1823	50	478	-1460	1150				
g_{15}	g_{24}	g_{31}	g_{32}	g_{33}				
24.9873	3.0280	16.9770	-51.8545	40.8443				
h_{15}	h_{24}	h_{31}	h_{32}	h_{33}				
1.0158	1.9791	-33.5315	-67.6476	14.3266				
Dielectric coefficients: $\epsilon_{ij}(\epsilon_0)$ and $\beta_{ij}(10^{-4}/\epsilon_0)$								
ϵ_{11}^S	ϵ_{22}^S	ϵ_{33}^S	ϵ_{11}^T	ϵ_{22}^T	ϵ_{33}^T			
6953	1847	291	8240	1865	3180			
β_{11}^S	β_{22}^S	β_{33}^S	β_{11}^T	β_{22}^T	β_{33}^T			
1.4383	5.4150	34.3440	1.2136	5.3619	3.1440			
Electromechanical coupling coefficients								
k_{15}	k_{24}	k_{31}	k_{32}	k_{33}	k_t			
0.40	0.10	0.35	0.86	0.87	0.19			

orientated using the Laue method with an accuracy of $\pm 0.5^\circ$. Each sample was cut and polished with three pairs of parallel surfaces perpendicular to each other. Gold electrodes were sputtered onto the [011] and $[0\bar{1}\bar{1}]$ faces of each sample. Then an external electric field ~ 0.4 MV/m was applied to pole these samples at room temperature. For the length-extensional resonance measurements, the aspect ratio of the resonators should exceed 5:1 in order to yield nearly pure resonance modes.²⁶

For orthorhombic symmetry, there are in total 17 independent material coefficients to be determined, i.e., nine elastic, five piezoelectric, and three dielectric coefficients.²⁷ In ultrasonic pulse-echo measurements, a 15 MHz longitudinal wave transducer (Ultran Laboratories, Inc.) and a 20 MHz shear wave transducer (Panametrics Com.) were used. The electric pulses used to excite these transducers were generated 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 measured along the three pure mode directions, [100], $[0\bar{1}\bar{1}]$, and [011], to obtain eight independent combinations of different material coefficients.²⁸

Three length-extensional and one thickness resonance measurements were conducted using an HP 4194A impedance/gain-phase analyzer. From the resonance and antiresonance frequencies we can calculate corresponding piezoelectric coefficients d_{31} and d_{32} , the elastic compliance s_{11}^E , s_{22}^E , and s_{33}^E , and the elastic stiffness c_{33}^D .²⁶ Dielectric measurements were carried out at 1 kHz using a Stanford Research System SR715 LCR meter. From capacitance measurements, the dielectric permittivity ϵ_{11}^T , ϵ_{22}^T , and ϵ_{33}^T were obtained. In addition, the piezoelectric strain coefficients d_{33} can be directly measured by quasistatic method using a ZJ-2 piezo d_{33} meter.

From these measurements we can obtain 17 independent coefficients: $c_{11}^E, c_{22}^E, c_{33}^E, c_{44}^E, c_{55}^E, c_{44}^D, c_{55}^D, c_{66}^E, s_{11}^E, s_{22}^E, s_{33}^E, \varepsilon_{11}^T, \varepsilon_{22}^T, \varepsilon_{33}^T, d_{31}, d_{32},$ and d_{33} . In order to check matrix consistency, we need to explicitly derive nine independent elastic coefficients $c_{\lambda\mu}^E$ or $s_{\lambda\mu}^D$, five independent piezoelectric coefficients $e_{i\lambda}$ or $d_{i\lambda}$, and three independent dielectric permittivity ε_{ij}^T or ε_{ij}^S ($i, j=1, 2, 3; \lambda, \mu=1-6$). The basic relationships to calculate them from the measured data are

$$s_{11}^E = \frac{c_{22}^E c_{33}^E - (c_{23}^E)^2}{C}, \quad (1)$$

$$s_{22}^E = \frac{c_{11}^E c_{33}^E - (c_{13}^E)^2}{C}, \quad (2)$$

$$s_{33}^E = \frac{c_{22}^E c_{11}^E - (c_{12}^E)^2}{C}, \quad (3)$$

where $C = (c_{11}^E c_{22}^E - (c_{12}^E)^2) c_{33}^E - c_{13}^E (c_{22}^E c_{13}^E - c_{12}^E c_{23}^E) - c_{23}^E (c_{11}^E c_{23}^E - c_{12}^E c_{13}^E)$, and c_{33}^E is given by

$$c_{33}^E = c_{33}^D (1 - k_7^2), \quad (4)$$

$$d_{15} = \sqrt{\varepsilon_{11}^T \left(\frac{1}{c_{55}^E} - \frac{1}{c_{55}^D} \right)}, \quad (5)$$

$$d_{24} = \sqrt{\varepsilon_{22}^T \left(\frac{1}{c_{44}^E} - \frac{1}{c_{44}^D} \right)}. \quad (6)$$

An iteration procedure is implemented while trying to determine the independent data set within the error limits. Using this procedure, we have derived a complete coefficient set of a [011] poled PZN-7%PT single crystal, as listed in Table I.

These properties are quite different from those of [001] poled PZN-7%PT.¹⁰ For example, the piezoelectric coefficient d_{15} of this system is 1823 pC/N, while for [001] poled crystal, d_{15} is only 176 pC/N. Moreover, the d_{24} of [011] poled crystal is only 50 pC/N but the d_{24} and d_{15} of [001] poled crystal are the same.¹⁰ It is worth mentioning that the shear anisotropy is very large in the [011] poled PZN-7%PT crystal, there is almost a 20 times difference between c_{44}^E and c_{55}^E . Moreover, c_{44}^E/c_{44}^D and c_{55}^E/c_{55}^D also exhibit a large difference, which is directly linked to the large difference between k_{24} and k_{15} . Most importantly, unlike [001] poled PZN-7%PT, there is a very large difference between the piezoelectric coefficients d_{32} and d_{31} in [011] poled PZN-7%PT crystals.

In summary, we have shown that [011] direction poled PZN-7%PT single crystals can produce a superlarge transverse d_{32} piezoelectric coefficient. Using a hybrid characterization technique, we have measured a complete set of material coefficients, including elastic, dielectric, and piezoelectric coefficients, based on macroscopic orthorhombic $mm2$ symmetry. The full matrix data allowed us to compre-

hensively evaluate the [011] direction poled multidomain crystal and compare the properties with that of [001] poled crystals. The largest improvement compared to [001] poled PZN-7%PT are the d_{32} and d_{15} , which can reach -1460 and 1823 pC/N, respectively. The electromechanical coupling coefficient k_{32} (0.86) is also very impressive, making the [011] poled PZN-7%PT an excellent candidate for transverse mode sensors, actuators and other electromechanical devices.

From both the results of [001] and [011] poled crystals we also verified a general rule in domain engineered crystals: larger piezoelectric coefficients always correspond to lower elastic stiffness coefficients or larger elastic compliance coefficients along the corresponding direction.

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