Complete set of elastic, dielectric, and piezoelectric constants of $[011]_C$ poled rhombohedral $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3\text{:Mn}$ single crystals

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Mn modified rhombohedral $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT:Mn) single crystals poled along $[011]_C$ crystallographic direction exhibit a “2R” engineered domain configuration, with macroscopic $mm2$ symmetry. The complete sets of material constants were determined using combined resonance and ultrasonic methods, and compared to $[001]_C$ poled PIN-PMN-PT:Mn crystals. The thickness shear piezoelectric coefficient d_{15} and electromechanical coupling factor k_{15} were found to be on the order of ~ 3000 pC/N and 0.92, respectively, with longitudinal piezoelectric coefficient d_{33} and coupling factor k_{33} being on the order of ~ 1050 pC/N and 0.90. Of particular importance is that PIN-PMN-PT:Mn single crystals exhibited high mechanical quality factor $Q_{33} \sim 1000$, comparable to “hard” PZT8 ceramics, which can also be confirmed by the low extrinsic contribution, being $\leq 2\%$ from the Rayleigh analysis. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4792661>]

I. INTRODUCTION

Relaxor-based single crystals, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PMN-PT), have attracted much attention over the past decades owing to their ultrahigh piezoelectric coefficients ($d_{33} > 1500$ pC/N) and electromechanical coupling factors ($k_{33} \sim 0.90$).^{1–6} However, the relatively low rhombohedral to tetragonal phase transition temperatures ($T_{RT} \sim 60\text{--}95^\circ\text{C}$) and Curie temperatures ($T_C \sim 130\text{--}170^\circ\text{C}$) of PMN-PT limit their usage temperature range. $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) based ternary single crystals have been reported to have T_{RT} more than 30°C higher than that of PMN-PT, with comparable piezoelectric coefficients ($d_{33} > 1500$ pC/N) and electromechanical coupling factors ($k_{33} \sim 0.90$). In addition, the coercive fields E_C were found to be around 5 kV/cm, twice of the binary PMN-PT crystals, offering much higher field stability and larger electric field operating range.^{7–10}

Both PMN-PT and PIN-PMN-PT single crystals show low mechanical quality factors $Q_m \sim 100$, which restricted their applications for high power transducers. Analogous to modified “hard” lead zirconate titanate (PZT) ceramics, it is expected that acceptor dopants, such as $\text{Mn}^{2+,3+}$, can improve the mechanical quality factor by the formation of acceptor-oxygen vacancy defect dipoles.^{11,12} Recently, manganese modified relaxor-PT crystals have been reported to exhibit enhanced mechanical quality factors Q_m and increased field stability.^{13,14} To date, however, the full matrix of electromechanical properties for rhombohedral PIN-PMN-PT:Mn single crystals has not been measured and the

effect of $\text{Mn}^{2+,3+}$ on relaxor-PT crystals is still not fully understood.

In this paper, the complete set of material constants was determined for $[011]_C$ poled rhombohedral PIN-PMN-PT:Mn crystals with two different compositions. The mechanical quality factors Q_m were evaluated for various vibration modes. Polarization and unipolar strain under high field were studied as a function of electric field. In addition, the intrinsic and extrinsic contributions to the longitudinal piezoelectric response were evaluated using Rayleigh analysis.

II. EXPERIMENTAL

Mn modified PIN-PMN-PT single crystals with a nominal starting composition of 0.26PIN-0.42PMN-0.32PT were grown using the modified Bridgman technique. The doped level of Mn was in the range of 1–5 mol. %. The as grown PIN-PMN-PT:Mn crystals were found to exhibit different phases along the growth direction due to the segregation of Ti. In this work, two sections of rhombohedral crystal were studied. Part A was compositionally far away from the nominal morphotropic phase boundary (MPB) with low PT, while part B was in close proximity to MPB composition with high PT. All samples were oriented by real-time Laue X-ray orientation system with an accuracy of 0.5° . Vacuum sputtered gold was applied to the desired surfaces as electrodes. The samples were poled at a dc electric field of 10 kV/cm at room temperature. For the $[011]_C$ poled crystals, the macroscopic symmetry is orthorhombic $mm2$, so there are 17 independent material constants: 9 elastic constants, 5 piezoelectric constants, and 3 dielectric permittivities. According to the IEEE standards on piezoelectricity,¹⁵ the pseudo-cubic crystallographic $[0\bar{1}1]_C$ direction is defined as the X axis, and $[100]_C$, $[011]_C$ are defined as the Y and Z

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FIG. 1. Dielectric permittivity (a) and dielectric loss (b) as a function of temperature for $[011]_c$ poled rhombohedral PIN-PMN-PT:Mn single crystals.

axes, respectively. The complete set of material constants was determined by combined resonance and ultrasonic methods. The resonance and antiresonance frequencies were measured using an HP4194A impedance-phase gain analyzer.¹⁶ Longitudinal and shear wave transducers were used to measure the phase velocities on cube samples with the dimensions of $5.0 \times 5.0 \times 5.0 \text{ mm}^3$, from which, corresponding elastic stiffness constants: c_{11}^E , c_{22}^E , c_{33}^E , c_{44}^E , c_{55}^E , c_{66}^E , and c_{12}^E could be calculated. The temperature dependence of the dielectric permittivity was determined on k_t type samples using HP4284A precision LCR meter at 1 kHz and 10 kHz, which were connected to a computer controlled high temperature furnace. Polarization and strain under high electric field were determined using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT) driven by a lock-in amplifier (Stanford Research system, Mode SR830). The Rayleigh analysis was performed on longitudinal bars using the same system.

III. RESULTS AND DISCUSSION

Fig. 1(a) shows the temperature dependence of dielectric permittivity and dielectric loss for two compositions of

FIG. 2. Polarization hysteresis loops of PIN-PMN-PT:Mn single crystals measured at ac electric field of 15 kV/cm at 1 Hz.

rhombohedral PIN-PMN-PT:Mn single crystals. The dielectric permittivity at room temperature was found to increase with increasing PT, due to the composition approaching to MPB. The Curie temperature of composition B was found to be $\sim 197^\circ\text{C}$, while the Curie temperature of composition A was found to be $\sim 188^\circ\text{C}$. For composition A, rhombohedral-monoclinic (T_{RM}) and monoclinic-tetragonal (T_{MT}) phase transitions were found to be $\sim 130^\circ\text{C}$ and 163°C , respectively, while for composition B, T_{RM} and T_{MT} phase transitions were found to be $\sim 106^\circ\text{C}$ and 121°C , respectively. The dielectric loss for PIN-PMN-PT:Mn single crystals exhibited peak values at the associated phase transitions, as given in Fig. 1(b).

Fig. 2 shows the polarization hysteresis loops for the two compositions of PIN-PMN-PT:Mn single crystals measured at 1 Hz. The remnant polarization for composition B was found to be on the order of 0.42 C/m^2 , slightly higher than that of composition A, which was 0.39 C/m^2 , while the coercive fields were found to be 5.1 kV/cm and 5.8 kV/cm , respectively, more than twice the value of binary PMN-PT crystals ($\sim 2.5 \text{ kV/cm}$)

FIG. 3. Unipolar strain as a function of electric field for compositions A and B of "2R" PIN-PMN-PT:Mn crystals at 1 Hz.

TABLE I. Measured and derived material constants for composition A [2R (A)] and composition B [2R (B)] of [011]_C poled rhombohedral PIN-PMN-PT:Mn single crystals. The data for [001]_C poled PIN-PMN-PT:Mn single crystals were listed for comparison.

Elastic stiffness constants: c_{ij}^E and c_{ij}^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			
2R (A) ^a	19.1	12.2	7.43	13.3	11.9	15.2	6.44	0.86	5.00			
2R (B) ^a	19.5	13.6	8.32	15.1	13.0	15.1	6.16	0.53	4.67			
4R ^b	12.8	11.1	10.8	12.8	10.8	11.3	6.5	6.5	3.6			
	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			
2R (A) ^a	19.2	12.0	7.75	14.6	9.61	19.2	7.19	4.64	5.00			
2R (B) ^a	19.5	13.4	8.64	16.4	10.7	19.1	6.99	3.56	4.67			
4R ^b	13.3	11.7	9.0	13.3	9.0	17.0	7.2	7.2	3.6			
Elastic compliance constants: s_{ij}^E and s_{ij}^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			
2R (A) ^a	18.0	−28.0	13.1	68.1	−39.4	30.9	15.5	116	20.0			
2R (B) ^a	23.5	−39.0	20.6	90.4	−56.4	43.8	16.2	189	21.1			
4R ^b	45.4	−15.9	−28.1	45.4	−28.1	62.4	15.4	15.4	27.8			
	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			
2R (A) ^a	10.7	−8.83	0.10	17.5	−5.20	7.79	13.9	21.6	20.0			
2R (B) ^a	11.7	−9.59	0.09	17.5	−5.46	8.27	14.3	28.1	21.4			
4R ^b	34.4	−26.9	−3.9	34.4	−3.9	9.2	13.9	13.9	27.8			
Piezoelectric coefficients: d_{ij} (10^{-12} C/N), e_{ij} (C/m ²), g_{ij} (10^{-3} Vm/N), and h_{ij} (10^8 V/m)												
	d_{15}	d_{24}	d_{31}	d_{32}	d_{33}	e_{15}	e_{24}	e_{31}	e_{32}	e_{33}		
2 R (A) ^a	2030	125	455	−1200	810	17.5	8.05	1.23	−8.52	14.8		
2R (B) ^a	2986	160	608	−1508	1053	15.8	9.86	1.08	−7.83	13.4		
4R ^b	133	133	−609	−609	1341	8.6	8.6	−5.2	−5.2	16.8		
	g_{15}	g_{24}	g_{31}	g_{32}	g_{33}	h_{15}	h_{24}	h_{31}	h_{32}	h_{33}		
2R (A) ^a	46.7	13.0	16.0	−42.2	28.5	21.6	9.37	2.19	−15.2	26.4		
2R (B) ^a	53.8	12.1	19.5	−48.7	33.8	19.1	8.43	2.37	−17.2	29.5		
4R ^b	11.3	11.3	−18.1	−18.1	39.7	8.3	8.3	−10.7	−10.7	34.2		
Dielectric: $\varepsilon_{ij}/\varepsilon_0$, β ($10^{-4}/\varepsilon_0$)												
	ε_{11}^S	ε_{22}^S	ε_{33}^S	ε_{11}^T	ε_{22}^T	ε_{33}^T	β_{11}^S	β_{22}^S	β_{33}^S	β_{11}^T	β_{22}^T	β_{33}^T
2R (A) ^a	912	970	635	4916	1084	3213	11.0	10.3	15.7	2.03	9.23	3.11
2R (B) ^a	934	1321	515	6274	1499	3523	10.7	7.57	19.4	1.59	6.67	2.84
4R ^b	1169	1169	553	1326	1326	3811	8.55	8.55	18.1	7.54	7.54	2.62
Electromechanical coupling factors: k_{ij}												
	k_{15}	k_{24}	k_{31}	k_{32}	k_{33}	k_t						
2R (A) ^a	0.90	0.32	0.64	0.86	0.86	0.45						
2R (B) ^a	0.92	0.34	0.71	0.90	0.90	0.46						
4R ^b	0.31	0.31	0.49	0.49	0.92	0.58						
Mechanical quality factors: Q_m												
	Q_{15}	Q_{24}	Q_{31}	Q_{32}	Q_{33}	Q_t						
2R(A) ^a	90	70	220	100	1000	200						
2R(B) ^a	130	110	260	140	1000	220						
4R ^a	60	60	500	500	700	100						

^aThis work.^bReference 14.

and comparable to that of pure PIN-PMN-PT crystals (~ 5.5 kV/cm).^{8,9} Of particular interest is that the internal bias was found to be on the order of 0.5–0.6 kV/cm. Mn modified relaxor-PT single crystals possess acceptor-oxygen defect

dipoles, forming anisotropic centers locally within a domain. When the crystals were poled, the dipoles realign along a preferential direction for the spontaneous polarization and move to the high stress areas of domain walls by diffusion. Thus, the

TABLE II. Comparison of electromechanical coupling factor k_{ij} and piezoelectric coefficient d_{ij} (pC/N) for “2R” domain engineered PIN-PMN-PT:Mn, PIN-PMN-PMN, and PMN-PT crystals.

	d_{15} (pC/N)	d_{24} (pC/N)	d_{31} (pC/N)	d_{32} (pC/N)	d_{33} (pC/N)	k_{15}	k_{24}	k_{31}	k_{32}	k_{33}	k_t
2R (A) ^a	2030	125	455	−1200	810	0.90	0.32	0.64	0.86	0.86	0.45
2R (B) ^a	2986	160	608	−1508	1053	0.92	0.34	0.71	0.90	0.90	0.46
PIN-PMN-28%PT ^b	2203	114	460	−1156	782	0.90	0.30	0.67	0.86	0.87	0.49
PIN-PMN-32%PT ^b	3354	162	744	−1781	1363	0.95	0.36	0.75	0.90	0.92	0.50
PMN-28%PT ^c	2816	234	723	−1761	1766	0.90	0.30	0.65	0.89	0.91	0.50
PMN-30%PT ^c	3262	289	813	−2116	1916	0.95	0.36	0.71	0.94	0.92	0.52

^aThis work.^bReference 19.^cReference 20.

internal bias is built up, which is believed to play an important role in clamping of domain wall motions and restricting polarization rotations, accounting for the enhanced mechanical Q_m and decreased dielectric loss.^{11,13}

The high field strain behavior as a function of electric field is given in Fig. 3. The electric field induced phase transition field level was found to be 27 kV/cm at room temperature for composition A. As expected, the induced phase transition field level of composition B was significantly lower, being ~ 17 kV/cm, owing to its composition at the proximity of MPB. It can be seen that the electric field threshold for the inducing orthorhombic phase was decreased with increasing the PT content (closer to MPB), with similar induced strain level being on the order of 0.26%, analogous to pure PIN-PMN-PT crystals.¹⁰ The piezoelectric coefficients d_{33} obtained from low fields were found to be 750–1100 pm/V, corresponding to the d_{33} values for PIN-PMN-PT: Mn crystals obtained from the resonance method. When the crystals transformed to orthorhombic phase under high electric field, the piezoelectric coefficient ($d_{33} \sim 150$ pm/V) was found to drop significantly, corresponding to the values for the single domain orthorhombic crystals.

Table I gives the complete set of elastic, piezoelectric, and dielectric constants of $[011]_C$ poled PIN-PMN-PT:Mn rhombohedral single crystals and compared to $[001]_C$ poled counterpart. All of the piezoelectric properties for composition B with “2R” engineered domain configuration were found to be higher than the values of composition A, where the piezoelectric coefficient d_{33} and electromechanical coupling factor k_{33} were found to be ~ 1050 pC/N and 0.90 for composition B crystals, respectively. Compared to “4R” domain engineered crystals ($[001]$ poled), higher thickness shear piezoelectric d_{15} and electromechanical coupling factor k_{15} were observed, being on the order of ~ 3000 pC/N and 92%, respectively. The mechanical quality factors Q_m were evaluated for various vibration modes, where the mechanical coupling factors Q_{31} (Q_{32}) for “4R” domain engineered crystals were found to be higher than those of “2R” crystals. In addition, the Q_{32} was lower than Q_{31} for “2R” crystals, exhibiting strong anisotropic mechanical properties in $[011]$ poled crystals. The longitudinal mechanical Q_{33} for “2R” domain engineered crystals was found to be ~ 1000 , comparable to “hard” PZT8 ceramics, and much higher than that of unmodified PIN-PMN-PT single crystals.¹⁷ All the studied shear mechanical quality factors were found to be low, due

to the facilitated “polarization rotation” and large rotation angle (90°) in the thickness shear vibration mode.^{1,18} In addition, the mechanical quality factors for composition B were found to be higher than the values of composition A. This may be due to the fact that the Mn dopant has large segregation along the growth direction, thus produced higher Mn doped level in composition B, leading to larger internal bias and enhanced mechanical Q_m .

FIG. 4. AC electric field dependent piezoelectric coefficient d_{33} for PIN-PMN-PT:Mn single crystals at 1 Hz for compositions A (a) and B (b). The comparison between the measured and calculated strain-electric field loops is given in the insets.

The electromechanical coupling factors k_{ij} and piezoelectric coefficients d_{ij} (pC/N) for “2R” domain engineered PIN-PMN-PT:Mn, PIN-PMN-PMN,¹⁹ and PMN-PT²⁰ crystals are listed in Table II for comparison. Analogous to “1O” single domain PIN-PMN-PT:Mn crystals, the piezoelectric properties for “2R” domain engineered crystals were found to be slightly lower than those values of unmodified binary PMN-PT and ternary PIN-PMN-PT crystals, due to the fact that the acceptor dopants $\text{Mn}^{2+,3+}$ induce internal bias, which pinned the domain wall motions and the “polarization rotation,” account for the decreased piezoelectric properties.

In order to understand the intrinsic and extrinsic contributions to the piezoelectric response of PIN-PMN-PT:Mn single crystals with “2R” domain engineered state, Rayleigh analysis was performed. The piezoelectric coefficient d_{33} was calculated from the slope of the unipolar strain measured at small amplitudes of electric field. The electric field dependence of piezoelectric coefficients d_{33} exhibiting a linear behavior can be described using the Rayleigh formula: $d(E_0) = d_{\text{init}} + \alpha E_0 \text{ pm/V}$,²¹ where E_0 is the amplitude of the electric field. The d_{init} is considered to arise from the intrinsic contribution and αE_0 represents the extrinsic contribution to the total piezoelectric response. Fig. 4 shows the ac electric field dependent piezoelectric coefficient d_{33} for compositions A and B of [011] poled PIN-PMN-PT:Mn single crystals. For A crystals, the values of d_{init} and α were found to be 850 pm/V and 10 cm/kV, respectively, with the extrinsic contribution being on the order of 1.2% (at applied field of 1 kV/cm). Correspondingly, the values of d_{init} and α for B crystals were found to be 1090 pm/V and 17 cm/kV, respectively, with the extrinsic contribution being on the order of 1.5% (at applied field of 1 kV/cm). The extrinsic contributions for the “2R” PIN-PMN-PT:Mn crystals were found to be lower than the value of [001]_C poled binary PMN-PT and ternary PIN-PMN-PT crystals, due to the reduced domain wall motions, which was effectively clamped by the internal bias.^{10,22}

IV. CONCLUSIONS

In summary, the full set of material constants for [011]_C poled rhombohedral PIN-PMN-PT:Mn single crystals was determined using the combined resonance and ultrasonic methods. The internal bias for Mn modified PIN-PMN-PT crystals was found to be 0.5–0.6 kV/cm, leading to higher mechanical quality factors $Q_m \sim 1000$ and smaller extrinsic contributions $\leq 2\%$ compared to their pure counterparts. The

high mechanical quality factor, together with the comparable piezoelectric and electromechanical properties, make PIN-PMN-PT:Mn crystals potential candidate for high power transducer applications.

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- ¹S. J. Zhang and F. Li, *J. Appl. Phys.* **111**, 031301 (2012).
- ²S. E. Park and T. R. Shrout, *J. Appl. Phys.* **82**, 1804 (1997).
- ³D. Damjanovic, M. Budimir, M. Davis, and N. Setter, *Appl. Phys. Lett.* **83**, 527 (2003).
- ⁴R. Zhang, B. Jiang, and W. Cao, *J. Phys. Chem. Solids* **65**, 1083 (2004).
- ⁵S. J. Zhang, J. Luo, R. Xia, P. W. Rehrig, C. A. Randall, and T. R. Shrout, *Solid State Commun.* **137**, 16 (2006).
- ⁶S. Zhang, S. Lee, D. Kim, H. Lee, and T. R. Shrout, *J. Am. Ceram. Soc.* **91**, 683 (2008).
- ⁷G. S. Xu, K. Chen, D. F. Yang, and J. B. Li, *Appl. Phys. Lett.* **90**, 032901 (2007).
- ⁸S. J. Zhang, J. Luo, W. Hackenberger, and T. R. Shrout, *J. Appl. Phys.* **104**, 064106 (2008).
- ⁹X. Z. Liu, S. J. Zhang, J. Luo, T. R. Shrout, and W. W. Cao, *J. Appl. Phys.* **106**, 074112 (2009).
- ¹⁰F. Li, S. J. Zhang, D. B. Lin, J. Luo, X. Zhou, X. Y. Wei, and T. R. Shrout, *J. Appl. Phys.* **109**, 014108 (2011).
- ¹¹K. Carl and K. H. Hardtl, *Ferroelectrics* **17**, 473 (1978).
- ¹²S. J. Zhang, R. Xia, L. Lebrun, D. Anderson, and T. R. Shrout, *Mater. Lett.* **59**, 3471 (2005).
- ¹³S. J. Zhang, S. M. Lee, D. H. Kim, H. Y. Lee, and T. R. Shrout, *Appl. Phys. Lett.* **93**, 122908 (2008).
- ¹⁴J. Luo, W. Hackenberger, S. Zhang, and T. Shrout, in *IEEE Ultrasonic Symposium* (IEEE, San Diego, California, 2010), pp. 68–71.
- ¹⁵*IEEE Standards on Piezoelectricity* (ANSI/IEEE, New York, 1987), p. 176.
- ¹⁶R. Zhang, B. Jiang, and W. W. Cao, *J. Appl. Phys.* **90**, 3471 (2001).
- ¹⁷S. J. Zhang, N. P. Sherlock, R. J. Meyer, Jr., and T. R. Short, *Appl. Phys. Lett.* **94**, 162906 (2009).
- ¹⁸F. Li, S. J. Zhang, Z. Xu, X. Y. Wei, and T. R. Shrout, *Adv. Funct. Mater.* **21**, 2118 (2011).
- ¹⁹E. W. Sun, S. J. Zhang, J. Luo, T. R. Short, and W. W. Cao, *Appl. Phys. Lett.* **97**, 032902 (2010).
- ²⁰M. Shanthi, L. C. Lim, K. K. Rajan, and J. Jin, *Appl. Phys. Lett.* **92**, 142906 (2008).
- ²¹D. Damjanovic, *The Science of Hysteresis* (Elsevier, New York, 2005), Vol. 3, p. 337.
- ²²F. Li, S. Zhang, X. Zhou, X. Wei, J. Luo, and T. Shrout, *J. Appl. Phys.* **108**, 034106 (2010).