Complete set of material constants of Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$−Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$−PbTiO$_3$ single crystal with morphotropic phase boundary composition

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Using combined resonance and ultrasonic methods, a full set of material constants has been measured for morphotropic phase boundary (MPB) composition xPb(In$_{1/2}$Nb$_{1/2}$)O$_3$−$(1-x-y)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$−yPbTiO$_3$ (PIN-PMN-PT) single crystals poled along $[001]_c$. Compared with the MPB composition $(1-x)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$−xPbTiO$_3$ (PMN-PT) single crystals, the PIN-PMN-PT single crystals have smaller anisotropy, higher Curie temperature ($T_c \approx 197$ °C), and higher rhombohedral to tetragonal phase transition temperature ($T_{R\text{-}T} \approx 96$ °C). The electromechanical properties obtained here are the best found so far for this ternary system with $d_{33} \approx 2742$ pC/N, $d_{31} \approx -1337$ pC/N, $k_{33} \approx 95\%$, and $k_{31} \approx 65\%$. © *2009 American Institute of Physics*. [doi:10.1063/1.3243169]

I. INTRODUCTION

Since the discovery of the superior piezoelectric and electromechanical coupling properties of $(1-x)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$−xPbTiO$_3$ (PMN-PT) and $(1-x)$Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$−xPbTiO$_3$ (PZN-PT) multidomain single crystals,[1] there have been intensive research on finding other crystal systems with even better properties and use them in practical applications. Typical devices utilizing these domain engineered crystals include ultrabroad band ultrasonic imaging transducers and high performance actuators. In principle, because the piezoelectric properties of these crystals are three to five times better than that of Pb(Ti,Zr)O$_3$ (PZT) ceramics and the manufacture price also comes down to an acceptable level, these domain engineered crystals could replace PZT in most electromechanical devices. However, some limitations of these crystals prevent them from replacing traditional PZT piezoelectric ceramics in many practical applications, despite their much superior electromechanical properties. The most noticeable inferior properties are the relatively low Curie point ($T_c \sim 145$ °C) and low rhombohedral-tetragonal transition temperature ($T_{R\text{-}T} \sim 70$ °C), which restrict the application temperature range and also make the piezoelectric properties temperature sensitive.

In order to increase the T_c and $T_{R\text{-}T}$, people have been trying to add different dopants to the binary compound PMN-PT. So far, the most successful system reported is the ternary compound xPb(In$_{1/2}$Nb$_{1/2}$)O$_3$−$(1-x-y)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$−yPbTiO$_3$ (PIN-PMN-PT), which can increase the T_c and $T_{R\text{-}T}$ without losing the superior electromechanical properties of the binary PMN-PT system. In this paper, we report the best properties found so far from this

PIN-PMN-PT system with composition close to the morphotropic phase boundary (MPB). In addition, a complete set of material constants has been accurately determined for this composition, which can facilitate practical applications of this ternary piezoelectric single crystal.

There are numerous published reports in the literature on PIN-PMN-PT ternary compounds. As an earlier work, ceramic PIN-PT and PIN-PMN-PT were fabricated and characterized.[2,3] Although the ceramic form of this ternary compound does not have ultrahigh piezoelectric properties, one found that the addition of lead indium niobate can drastically increase the phase transition temperature T_c and the rhombohedral to tetragonal transition temperature $T_{R\text{-}T}$. The $[001]_c$ poled multidomain single crystals exhibited excellent dielectric and piezoelectric properties with $\varepsilon_{33}^T \sim 5000$ and $d_{33} \sim 2200$ pC/N and the phase transition temperatures are also increased ($T_c \sim 192$ °C and $T_{R\text{-}T} \sim 119$ °C).[4] Tian *et al.* demonstrated that ternary PIN-PMN-PT crystals can be grown in large size by a modified Bridgman method, and they reported high coercive field ($E_C \sim 6.0$ kV/cm) and increased depoling temperature ($T_{R\text{-}T} \sim 100-117$ °C).[5] The elastic, dielectric, and piezoelectric properties of ternary PIN-PMN-PT crystals with $26\% \sim 59\%$ PIN were measured using resonance technique and it was found that the ternary system can have excellent piezoelectric properties comparable to that of PMN-PT single crystals.[6] The PIN-PMN-PT single crystals were also investigated earlier by Hosono and Yamashita who reported higher phase transition temperatures: $T_c = 184$ °C and $T_{R\text{-}T} = 89$ °C, and excellent dielectric and piezoelectric properties.[7] Zhang *et al.*[8] reported an investigation on PIN-PMN-PT system using a larger crystal boule of 50 mm in diameter and 100 mm in length. They reported full set material constants measured using resonance method for three different sections from the same crystal boule. The compositions were found to change along the growth direc-

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TABLE I. Relationships between phase velocities and elastic constants for 4*mm* symmetry the measured values of phase velocities in 0.27PIN-0.40PMN-0.33PT multidomain single crystals poled along $[001]_c$.

Phase velocities	$v_l^{[001]}$	$v_s^{[001]}$	$v_l^{[100]}$	$v_{s\perp}^{[100]}$	$v_{s\parallel}^{[100]}$	$v_l^{[110]}$
Related elastic constants	c_{33}^D	c_{44}^E	c_{11}^E	c_{66}^E	c_{44}^D	$\frac{1}{2}(c_{11}^E+c_{12}^E+2c_{66}^E)$
Measure phase velocity (m/s)	4571	2900	3850	2750	2962	4675

tion so that the exact composition of each section was difficult to determine, therefore, a range of properties was reported with the best results comparable to that of PMN-29%PT.[8] Because the resonance technique has strict demand for sample geometries and the properties are strongly influenced by the geometries of the sample due to the change of domain configuration, properties determined using resonance technique alone often have very large uncertainties.

In this work, we have grown and characterized the MPB composition of this system with nominal composition of 0.27PIN-0.40PMN-0.33PT. The crystals have rhombohedral symmetry and were being polarized along $[001]_c$ to produce effective tetragonal macroscopic symmetry. By using combined ultrasonic and resonance methods,[9–11] we accurately measured a complete set of material properties for this multidomain system. It was found that this MPB composition has the best electromechanical properties of the PIN-PMN-PT system reported so far, which are comparable to that of the PMN-0.33PT system, while the $T_{R\text{-}T}$ and T_c have been increased by more than 27 °C.

II. EXPERIMENTAL PROCEDURE

The crystals used in the study were grown by a modified Bridgman method and the crystal symmetry is rhombohedral 3*m* according to the XRD pattern. After being poled along $[001]_c$, the effective symmetry of the multidomain system becomes tetragonal 4*mm*, which has 11 independent electromechanical constants: six elastic, three piezoelectric, and two dielectric constants.

All samples were oriented using the Laue x-ray machine and vacuum sputtered with gold on the parallel ⟨001⟩ faces. The samples were poled along $[001]_c$ at room temperature using an electric field of 20 kV/cm. The frequency spectra were measured by an HP 4194A impedance-phase gain analyzer. A 15 MHz longitudinal wave transducer (Ultra Laboratories, Inc.) and 20 MHz shear wave transducer (Panametrics) were used for the pulse-echo measurements. The electric pulses used to excite transducers were generated by a Panametrics 200 MHz pulser/receiver (5900PR), and the time-of-flight between echoes were measurement by a Tektronix 460A digital oscilloscope.

The free and clamped permittivity (ε_{11}^T, ε_{33}^T, ε_{11}^S, and ε_{33}^S) were calculated from the low (1 kHz) and high frequency ($\sim 2f_a$) capacitances using the parallel capacitor approximation. The electromechanical coupling factors k_{15}, k_{31}, k_{33}, and k_t, and the elastic compliance s_{11}^E, s_{33}^D, and s_{33}^E, were calculated from the resonance and antiresonance frequencies of resonators with geometries defined in the IEEE standards. The elastic constants c_{33}^D, c_{44}^E, c_{11}^E, c_{66}^E, c_{44}^D, and c_{12}^E were determined from the phase velocities of ultrasonic waves propagating along certain crystallographic directions. After that, d_{31}, d_{33}, e_{31}, and e_{33} can be calculated with the measured properties, while c_{13}^E can be calculated from the formula $c_{13}^E=(e_{33}-d_{33}c_{33}^E)/2d_{31}$. Over all, we made 18 indepen-

TABLE II. Measured and derived material constants of 0.27PIN-0.40PMN-0.33PT multidomain single crystal poled along $[001]_c$ (density: $\rho=8198$ kg/m³).

	Elastic stiffness constants, c_{ij} (10^{10} N/m²)										
c_{11}^E [a]	c_{12}^E [a]	c_{13}^E	c_{33}^E [a]	c_{44}^E [a]	c_{66}^E [a]	c_{11}^D	c_{12}^D	c_{13}^D	c_{33}^D [a]	c_{44}^D [a]	c_{66}^D [a]
12.2	11.3	10.8	11.2	6.9	6.2	12.3	11.4	9.9	17.1	7.5	6.2

	Elastic compliance constants, s_{ij} (10^{-12} N/m²)										
s_{11}^{E*}	s_{12}^E	s_{13}^E	s_{33}^E [a]	s_{44}^E	s_{66}^E	s_{11}^D	s_{12}^D	s_{13}^D	s_{33}^D [a]	s_{44}^D	s_{66}^D
75.5	−38.3	−35.8	77.8	14.5	16.1	61.0	−52.8	−4.7	11.3	13.3	16.1

	Piezoelectric coefficients, $e_{i\lambda}$ (C/m²)			$d_{i\lambda}$ (10^{-12} C/N)			$g_{i\lambda}$ (10^{-3} Vm/N)			$h_{i\lambda}$ (10^8 V/m)	
e_{15}	e_{31}	e_{33}	d_{15}	d_{31}	d_{33}	g_{15}	g_{31}	g_{33}	h_{15}	h_{31}	h_{33}
16.0	−2.7	18.6	232	−1337	2742	2.6	−13.4	42.7	3.8	−4.6	31.9

	Dielectric constants, $\varepsilon(\varepsilon_0)$			β ($10^{-4}/\varepsilon_0$)				Electromechanical coupling factors			
ε_{11}^S [a]	ε_{33}^S [a]	ε_{11}^T [a]	ε_{33}^T [a]	β_{11}^S	β_{33}^S	β_{11}^T	β_{33}^T	k_{15} [a]	k_{31} [a]	k_{33} [a]	k_t [a]
4736	659	10 081	7244	2.1	15.2	1.0	1.4	0.20	0.65	0.95	0.59

[a]Directly measured properties.

TABLE III. Comparison of some important constants for several different single crystals.

Compound	T_c (°C)	T_{rt} (°C)	P_r (μC/cm^2)	E_c (kV/cm)	d_{33} (pC/N)	k_{33}	$\varepsilon_{33}^T/\varepsilon_0$
PMN-29%PT[a]	137	93	26.5	2.0	1540	0.91	5400
PMN-33%PT[b]	149	69	27.0	2.3	2820	0.94	8200
PMN-42%PT[c]	190–193	/	42.0	5.3	260	0.78	660
PIN-PMN-PT[a] (part C)	191	125	25.0	5.5	1510	0.92	4400
PIN-PMN-PT (in this study)	197	96	34.0	5.5	2742	0.95	7244

[a]See Ref. 8.
[b]See Ref. 12.
[c]See Ref. 14.

dent measurements, which provided seven control checks to guarantee self-consistency of the 11 independent constants being determined.

The measured sound velocities for the five pure modes are listed in Table I. In order to see the better accuracy of our combined method than the resonance method, let us analyze a specific measurement for c_{12}^E. From the sound velocity measurement $v_l^{[110]}$, we can obtain c_{12}^E following the formula in Table I. Considering the resolutions for the time of flight and the sample thickness measurements are 1 ns and 0.01 mm, respectively, and there are small errors in orientation and parallelness of the sample surfaces, the overall error of sound velocity measurements is about 1.0%. On the other hand, if one uses the resonance technique, the elastic constant c_{12}^E is derived from following formula:

$$c_{12}^E = \frac{\varepsilon_{33}^T - \varepsilon_{33}^S - d_{31}^2 c_{11}^E - 2d_{33}e_{33} + d_{33}^2 c_{33}^E}{2d_{31}^2}$$
$$= \frac{\varepsilon_{33}^T - \varepsilon_{33}^S - 2d_{33}e_{33} + d_{33}^2 c_{33}^E}{2d_{31}^2} - \frac{c_{11}^E}{2}. \quad (1)$$

The relative errors may be estimated by

$$\frac{\Delta c_{12}^E}{c_{12}^E} = \frac{\frac{\varepsilon_{33}^T}{2}\left(\frac{\Delta\varepsilon_{33}^T}{\varepsilon_{33}^T}\right) + \frac{\varepsilon_{33}^S}{2}\left(\frac{\Delta\varepsilon_{33}^S}{\varepsilon_{33}^S}\right) + (2e_{33} + 2d_{33}c_{33}^E)d_{33}\left(\frac{\Delta d_{33}}{d_{33}}\right) + 2d_{33}e_{33}\left(\frac{\Delta e_{33}}{e_{33}}\right) + d_{33}^2 c_{33}^E\frac{\Delta c_{33}^E}{c_{33}^E} + 2(\varepsilon_{33}^T - \varepsilon_{33}^S - 2d_{33}e_{33} + d_{33}^2 c_{33}^E)\left(\frac{\Delta d_{31}}{d_{31}}\right) + d_{31}^2 c_{11}^E\left(\frac{\Delta c_{11}^E}{c_{11}^E}\right)}{\varepsilon_{33}^T - \varepsilon_{33}^S - d_{31}^2 c_{11}^E - 2d_{33}e_{33} + d_{33}^2 c_{33}^E}. \quad (2)$$

For the PIN-PMN-PT crystal, Eq. (2) may be quantified as

$$\frac{\Delta c_{12}^E}{c_{12}^E} = 0.02\frac{\Delta\varepsilon_{33}^T}{\varepsilon_{33}^T} + 0.003\frac{\Delta\varepsilon_{33}^S}{\varepsilon_{33}^S} + 2.67\frac{\Delta d_{33}}{d_{33}} + 0.10\frac{\Delta e_{33}}{e_{33}}$$
$$+ 1.28\frac{\Delta c_{33}^E}{c_{33}^E} + 2.43\frac{\Delta d_{31}}{d_{31}} + 0.22\frac{\Delta c_{11}^E}{c_{11}^E}. \quad (3)$$

Thus, if there is 2.0% error in the measurement of d_{31} and d_{33}, the error of c_{12}^E will exceed 10.0%. Therefore, c_{12}^E obtained from the ultrasonic measurement is much more reliable. By selecting only dependable formulas for the constants, the combined ultrasonic and resonance technique offers much better accuracy in the full matrix property characterization of these multidomain single crystals.

III. RESULTS AND DISCUSSIONS

The measured elastic, piezoelectric, and dielectric constants for the MPB composition PIN-PMN-PT single crystal are given in Table II, and some important parameters are listed in Table III for comparison among several different systems. One can see from Table III that the properties obtained here are comparable to that of the $[001]_c$ poled PMN-0.33PT,[12] which is the MPB composition of the PMN-PT binary system. The piezoelectric coefficients $d_{33}(\approx2742$ pC/N) as well as $d_{31}(\approx-1337$ pC/N) are very large, and the corresponding electromechanical coupling factors k_{33} ($\approx95\%$) as well as k_{31} ($\approx65\%$) are even better than that of PMN-0.33PT. Because the composition of this crystal is at the MPB, its electromechanical properties are better
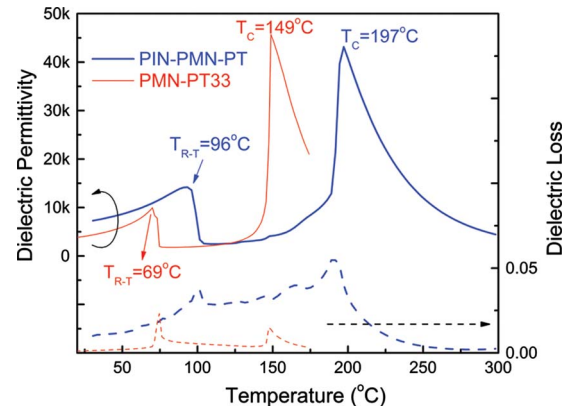

FIG. 1. (Color online) Dielectric constant ε_{33}^T and dielectric loss as a function of temperature for PMN-0.33PT and 0.27PIN-0.40PMN-0.33PT single crystals.

TABLE IV. Anisotropies of measured material properties for several different single crystals.

Compound	$\varepsilon_{11}^T/\varepsilon_{33}^T$	$\varepsilon_{11}^S/\varepsilon_{33}^S$	s_{33}^E/s_{11}^E	s_{33}^D/s_{11}^D	s_{44}^E/s_{66}^E	s_{13}^E/s_{12}^E	s_{13}^D/s_{12}^D
PMN-29%PT[a]	0.28	1.47	0.87	1.33	1.80	0.94	0.82
PMN-33%PT[b]	0.20	2.1	1.73	0.25	0.95	5.01	0.12
PMN-42%PT[c]	13.00	11.79	2.04	0.95	2.88	3.65	0.67
PIN-PMN-PT[a] (part C)	0.31	1.75	1.34	0.24	0.37	1.71	0.11
PIN-PMN-PT (in this study)	1.39	7.2	1.18	0.18	0.90	0.93	0.09

[a]See Ref. 8.
[b]See Ref. 12.
[c]See Ref. 14.

than those reported earlier for PIN-PMN-PT system with lower PT content, but the T_{R-T} here is about $10-20$ °C lower than those reported earlier.[5,8,13] Even though, compared to PMN-0.33PT, the phase transition temperatures T_c (from cubic to tetragonal) and T_{R-T} (from rhombohedral to tetragonal) of the 0.27PIN-0.40PMN-0.33PT crystal increased by 48 and 27 °C, respectively. The temperature dependence of the dielectric properties has been measured for both PMN-0.33PT and 0.27PIN-0.40PMN-0.33PT single crystals. As one can see from Fig. 1 that the T_c and T_{R-T} of 0.27PIN-0.40PMN-0.33PT are much higher.

In order to check the anisotropy of the multidomain 0.27PIN-0.40PMN-0.33PT single crystals, some constant ratios are calculated and listed in Table IV. It was found that the measured elastic anisotropies of 0.27PIN-0.40PMN-0.33PT single crystal are much less than that of PMN-29%PT,[8] PMN-33%PT,[12] and PMN-42%PT[14] and other compositions of PIN-PMN-PT.[5,8]

IV. SUMMARY AND CONCLUSIONS

In summary, we have grown the MPB composition PIN-PMN-PT single crystal by a modified Bridgman method and performed accurate property characterization by using combined ultrasonic and resonance technique. A complete set of material constants for $[001]_c$ polarized multidomain crystals has been obtained. It was found that the piezoelectric properties $d_{33} \approx 2742$ pC/N, $d_{31} \approx -1337$ pC/N of this MPB composition PIN-PMN-PT are comparable to that of the counterpart PMN-PT single crystals, while the electrome-chanical coupling factors $k_{33} \approx 95\%$ and $k_{31} \approx 65\% k_{33}$ are even better. Most importantly, the depoling temperature T_{R-T}, which restricts the temperature range of practical applications of these piezoelectric crystals, has been increased by more than 27 °C, which can greatly enlarge the application range of these outstanding piezoelectric single crystals.

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