Characterization of $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ ferroelectric crystal with enhanced phase transition temperatures

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The full set of material constants for relaxor-based ternary single crystals $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PIN-PMN-PT) were determined and compared to binary $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PMNT) crystals. The Curie temperature for rhombohedral compositions of PIN-PMN-PT was found to be in the range of 160–200 °C with ferroelectric rhombohedral to tetragonal phase transition on the order of 120–130 °C, more than 30 °C higher than that found for PMNT. The piezoelectric coefficients (d_{33}) were in the range of 1100–1500 pC/N, with electromechanical coupling factors (k_{33}) about 89%–92% comparable to PMNT crystals. The coercive field of the ternary crystal was found to be 5.5 kV/cm, double the value of the binary counterparts. The dielectric behavior under varying dc bias exhibited a similar trend as observed in PMNT with a much broader usage temperature range. Together with its enhanced field induced phase transition level, the ternary PIN-PMN-PT crystals are promising candidates for high temperature and high drive transducer applications. © 2008 American Institute of Physics. [DOI: 10.1063/1.2978333]

I. INTRODUCTION

Relaxor-based single crystals, such as $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}x\text{PbTiO}_3$ (PMNT) ($x=0.28\text{--}0.32$) with morphotropic phase boundary (MPB) composition have attracted much attention over the past decade owing to its ultrahigh piezoelectric coefficients ($d_{33}=1500\text{--}2500$ pC/N) and electromechanical coupling factors ($k_{33}>90\%$).^{1–3} However, their relatively low Curie temperatures (130–170 °C) limit their application in transducers and actuators, in which thermal stability is expected in relation to dielectric and piezoelectric property variations and depolarization as a result of postfabrication processes. In addition, the strongly curved MPB results in rhombohedral to tetragonal phase transformation temperature of only 60–95 °C, further limiting their applicability. A broader temperature and/or electric field operating range would allow for greater device design flexibility and therefore a wider range of potential applications. Thus, new single crystal piezoelectric compositions that will operate at higher temperature and/or higher electric field than current state-of-the-art PMNT single crystals are desirable. Extensive investigations have been carried out on single crystals with high Curie temperature over the past few years^{4–17} in order to find the possibility of single crystals for the next generation of transduction devices.

In the reported relaxor- PbTiO_3 systems, $\text{Pb}(\text{Sc}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--PbTiO}_3$, $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--PbTiO}_3$, and $\text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--PbTiO}_3$ (PYNT) were found to possess relative high Curie temperatures near their respective MPBs, being on the order of 260–360 °C.^{4–6} The PYNT single crystals are very promising with the highest Curie tempera-

ture of 350 °C and rhombohedral to tetragonal phase transition temperature is on the order of ~ 160 °C. However, it was reported that the PYNT crystals can only be obtained from high temperature solution method due to its poor perovskite stability with crystal sizes only on the order of few millimeters.^{7,8} Bismuth based perovskite ferroelectric single crystals $\text{BiScO}_3\text{--PbTiO}_3$ (BSPT) were reported to possess much higher Curie temperatures, being on the order of 400 °C. Of particular interest is its high ferroelectric phase transition temperature of 350 °C with excellent piezoelectric properties ($d_{33}\sim 1200$ pC/N and $k_{33}=90\%$), expanding its temperature usage range significantly.^{9,10} As for the PYNT system, BSPT crystals can only be grown using the flux method, with crystals on the order of few millimeters obtained.

Recently, it was reported that large ternary PIN-PMN-PT single crystals (>50 mm in diameter) can be grown from the melt directly by the Bridgman method, with Curie temperatures on the order of ~ 200 °C, while maintaining the excellent piezoelectric properties.^{15–17} In this work, the dielectric permittivity, piezoelectric coefficient, elastic con-

FIG. 1. (Color online) Photo of as grown PIN-PMN-PT crystal with 50 mm in diameter.

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TABLE I. Measured and derived elastic compliance constants s_{ij} (10^{-12} m²/N) and elastic stiffness constants c_{ij} (10^{10} N/m²) for PIN-PMN-PT crystals, compared to PMNT29.

Material	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
Part A	42.3	-18.4	-20.9	45.7	15.6	33.0	33.9	-26.7	-3.6	9.9	14.4	33.0
Part B	49.0	-20.0	-26.5	57.3	15.2	39.4	38.2	-30.8	-4.0	10.3	14.3	39.4
Part C	51.2	-18.3	-31.3	68.4	15.8	43.0	38.2	-31.3	-3.7	10.0	14.5	43.0
PMNT29	52.1	-24.6	-26.4	59.9	16.0	28.3	41.8	-34.8	-3.9	10.3	14.0	28.3
Material	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
Part A	11.2	9.6	9.5	10.9	6.4	3.0	11.7	10.1	7.9	15.9	6.9	3.0
Part B	11.9	10.5	10.4	11.4	6.6	2.5	12.3	10.9	9.0	16.7	7.0	2.5
Part C	12.2	10.7	10.5	11.0	6.4	2.3	12.7	11.2	8.8	16.4	6.9	2.3
PMNT29	12.4	11.1	10.4	10.8	6.3	3.5	12.6	11.3	9.3	16.8	7.1	3.5

stant, and electromechanical coupling factors of PIN-PMN-PT crystals were measured and/or derived. The ability to utilize the ternary crystals over a wider temperature and external electric field range is demonstrated in contrast to the binary PMNT counterpart.

II. EXPERIMENTAL

Ternary PIN-PMN-PT single crystals were grown by the Bridgman technique using the [011] oriented seed crystals. The starting composition was selected as $[x\text{PIN}-(1-x-y)\text{PMN}-y\text{PT}]$ with $x > 0.25-0.35$ and $y > 0.30-0.32$. An obtained crystal boule with 50 mm in diameter and 100 mm in length is shown in Fig. 1. As reported for PMNT crystals, the composition along the growth direction is varied due to the segregation of titanium in PIN-PMN-PT crystals, with lower PT content at the bottom part of the crystals and the crystal near the top of the boule was found to be in tetragonal phase. The obtained crystal boule was divided into five parts, rhombohedral A, B, and C, and MPB region, and tetragonal, as shown in Fig. 1. All the samples for characterization in this work belong to the rhombohedral phase, considering the low ferroelectric phase transition temperature associated with the MPB composition(s), the MPB region was not studied in this work. The full set of material constants were determined using the resonance method and five types of Z-cut samples

were prepared according to IEEE standards.^{10,11,18-22} All the samples were oriented along their crystallographic directions [001] and [110] using real-time Laue and sputtered with gold on the parallel [001] faces. The samples were poled at 20 kV/cm at room temperature. High field polarization and strain measurements at room temperature were performed on the [001] oriented plate samples using a modified Sawyer-Tower circuit and linear variable differential transducer driven by a lock-in amplifier. The resonance and antiresonance frequencies were obtained by an HP 4194A impedance-phase gain analyzer. The Curie temperature and ferroelectric phase transition temperatures were determined from the dielectric temperature dependence using a multifrequency LCR meter (HP4284A), connected to a computer controlled temperature chamber. Dielectric behavior under external dc bias was measured as a function of temperature on the [001] oriented samples, with dc bias varying from 0 to 20 kV/cm and in 1 kV/cm step, with a blocking circuit to protect the LCR meter under high dc bias field, which was supplied by a Trek609C-6 high-voltage dc amplifier.

III. RESULTS AND DISCUSSIONS

A. Material constants at room temperature

Tables I-III list the full set of elastic constants, piezo-

TABLE II. Piezoelectric coefficients, d_{ij} (pC/N), e_{ij} (C/m²), g_{ij} (10^{-3} Vm/N), and h_{ij} (10^8 V/m), and electromechanical coupling factors, k_{ij} , for PIN-PMN-PT crystals, compared to PMNT29.

Material	d_{33}	d_{31}	d_{15}	e_{33}	e_{31}	e_{15}
Part A	1130	-544	119	19.1	-6.1	7.6
Part B	1320	-634	105	18.6	-4.8	6.9
Part C	1510	-712	119	17.1	-5.4	7.6
PMNT29	1540	-699	164	22.3	-3.9	10.3
Material	g_{33}	g_{31}	g_{15}	h_{33}	h_{31}	h_{15}
Part A	31.8	-15.4	9.9	26.2	-8.4	7.0
Part B	35.6	-17.0	8.8	28.9	-7.4	6.5
Part C	38.7	-18.3	10.2	31.4	-9.8	7.9
PMNT29	32.2	-14.6	11.9	27.7	-4.8	8.7
Material	k_{33}	k_{31}	k_{15}	k_t	k_{31} (45 °C)	
Part A	0.89	0.44	0.27	0.56	0.77	
Part B	0.91	0.47	0.25	0.57	0.80	
Part C	0.92	0.50	0.28	0.57	0.82	
PMNT29	0.91	0.44	0.35	0.60	0.81	

TABLE III. Dielectric constants ϵ_{ij} (ϵ_0) and dielectric impermeability constants β ($10^{-4}/\epsilon_0$) for PIN-PMN-PT crystals, compared to PMNT29.

Material	ϵ_{33}^T	ϵ_{11}^T	ϵ_{33}^S	ϵ_{11}^S	β_{33}^T	β_{11}^T	β_{33}^S	β_{11}^S
Part A	4000	1360	822	1230	2.50	7.35	12.17	8.13
Part B	4200	1335	729	1200	2.38	7.49	13.72	8.33
Part C	4400	1320	617	1080	2.27	7.58	16.21	9.26
PMNT29	5400	1560	910	1340	1.85	6.41	10.99	7.46

electric coefficients, electromechanical coupling factors, and dielectric permittivity for PIN-PMN-PT and compared to PMNT, respectively. As found in PMNT crystal boules, the PT content in PIN-PMN-PT was found to vary along the growth direction, with lower PT observed in the early growth stage and higher PT in the final growth stage. As shown in Fig. 1, parts A–C are in the rhombohedral region, with the highest PT found in part C. The elastic compliance constants (s_{11}^E, s_{33}^E) were found to increase slightly with increasing PT, while the elastic stiffness constants (c_{11}, c_{33} , and c_{44}) exhibited similar values, demonstrating that the rhombohedral PIN-PMN-PT crystals have similar longitudinal and shear wave sound velocities related to the above constants regardless of the variation in PT content. However, the elastic stiffness c_{66} were found to decrease slightly with increasing PT, indicating slower shear wave (with both the propagation and displacement perpendicular to the poling direction) sound velocity due to the domain wall motion, which makes extrinsic contribution to the dielectric and piezoelectric properties.²¹ The piezoelectric strain coefficients d_{33} were found to increase with increasing PT. The piezoelectric stress coefficient e_{33} values were found to decrease with increasing PT contents, associated with a decrease in clamped dielectric permittivity. All the piezoelectric properties are comparable to PMNT29 single crystals.

B. Ferroelectric properties at room temperature

Figure 2 shows the bipolar polarization hysteresis for PIN-PMN-PT crystals and compared to PMNT. The remnant polarization was found to be on the order of 0.25 C/m² for PIN-PMN-PT, comparable to PMNT (~ 0.265 C/m²). Of particular interest is the high coercive field of PIN-PMN-PT,

FIG. 2. Polarization hysteresis measured at a field of 20 kV/cm for PIN-PMN-PT crystals and compared to PMNT.

being on the order of 5.5 kV/cm, more than twice of the value of PMNT (~ 2 kV/cm). The high field strain behavior as a function of electric field is given in Fig. 3, in which the electric field induced phase transformation field level of PMNT crystals was found to be ~ 15 kV/cm, while the induced transition field level was on the order of 46 kV/cm for the ternary system. The piezoelectric coefficients obtained from the low-field slope were found to be 1100–1500 pm/V, corresponding to the d_{33} value of the rhombohedral crystals obtained from the resonance method. Upon strain saturating, i.e., tetragonal phase induced, the piezoelectric d_{33} was found to drop significantly, being on the order of 250 pm/V for PMNT crystal and ~ 400 pm/V for PIN-PMN-PT system.

C. Properties as a function of temperature

Figure 4 shows the dielectric permittivity and dielectric loss as functions of temperature for rhombohedral PIN-PMN-PT with different PT contents, and compared to PMNT29, respectively. The room temperature dielectric permittivity was found to be ~ 4000 for part A, increasing to ~ 4400 for part C, lower than binary PMNT29 crystal (~ 5400). The Curie temperature increased from 164 to 191 °C, depending on the different PT contents. Of particular interest is the rhombohedral to tetragonal phase transition temperature for most of the rhombohedral region, being on the same order of ~ 125 °C, 30 °C higher than the binary counterpart. The dielectric permittivity variation for PIN-PMN-PT in the range of room temperature to 100 °C was found to be on the order of 50–90/K, much lower when compared to PMNT crystal (~ 220 /K), exhibiting a much flatter and more stable dielectric behavior. The dielectric loss

FIG. 3. Unipolar strain as a function of electric field for PIN-PMN-PT and compared to PMNT.

(a)

(b)

FIG. 4. Dielectric permittivity (a) and dielectric loss (b) as a function of temperature for PIN-PMN-PT and compared to PMNT.

for PIN-PMN-PT crystals, as shown in Fig. 4(b), exhibited similar trend as dielectric permittivity, with peak values located at the phase transition temperature.

Figure 5 shows the variation in electromechanical coupling k_{31} and piezoelectric coefficient d_{31} as functions of temperature for PIN-PMN-PT crystals, compared to PMNT. It was observed that the electromechanical coupling factor maintained similar values with increasing temperature, decreasing sharply above the phase transition temperature ($\sim 125^\circ\text{C}$ for PIN-PMN-PT) due to the partial depolarization of the crystals in the tetragonal phase. The piezoelectric coefficients were found to increase with increasing temperature and reach a maxima at the phase transition temperature, whereupon they decrease significantly.

D. Usage temperature range under dc bias

Usage temperature range for a ferroelectric single crystal is not only limited by their ferroelectric phase transition temperature but to the applied external electric fields, which results in lower phase transition temperatures. Thus, it is important to understand the behavior of crystals under dc bias field. Figure 6 presents the Curie temperature and rhombohedral to tetragonal phase transition temperatures for PIN-PMN-PT crystals with different PT contents as a function of dc bias. As found for other ferroelectric crystal systems,¹⁴ the Curie temperature was found to shift to lower temperatures when the dc bias was lower than a specific threshold field,

(a)

(b)

FIG. 5. Variation in lateral electromechanical coupling factor (a) and variation in lateral piezoelectric coefficient (b) as a function of temperature for PIN-PMN-PT and compared to PMNT.

which is related to the magnitude of the random internal field in relaxor systems. Above the critical field, the Curie temperature increased with increasing dc bias; meanwhile, the rhombohedral to tetragonal phase transition temperatures were found to decrease linearly with increasing dc bias. This

FIG. 6. Curie temperature and rhombohedral to tetragonal phase transition temperature as a function of external dc bias for PIN-PMN-PT crystals. (The inset shows the usage temperature range of PIN-PMN-PT and compared to PMNT crystal.)

behavior reflects the stabilizing of the tetragonal phase, owing to the fact that the spontaneous polarization direction [001] in tetragonal phase is along the dc bias direction. The small inset in Fig. 6 shows the usage temperature range (phase transition temperature) for PIN-PMN-PT under different dc biases compared to PMNT. The usage temperature range for PIN-PMN-PT was found to be on the order of 125 °C (zero bias) and decreases to 90 °C at an applied field of 20 kV/cm, being 30 °C higher than PMNT counterpart.

IV. SUMMARY

In summary, large size (50 mm in diameter) PIN-PMN-PT crystals were grown directly from the melt using the Bridgman technique. Of the obtained crystal boules, 70% of which belongs to the rhombohedral phase, with modest PT segregation along the growth direction. The piezoelectric properties of rhombohedral PIN-PMN-PT crystals are comparable to binary PMNT crystals. Of particular interest, the ferroelectric phase transition temperatures observed, being on the order of 125 °C, were 30 °C higher than PMNT29 crystals. Due to the higher Curie temperature, PIN-PMN-PT crystals were found to possess higher coercive field of ~5.5 kV/cm, more stable dielectric and piezoelectric properties, and much broader usage temperature range, when compared to PMNT crystals, which make the ternary crystals promising candidates for wider range of potential transducer applications.

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