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Complete set of properties of $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ single crystal with engineered domains

Rui Zhang, Bei Jiang, Wenhua Jiang, Wenwu Cao*

Materials Research Institute, The Pennsylvania State University, 164 University Park, PA 16802-4800, USA

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Abstract

This paper reports the complete set of elastic, piezoelectric and dielectric constants of $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.08\text{PbTiO}_3$ domain engineered single crystal. We found that the piezoelectric strain constant d_{33} and dielectric permittivity ϵ_{33}^T of this crystal are larger than that of $0.955\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$ reported earlier. Fluctuations of the values of piezoelectric and dielectric constants from sample to sample of this single crystal system were observed because the composition is very close to the morphotropic phase boundary.

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1. Introduction

The relaxor-based $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ (PZN–PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$ (PMN–PT) domain engineered single crystal systems exhibit superior electromechanical property comparing to the conventional PZT ceramics. Due to the extremely attractive application potential in ultrasonic transducers and piezoelectric actuators, extensive studies have been conducted on these crystals in recent years [1–7].

For both fundamental study and device design purposes, it is necessary to measure the complete set of matrix properties of these crystals. Such a complete set of elastic, piezoelectric and dielectric constants for

$0.95\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.045\text{PbTiO}_3$ [PZN–4.5%PT] single crystal system has already been reported earlier [8]. However, it is known that PZT–4.5%PT [2] is fairly far away from the morphotropic phase boundary (MPB) composition (PZN–8.5%PT), therefore, it does not represent the maximum electromechanical capability of this solid solution single crystal system. It is expected that the PZN–PT system with composition near to MPB should have the largest piezoelectric strain constant d_{33} and dielectric permittivity ϵ_{33}^T . On the other hand, it is very difficult to control the property of PZN–8.5%PT because the property will be reduced drastically if the structure becomes tetragonal.

For this reason, we have characterized the PZN–8%PT and report its full set of matrix properties in this letter. This composition is almost on the morphotropic phase boundary near room temperature and is in the

* Corresponding author. Tel.: +1-814-863-9884; fax: +1-814-865-8126.

E-mail address: cao@math.psu.edu (W. Cao).

rhombohedral phase, which has the best piezoelectric property. After poled along the [001] of the cubic direction, the multi-domain single crystal has a pseudo-tetragonal symmetry. As expected, the PZN–8%PT system has much larger d_{33} and ε_{33}^T compared with that of the PZN–4.5%PT crystal. Issues regarding self-consistency and uncertainty among different samples are discussed.

2. Experiment procedure

Following the same argument in previous studies [3–8], we treat the PZN–8%PT single crystal poled along [001] direction of the original cubic axial with pseudo-tetragonal 4 mm symmetry. For the 4 mm symmetry, there are a total of 11 independent material constants: 6 elastic, 3 piezoelectric and 2 dielectric

constants. In order to determine them unambiguously, we have employed both the ultrasonic pulse-echo and resonance methods. Details of the technique have been given in Refs. [8,9]. The elastic stiffness constants $c_{11}^E, c_{33}^D, c_{44}^E, c_{66}^E, c_{12}^E$ and c_{44}^D can be directly determined from the measurements of phase velocities of ultrasonic waves propagating along appropriate pure mode directions [8]. The elastic compliances s_{11}^E, s_{33}^E and the electromechanical coupling coefficients, k_{33}, k_{31} and k_t , are determined from the measured resonance and anti-resonance frequencies of the length-extensional vibration bars and thickness-extensional vibration plate, respectively. Also, the piezoelectric strain constants d_{33} can be directly measured by using quasi-static method. The dielectric constants ε_{11}^T and ε_{33}^T were obtained from the low-frequency capacitances using the parallel plate capacitor approximation.

Table 1
Measured and derived material properties of PZN–8%PT and PZN–4.5%PT^a single crystal poled along [001]

Elastic stiffness constants												
	c_{ij} (10^{10} N/m ²)											
PT (%)	c_{11}^{E*}	c_{12}^{E*}	c_{13}^E	c_{33}^E	c_{44}^{E*}	c_{66}^{E*}	c_{11}^D	c_{12}^D	c_{13}^D	c_{33}^{D*}	c_{44}^{D*}	c_{66}^D
8	11.5	10.5	10.9	11.51	6.34	6.50	11.8	10.8	10.0	14.3	6.76	6.50
4.5 ^a	11.1	10.2	10.1	10.5	6.4	6.3	11.3	10.4	9.5	13.5	6.7	6.3
Elastic compliance constants												
	s_{ij} (10^{-12} m ² /N)											
PT (%)	s_{11}^{E*}	s_{12}^{E*}	s_{13}^E	s_{33}^E	s_{44}^{E*}	s_{66}^{E*}	s_{11}^D	s_{12}^D	s_{13}^D	s_{33}^{D*}	s_{44}^{D*}	s_{66}^D
8	87.0	–13.1	–70.0	141	15.8	15.4	55.8	–44.2	–8.2	18.5	14.8	15.4
4.5 ^a	82.0	–28.5	–51.0	108	15.6	15.9	61.5	–49.0	–9.0	20.6	14.9	15.9
Piezoelectric constants												
	e_{iz} (C/m ²)			d_{iz} (10^{-12} C/N)			g_{iz} (10^{-3} V m/N)			h_{iz} (10^8 V/m)		
PT (%)	e_{15}	e_{31}	e_{33}	d_{15}	d_{31}	d_{33}^*	g_{15}	g_{31}	g_{33}	h_{15}	h_{31}	h_{33}
8	10.1	–5.1	15.4	159	–1455	2890	6.2	–21.3	42.4	4.2	–5.8	17.7
4.5 ^a	8.9	–3.7	15.0	140	–970	2000	5.0	–21.0	44	3.4	–4.3	17
Dielectric constants												
	$\varepsilon(\varepsilon_0)$				$\beta(10^{-4}/\varepsilon_0)$				Electromechanical coupling constants			
PT (%)	ε_{11}^S	ε_{33}^S	ε_{11}^{T*}	ε_{33}^{T*}	β_{11}^S	β_{33}^S	β_{11}^T	β_{33}^T	k_{15}	k_{31}^*	k_{33}^*	k_t^*
8	2720	984	2900	7700	3.68	10.2	3.45	1.30	0.25	0.60	0.94	0.45
4.5 ^a	3000	1000	3100	5200	3.4	10.0	3.2	1.9	0.23	0.50	0.91	0.50

Density: $\rho = 8315$ kg/m³ (PZN–8%PT); $\rho = 8310$ kg/m³ (PZN–4.5%PT).

(*) Measure properties.

^a The complete set of constants of PZN–4.5%PT single crystal are from Ref. [8].

3. Results and discussions

A complete set of elastic, piezoelectric and dielectric constants of PZN–8%PT is listed in Table 1. In the table, material constants marked with an asterisk (*) were determined directly by measurements and the others were derived quantities. The relevant constants of PZN–4.5%PT reported in Ref. [8] are also listed in Table 1 for comparison. It is seen that the difference in elastic stiffness constants under constant electric field is very small between the two systems. We therefore conclude that the PT composition in PZN–PT system has little influence on the elastic stiffness under constant electric field. The most pronounced differences between the two systems listed in Table 1 are in the values of s_{33}^E , d_{33} and ϵ_{33}^T . The values of those constants of PZN–8%PT are 1.34, 1.45 and 1.48 times of the corresponding values of PZN–4.5%PT, respectively. Our results seem to confirm the previous reported phenomena that larger d_{33} is associated with larger s_{33}^E [2].

As indicated in Table 1, the values of some constants are derived indirectly. There is usually more than one relationship to derive a given constant. Therefore, consistency of these relations needs to be examined. Our error analysis showed that data inconsistency mainly comes from property variation from sample to sample. The situation is more serious for the PZN–8%PT system because its extraordinarily large piezoelectric coefficients, d_{31} and d_{33} , and high coupling coefficient, k_{33} , are very sensitive to com-

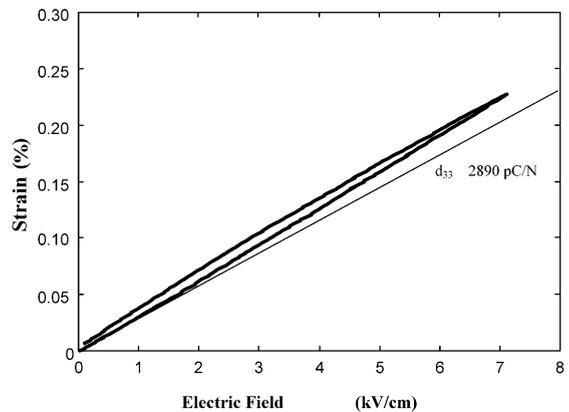


Fig. 2. A typical strain vs. electric field behavior along [001] of cubic direction for a PZN–8%PT single crystal sample. The d_{33} value increases with driving field.

positional variations. The property change can be substantial in many cases, for example, the dielectric constant ϵ_{33}^T can change more than 50% and the piezoelectric coefficient e_{31} could even have the wrong sign. In order to reduce this uncertainty, we have made 16 different measurements for the 11 independent unknown constants. Those additional independent measurements provide consistency checks.

Because the growth method and the nature of the crystal, Pb loss is extremely difficult to avoid. Usually, 5% compositional variation is common in a large crystal boule. This will greatly affect the consistency of the measured data set, particularly for crystal near the morphotropic phase boundary composition, for which the properties can change drastically with composition. For samples cut from different parts of the same crystal boule, the measured value of d_{33} is in the range of 2000–4000 (pC/N) and the value of ϵ_{33}^T ranges from 5000 to 8000. In order to examine the PT composition in each sample, the temperature dependence of dielectric permittivity is measured, which shows the phase transition temperature. As shown in Fig. 1, the PT composition could change as much as 8% from different parts of the same crystals we have received, which were claimed to have the same chemical composition. The data set given in Table 1 is obtained from those samples with the same 8%PT composition based on the onset of phase transition temperature.

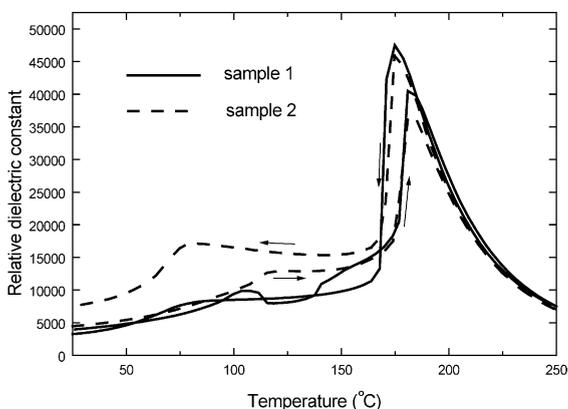


Fig. 1. Temperature dependence of the dielectric constants of PZN–8%PT single crystal samples 1 and 2 measured at 1 kHz.

Due to its multi-domain nature, properties of samples with the same chemical composition also depend strongly on the domain patterns produced, while these domain patterns are determined by the geometry of the sample and the poling process. There are of course other factors affecting the effective materials properties, such as voids, defect inclusions and cracks. They will increase the coercive field, decrease electromechanical coupling factors, and reduce the effective remnant polarization. Considering these problems, samples were carefully examined under optical microscope before conducting further measurements. The relationship between piezoelectric coefficient d_{33} and the driving field of one typical sample used in our measurement is shown in Fig. 2, from which it could be seen that the piezoelectric coefficient d_{33} of the sample is about 2890 pC/N, and d_{33} indeed increases a little with the driving field.

4. Summary

A complete set of elastic, piezoelectric and dielectric constants for the PZN–8%PT single crystals have been determined. Since the PZN–8%PT system is very near the morphotropic phase boundary, the system has much larger piezoelectric and dielectric constants compared with PZN–4.5%PT system. It is also observed that the PT composition has little influence on the elastic stiffness constants $c_{\alpha\beta}^E$. Large variations have been observed in piezoelectric and

dielectric properties from sample to sample due to the chemical inhomogeneity and the domain pattern difference. We have used over-determination technique to eliminate some of these uncertainties.

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