

## Complete set of material constants of 0.93Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.07PbTiO<sub>3</sub> domain engineered single crystal

RUI ZHANG, BEI JIANG, WENWU CAO

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

E-mail: cao@math.psu.edu

AHMED AMIN

Naval Sea System Command, Newport, RI 02841, USA

The relaxor based Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PZN-PT) and Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> (PMN-PT) domain engineered single crystal systems exhibit superior electromechanical property compared to the conventional PZT ceramics, which have been dominating piezoelectric applications for more than 40 years. The theoretical studies for the physical mechanism of this multi-domain system have generated a great deal of interests in scientific community [1–6]. From both fundamental study and device design purpose, it is necessary to get the complete set of matrix properties for those crystals.

Recently, such a complete set of elastic, piezoelectric and dielectric constants has been reported for 0.95Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.045PbTiO<sub>3</sub> (PZN-4.5%PT) and 0.92Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.08PbTiO<sub>3</sub> (PZN-8.0%PT) single crystal systems [7–9]. It is known that PZT-4.5%PT single crystal system [2] is fairly far away from the morphotropic phase boundary (MPB) composition, therefore, it does not represent the maximum electromechanical capability of this solid solution system. It has been shown that the PZN-8.0%PT single crystal system possesses much larger piezoelectric strain constant  $d_{33}$  than that of PZT-4.5%PT [9]. The electromechanical coupling coefficient  $k_{33}$  of PZN-8.0%PT could reach 0.94, which is higher than that of PZT-4.5%PT. However, PZN-PT single crystal systems near the MPB composition exhibit strong property fluctuations. We have measured several PZN-8.0%PT samples cut from different parts of the same crystal boule and found that although the fluctuation in PT composition of all samples were within  $\pm 2\%$ , the measured value of  $d_{33}$  varied from 2000 to 4000 (pC/N) and the value of  $\varepsilon_{33}^T$  varied from 5000 to 8000, which makes PZN-8.0%PT single crystal unsuitable for many practical device applications.

On the other hand, it is very difficult to control the composition accurately because of the lead loss during growth. Therefore, we focused our attention to 0.93Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.07PbTiO<sub>3</sub> (PZN-7.0%PT) which has the PT composition slightly away from the morphotropic phase boundary and is in the rhombohedral phase at room temperature. A full set of matrix properties of PZN-7.0%PT was measured and is reported in this paper. The electromechanical coupling property fluctuation was also investigated as a reference for people who will use these material properties.

After being poled along [001] of the cubic coordinates at room temperature, the multi-domain PZN-7.0%PT single crystal could be treated as pseudo-tetragonal 4 mm symmetry [1–10]. For materials with 4 mm symmetry, there are 11 independent material constants altogether: 6 elastic, 3 piezoelectric and 2 dielectric constants. In order to determine them unambiguously, an improved hybrid method combining the advantages of ultrasonic pulse-echo and resonance methods was used. The main ideas of this technique have been given in Refs. [8–11].

In previous measurements, usually  $e_{31}$  and  $e_{33}$  were derived from the measured  $c_{11}^E, c_{12}^E, c_{13}^E, c_{33}^E, d_{31}$  and  $d_{33}$  by using the following equations

$$e_{31} = d_{31}(c_{11}^E + c_{12}^E) + d_{33}c_{13}^E \quad (1)$$

$$e_{33} = 2d_{31}c_{13}^E + d_{33}c_{33}^E \quad (2)$$

From the standard error analysis, we found that even very small variations in the values of  $c_{12}^E$  and  $c_{13}^E$  will cause large variations in the calculated values of  $e_{31}$  and  $e_{33}$  if the amplitudes of  $d_{31}$  and  $d_{33}$  are very large. For PZN-7.0%PT, the enlarged errors for  $e_{31}$  associated with  $c_{12}$  and  $c_{13}$  are given by

$$\frac{\Delta e_{31}}{e_{31}} = 54.2 \left( \frac{\Delta c_{12}^E}{c_{12}^E} \right) \quad (3)$$

$$\frac{\Delta e_{31}}{e_{31}} = 112.6 \left( \frac{\Delta c_{13}^E}{c_{13}^E} \right) \quad (4)$$

Similarly, the errors of  $e_{33}$  caused by the uncertainty of  $c_{13}^E$  and  $c_{33}^E$  are

$$\frac{\Delta e_{33}}{e_{33}} = 17.9 \left( \frac{\Delta c_{13}^E}{c_{13}^E} \right) \quad (5)$$

$$\frac{\Delta e_{33}}{e_{33}} = 34.4 \left( \frac{\Delta c_{33}^E}{c_{33}^E} \right) \quad (6)$$

For comparison, error analysis was performed for PZN-4.5%PT, PZN-8%PT and BaTiO<sub>3</sub>, respectively, as listed in Table I. The  $d_{31}$  and  $d_{33}$  values are also shown in the table. In general, the larger are the amplitudes of  $d_{31}$  and  $d_{33}$ , the greater are the fluctuations of calculated

TABLE I Error amplifications of derived piezoelectric coefficients  $e_{31}$  and  $e_{33}$  caused by the relative error of some elastic constants

	PZN-4.5%PT $d_{31} = -970$ $d_{33} = 2000$	PZN-7.0%PT $d_{31} = -1204$ $d_{33} = 2455$	PZN-8.0%PT $d_{31} = -1450$ $d_{33} = 2900$	BaTiO <sub>3</sub> $d_{31} = -34.5$ $d_{33} = 85.6$
$(\frac{\Delta e_{31}}{e_{31}}) / (\frac{\Delta c_{12}^E}{c_{12}^E})$	21.5	54.2	52.5	2.3
$(\frac{\Delta e_{31}}{e_{31}}) / (\frac{\Delta c_{13}^E}{c_{13}^E})$	43.8	112.6	109	4.9
$(\frac{\Delta e_{33}}{e_{33}}) / (\frac{\Delta c_{33}^E}{c_{33}^E})$	14.9	17.9	19.2	3.9
$(\frac{\Delta e_{33}}{e_{33}}) / (\frac{\Delta c_{13}^E}{c_{13}^E})$	28.7	34.4	36.6	7.2

values of  $e_{31}$  and  $e_{33}$ . One can see that when Equations 1 and 2 were used for BaTiO<sub>3</sub>, there is no problem because the relatively small piezoelectric coefficients do not introduce large error amplification. But, those conversion formulas became unstable when used for PZN-PT single crystals since both  $d_{31}$  and  $d_{33}$  are very large. Therefore,  $c_{12}^E$ ,  $c_{13}^E$  and  $c_{33}^E$  must be determined very accurately in order for the  $e_{31}$  and  $e_{33}$  to have relatively reliable values. On the other hand, the changes of  $e_{31}$  and  $e_{33}$  have little influence on the value of  $c_{12}^E$ ,  $c_{13}^E$  or  $c_{33}^E$ . Therefore, a reverse strategy was used in our measurements, i.e., the values of  $e_{31}$  and  $e_{33}$  were determined first, then the values of  $c_{12}^E$  and  $c_{13}^E$  were deduced from measured  $e_{31}$  and  $e_{33}$  by using Equations 1 and 2. In addition to the thickness extensional resonance sample used to determine  $e_{33}$  directly, an edge-excited thickness resonance sample was made and used to measure  $e_{31}$  directly. Thus, a self-consistent complete set of materials constants is obtained.

The measured complete set of elastic, piezoelectric and dielectric constants of PZN-7.0%PT are shown in Table II. Material constants marked with a star (\*) were determined directly by measurements and the others were derived values. The relevant constants of PZN-4.5%PT single crystal reported in Ref. [8] are also listed in Table II for comparison. It is seen that the difference in elastic stiffness constants under constant electric field are very small between the two systems. Therefore, we 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 are in the values of  $s_{33}^E$ ,  $d_{33}$  and  $\varepsilon_{33}^T$ . The values for PZN-7.0%PT are 1.34, 1.23 and 1.08 times of the corresponding values of PZN-4.5%PT, respectively. The values of PZN-7.0%PT are generally less than those of PZN-8.0%PT single crystal except  $s_{33}^E$ , which is almost equal to that of PZN-8.0%PT. We found that  $s_{33}^E$  of all three PZN-PT

TABLE II Measured and derived material properties of PZN-7.0%PT, PZN-8.0%PT and PZN-4.5%PT single crystal poled along [001]

		PZN-7.0%PT			Density: $\rho$ (kg/m <sup>3</sup> )				PZN-8.0%PT				PZN-4.5%PT	
		8350			8315				8310					
		Elastic stiffness constants: $c_{ij}$ (10 <sup>10</sup> N/m <sup>2</sup> )												
PT (%)		$c_{11}^{E*}$	$c_{12}^E$	$c_{13}^E$	$c_{33}^E$	$c_{44}^{E*}$	$c_{66}^{E*}$	$c_{11}^D$	$c_{12}^D$	$c_{13}^D$	$c_{33}^{D*}$	$c_{44}^{D*}$	$c_{66}^D$	
7.0		11.3	10.3	10.5	10.91	6.30	7.10	11.37	10.37	10.0	14.0	6.80	7.10	
8.0		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 <sup>†</sup>		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 <sup>-12</sup> m <sup>2</sup> /N)												
PT (%)		$s_{11}^{E*}$	$s_{12}^E$	$s_{13}^E$	$s_{33}^E$	$s_{44}^{E*}$	$s_{66}^{E*}$	$s_{11}^D$	$s_{12}^D$	$s_{13}^D$	$s_{33}^{D*}$	$s_{44}^{D*}$	$s_{66}^D$	
7.0		85.9	-14.1	-69.0	142	15.9	14.1	56.7	-43.3	-9.6	20.9	14.7	14.1	
8.0		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 <sup>†</sup>		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: $e_{i\lambda}$ (C/m <sup>2</sup> ) $d_{i\lambda}$ (10 <sup>-12</sup> C/N) $g_{i\lambda}$ (10 <sup>-3</sup> Vm/N) $h_{i\lambda}$ (10 <sup>8</sup> V/m)												
PT (%)		$e_{15}$	$e_{31}^*$	$e_{33}^*$	$d_{15}$	$d_{31}$	$d_{33}^*$	$g_{15}$	$g_{31}$	$g_{33}$	$h_{15}$	$h_{31}$	$h_{33}$	
7.0		11.1	-2.3	15.1	176	-1204	2455	6.6	-24.2	49.3	4.5	-3.1	20.7	
8.0		10.1	-5.1	15.4	159	-1455	2890	6.2	-21.3	42.4	4.2	-5.8	17.7	
4.5 <sup>†</sup>		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 (%)		$\varepsilon_{11}^S$	$\varepsilon_{33}^S$	$\varepsilon_{11}^{T*}$	$\varepsilon_{33}^{T*}$	$\beta_{11}^S$	$\beta_{33}^S$	$\beta_{11}^T$	$\beta_{33}^T$	$k_{15}$	$k_{31}^*$	$k_{33}^*$	$k_t^*$	
7.0		2779	823	3000	5622	3.60	12.2	3.33	1.78	0.27	0.58	0.92	0.47	
8.0		2720	984	2900	7700	3.68	10.2	3.45	1.30	0.25	0.60	0.94	0.45	
4.5 <sup>†</sup>		3000	1000	3100	5200	3.4	10.0	3.2	1.9	0.23	0.50	0.91	0.50	

\*Measure properties.

<sup>†</sup>Data from Ref. [8].

TABLE III The relevant constants determined from resonance measurements for different length expander bar resonators. The units of all the constants are the same as in Table II

Sample no.	Length (mm)	Width (mm)	Height (mm)	$s_{33}^E$	$d_{33}$	$\epsilon_{33}^T$	$k_{33}$
PZN-7.0%PT							
1	11.73	4.183	4.208	140.5	2420	5516	0.924
2	12.04	4.184	4.198	143.5	2490	5727	0.923
3	10.61	2.607	2.611	142.2	2457	5621	0.923
$\delta$ (%)	–	–	–	$\pm 1.1$	$\pm 1.5$	$\pm 1.9$	$\pm 0.1$
PZN-8.0%PT							
4	8.13	1.17	1.09	120.9	2135	5010	0.922
5	6.02	0.93	0.97	142.0	2920	7630	0.943
6	4.39	0.91	0.87	140.6	2736	6891	0.934
$\delta$ (%)	–	–	–	$\pm 10.1$	$\pm 17.8$	$\pm 23.0$	$\pm 1.2$

single crystal systems are much larger than conventional ceramics, which further confirms the previous reported phenomenon that larger  $d_{33}$  is associated with larger  $s_{33}^E$  [2].

In order to investigate the fluctuation in electromechanical properties of PZN-7.0%PT single crystal system, several extension bars of differing lengths and with exciting electric field parallel to their length were cut from different part of a crystal boule. From the measurement of series and parallel resonance frequencies as well as capacitances of those bar resonators, the material constants  $\epsilon_{33}^T$ ,  $s_{33}^E$ ,  $d_{33}$  and  $k_{33}$  were determined. The results are listed in Table III, where  $\delta$  denotes the relative deviation of related constants. It can be easily seen that the property fluctuation of PZN-7.0%PT single crystal system is much smaller than that of PZN-8.0%PT single crystal. This is because the composition of the PZN-7.0%PT is a little away from the morphotropic boundary composition, its piezoelectric and dielectric properties are much less sensitive to the variation of PT composition. Among the domain engineered PZN-PT single crystal systems, PZN-7.0%PT single crystal system might be the best candidate for device applications since its properties are comparable to that of PZN-8.0%PT but much more stable.

### Acknowledgments

This research was sponsored by the ONR under Grant # N00014-01-1-0960 and the NIH under Grant #

RR11795-05. We would like to thank Dr. M. Matsushita of Kawatetsu Mining Co. Ltd, Research laboratory, Japan for providing the PZN-7.0% PT crystal used in this work.

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Received 24 June

and accepted 7 August 2002