Domain size engineering in tetragonal $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ crystals

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The effect of domain size on the dielectric and piezoelectric properties of [111]-oriented tetragonal $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ crystals was investigated. The dielectric permittivity ($\epsilon_{33}^T/\epsilon_0$) and piezoelectric coefficient (d_{33}) were found to be on the order of 13 800 and 1630 pC/N, respectively, for samples with domain size of ~ 500 nm, a 3-fold increase to crystals with domain size of ~ 50 μm . Rayleigh analysis revealed that the extrinsic contribution to the piezoelectric response increased from $\sim 8\%$ to 30% with decreasing domain size, due to the increased domain wall density and associated irreversible domain wall motion. The enhanced properties were thought to relate to the fine domain structures, however, showing a poor electric field and temperature stabilities with domain size of 500 nm. Of particular significance is that samples with domain size being on the order of 5 μm exhibit field and temperature stabilities, with yet high piezoelectric properties, make it potential for transducer applications. © 2011 American Institute of Physics. [doi:10.1063/1.3654137]

I. INTRODUCTION

Domain wall engineering in ferroelectric materials is an approach to enhance piezoelectric related properties. The piezoelectric properties of BaTiO_3 single crystals have been investigated as a function of domain size,^{1–4} where the piezoelectric properties were found to significantly increase with decreasing domain size. The piezoelectric coefficient (d_{31}) and lateral electromechanical coupling factor (k_{31}) were found to increase from -98 pC/N to -230 pC/N and from 25.9% to 47.5%, respectively, with corresponding domain sizes of 40 μm and 5.5 μm .^{1,2} The piezoelectric coefficient (d_{33}) in BaTiO_3 was projected to be as high as 8000 pC/N for domain size in the nanoregion,⁴ though this has to be experimentally confirmed. The experimental results revealed that the enhanced piezoelectric coefficients were associated with the high domain wall density.^{1–3} Generally, the extrinsic contribution (irreversible domain wall motion) will increase with increasing domain wall density. In previous work, Rayleigh law has been used to investigate the extrinsic contribution to the dielectric and piezoelectric responses in ferroelectric materials.^{5–10} Therefore, Rayleigh law gives a way to investigate the domain size (reciprocal of domain wall density) effect in domain engineered single crystals.

Relaxor- PbTiO_3 single crystals have been extensively studied due to the high piezoelectric and electromechanical properties. The temperature usage range of these crystals, however, was limited by the low ferroelectric-ferroelectric phase transition temperatures (T_{R-T}), being on the order of 60°C – 95°C .

The tetragonal $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PIN-PMN-PT) crystals exhibit high Curie temperature ($T_C > 180^\circ\text{C}$), with no ferroelectric-ferroelectric phase transition above room temperature, expanding the temperature usage range greatly.¹¹ The piezoelectric d_{33} values are only about 400–450 pC/N in [001]-oriented tetragonal PIN-PMN-PT crystals,¹¹ thus limits their usage. Following the research on the domain wall engineered tetragonal BaTiO_3 crystals,⁴ [111]-oriented tetragonal PIN-PMN-PT crystals with enhanced piezoelectric properties will be expected, due to the engineered domain configuration “3T.”¹² In this study, the domain size (domain wall density) of the [111] oriented tetragonal crystals was studied, the extrinsic (irreversible domain wall motion) contribution to the enhanced properties was investigated using Rayleigh analysis. The field and temperature stabilities of the domain wall engineered PIN-PMN-PT crystals were explored as a function of pulse-field/cycle and temperature.

II. EXPERIMENTAL

A. Sample preparation and measurements

The PIN-PMN-PT crystals used in this work were grown using the modified Bridgman technique.¹³ Crystal samples with [111] directions were oriented by real-time Laue X-ray system. Samples with size of $6 \times 1 \times 1$ mm³ were polished to allow in-situ microscopic observation of the domain structure. Gold electrodes were sputtered on the (111) end faces to allow electrical property measurements. Domain size was controlled by applying dc electric field (Stanford Research PS325) along the [111] direction at different temperatures.² The domain structure was subsequently observed using a

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polarizing light microscope (PLM) (Zeiss Axioskop) with a digital camera (Pixelink) connecting to a computer.

The dielectric permittivity of PIN-PMN-PT crystals was calculated from the capacitance measured by HP4284A multi-frequency LCR meter at 1 kHz. The $d_{33(\text{cal.})}$ was determined by the impedance method according to IEEE standards,¹⁴ using an HP 4294 A impedance-phase gain analyzer. The $d_{33(\text{meter})}$ was measured using a piezo- d_{33} meter (ZJ-2). Polarization versus electric field (P-E) and strain versus electric field (S-E) were measured on samples with size of $5 \times 5 \times 1 \text{ mm}^3$, using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT), driven by a lock-in amplifier (Stanford Research Systems, Model SR830). The high field piezoelectric coefficients (d_{33}^*) were calculated from the slope of the unipolar strain curves. An Olympus Panametrics 200 MHz computer-controlled pulser/receiver with duration of 5 ns was used to investigate the field stability of the domain wall engineered crystals. The temperature dependence of dielectric permittivity was measured using a multi-frequency LCR meter (HP4284A), connected to a special designed furnace. The electromechanical coupling factors and piezoelectric coefficients as function of temperature were obtained using an HP 4294 A impedance-phase gain analyzer connected to a furnace.

B. Rayleigh analysis

In general, if cyclic electric field is applied to the samples with peak amplitudes (E_0) approximately up to 50% of the coercive field (E_C), the Rayleigh law can be expressed using the following formulae^{12,15,16}

$$S(E) = (d_{\text{init}} + \alpha E_0)E \pm \alpha(E_0^2 - E^2)/2, \quad (1)$$

$$d(E_0) = (d_{\text{init}} + \alpha E_0)PC/N, \quad (2)$$

where $S(E)$ is the electric-field-induced strain and E_0 is the peak value of applied electric field. The piezoelectric coefficient d_{init} is from an intrinsic contribution, following the analysis given in Refs. 12 and 15. αE_0 reveals the extrinsic contribution to the total piezoelectric response. Equation (1) describes the Rayleigh hysteresis where the sign “+” or “-” corresponds to decreasing and increasing electric field, respectively. For the Rayleigh measurements, the total piezoelectric coefficient d_{33} was calculated from the peak to peak strain ($S_{p+} - S_{p-}$) and the applied electric field (E_0), following equation:

$$d_{33} = \frac{S_{p+} - S_{p-}}{2E_0}. \quad (3)$$

The amplitude of the applied electric fields was selected from 0.1 kV/cm to 1 kV/cm, far below $1/2 E_C$.

III. RESULTS AND DISCUSSION

A. Domain structure with various sizes

The sub-micrometer and micrometer sized ($0.5 \sim 50 \mu\text{m}$) domain structures in [111]-poled PIN-PMN-PT crystals can be directly observed by PLM under a crossed polarizer/

analyzer (P/A) pair, as shown in Fig. 1. Fig. 1(a) illustrates the sample for domain observation and electric property measurement. It can be seen from Fig. 1(a) that the domain size was about $20 \mu\text{m}$ in the unpoled tetragonal PIN-PMN-PT crystals. The samples with domain sizes of $50 \mu\text{m}$, $20 \mu\text{m}$, $5 \mu\text{m}$, $2 \mu\text{m}$, and 500 nm after the controlled poling were given in Figs. 1(b)–1(f), respectively. The domain walls were found to be parallel in the crystals with larger domain sizes of $50 \mu\text{m}$ and $20 \mu\text{m}$, while being curved and skewed with further decreasing the domain size, indicating that the non- 180° domain walls observed in Figs. 1(d)–1(f) were not 90° domain walls. The optimum poling conditions for achieving various domain sizes, including the poling temperature and applied electric field, were summarized in Table I. It was found that higher poling temperatures favor smaller domain size at similar poling field, however, the domain size increases when poling temperature further increase to 240°C , far above the Curie temperature of the studied PIN-PMN-PT crystals ($\sim 210^\circ\text{C}$).

B. Domain size effect

The piezoelectric coefficients ($d_{33(\text{meter})}$, d_{33}^* , and $d_{33(\text{cal.})}$) for [111]-poled tetragonal PIN-PMN-PT crystals as a function of domain sizes are shown in Fig. 2. The piezoelectric coefficient $d_{33(\text{meter})}$ was found to be similar with the high field d_{33}^* , both much higher than the $d_{33(\text{cal.})}$, calculated based on IEEE

FIG. 1. (Color online) (a) PIN-PMN-PT crystal sample for domain observation and electrical property measurement; domain structure of PIN-PMN-PT crystals with various domain sizes: (b) $50 \mu\text{m}$, (c) $20 \mu\text{m}$, (d) $5 \mu\text{m}$, (e) $2 \mu\text{m}$, (f) 500 nm .

TABLE I. Dielectric, piezoelectric, and ferroelectric properties of [111]-poled tetragonal PIN-PMN-PT crystals with various domain sizes.

Domain size (μm)	Poling Temp. ($^{\circ}\text{C}$)/ E-field (kV/cm)	$\epsilon_{33}^T/\epsilon_0$	$\tan\delta(\%)$	$s_{33}^E(\text{pm}^2/\text{N})$	$k_{33}(\%)$	$d_{33(\text{Cal.})}(\text{pC/N})$	Q	$d_{33(\text{meter})}(\text{pC/N})$	$d_{33}^*(\text{pm/V})$
50	150/4	3000	0.4	10.71	72.8	390	360	450	480
20	180/3.5	5900	0.5	11.38	74.4	570	280	610	700
5	200/3.5	7700	0.5	11.84	75.4	680	220	1120	1100
2	205/4	11300	0.6	12.80	77.4	880	170	1290	1260
0.5	210/4	13800	0.7	14.73	80.5	1080	130	1630	1590
0.4	210/4 ^a	13800	0.7	14.81	80.6	1080	/	1630	/

^aSlow cooling down.

standard. The detail results of PIN-PMN-PT crystals with various domain sizes were listed in Table I. In order to fitting the experimental data of $d_{33(\text{meter})}$ versus domain size, exponential decay function was used. The relationship between $d_{33(\text{meter})}$ and domain size follow the formula:

$$d_{33} = 450 + 1180 \times \exp(-W_d/11), \quad (4)$$

where W_d is defined as domain size. According to the formula, the d_{33} was significantly increased as the domain size decreased from 70 μm to 500 nm, while maintaining same piezoelectric properties with further decreasing the domain size.

The impedance and phase characteristics of the longitudinal bar samples with domain sizes of 50 μm and 500 nm are given in Fig. 3, respectively. The phase angle between the resonance frequency (f_r) and antiresonance frequency (f_a) was close to $+90^{\circ}$, indicating complete poling treatment for the domain wall engineered PIN-PMN-PT crystals.² Based on the measured f_r and f_a , the electromechanical coupling factor (k_{33}), elastic compliance (s_{33}^E), piezoelectric coefficient ($d_{33(\text{cal.})}$), and mechanical Q were calculated and listed in Table I. All piezoelectric-related coefficients were found to increase with decreasing domain size, where the PIN-PMN-PT crystal with domain size of 500 nm exhibited the highest piezoelectric coefficient ($d_{33(\text{Cal.})} = 1080$), with electromechanical coupling factor (k_{33}) and dielectric permittivity ($\epsilon_{33}^T/\epsilon_0$) being on the order of 80.5% and

13 800, respectively. The ferroelectric properties, such as remnant polarization (P_r) and coercive field (E_c), were found to be insensitive to the domain size, being on the order of $32.5 \mu\text{C}/\text{cm}^2$ and 8.6 kV/cm, respectively, as shown in Fig. 4. The dielectric loss and mechanical loss (inverse of mechanical quality factor Q) were both found to increase with decreasing domain size, due to the higher domain wall density.

The high-field piezoelectric behavior for the domain wall engineered PIN-PMN-PT single crystals with various domains sizes were given in Fig. 5. The high field d_{33}^* was found to increase significantly with decreasing domain size, with the values being on the order of 480, 1100, and 1590 pm/V for the samples with domain sizes of 50 μm , 5 μm , and 500 nm, respectively.

Strain hysteresis was calculated from equation:¹⁷

$$\text{Strain Hysteresis } (\%) = \frac{\Delta S}{S_{\text{max}}} \times 100\%, \quad (5)$$

where S_{max} is the maximum strain and ΔS is the strain deviation during the rise and fall of the field at half of the maximum electric field. As shown in Fig. 5, the strain hysteresis was increased from 6% to 19% with decreasing domain size, implying that the extrinsic domain wall contribution to the piezoelectric response increased with domain size decrease.

FIG. 2. (Color online) The piezoelectric coefficients $d_{33(\text{meter})}$, d_{33}^* , and $d_{33(\text{cal.})}$, as a function of domain size in [111]-oriented tetragonal PIN-PMN-PT crystals.

FIG. 3. Frequency dependence of impedance and phase for longitudinal mode [111]-poled tetragonal PIN-PMN-PT crystals with domain sizes of 50 μm and 500 nm.

FIG. 4. Polarization versus electric field (P-E) for [111]-oriented tetragonal PIN-PMN-PT crystals with domain sizes of 50 μm and 500 nm.

C. Domain wall contribution

From Table I, the piezoelectric coefficient $d_{33(\text{meter})}$ was similar to the high field d_{33}^* value, but much higher than the calculated $d_{33(\text{cal.})}$. In order to interpret the discrepancy of the d_{33}^* and $d_{33(\text{cal.})}$, Rayleigh analysis was carried out. Fig. 6(a) shows the ac field dependent $d_{33}(E_0)$ for [111]-poled PIN-PMN-PT crystals with various domain sizes. By fitting Eq. (2), the values of d_{init} and α were found to be on the order of 1110 pC/N and 480 cm/kV for samples with domain size of 500 nm, respectively, indicating that the extrinsic contribution (irreversible domain wall motion) to the piezoelectric response was about 30%. Following this procedure, the ratio of extrinsic contribution to the total piezoelectric response for [111]-oriented PIN-PMN-PT crystals with domain sizes of 50 μm , 20 μm , 5 μm , and 2 μm , were calculated, and shown in Fig. 6(b). The extrinsic contribution was found to be 8% for samples with domain size of 50 μm , increasing to 30% for samples with smaller domains. Of par-

FIG. 6. (Color online) (a) The ac electric field dependent piezoelectric coefficient d_{33} for [111]-oriented tetragonal PIN-PMN-PT crystals with various domain size, (b) the level of extrinsic contribution to piezoelectric response at $E_0 = 1$ kV/cm for [111]-oriented tetragonal PIN-PMN-PT crystals with various domain sizes.

ticular interest, small signal $d_{33(\text{Cal.})}$ values were lower than the high field d_{33}^* , but similar to the d_{init} values analyzed by Rayleigh approach. Thus, it can be concluded that the extrinsic contribution (non-180° domain wall motion) increased with decreasing domain size, revealing that the irreversible domain wall motion is the dominant factor for the enhanced piezoelectric properties.

It is well accepted that the piezoelectric effect observed in the perovskite-based ferroelectrics originates from the electrostrictive effect,^{18,19} which can be expressed as

$$d_{33} = 2Q_{33}\epsilon_{33}^T P_s, \quad (6)$$

where Q_{33} is the electrostrictive coefficient, ϵ_{33}^T and P_s are dielectric permittivity and polarization of the crystal, respectively. In this study, it was presumed that the Q_{33} and P_s maintained the same values. As summarized in Table I, the d_{33} was 1630 pC/N in samples with domain size < 500 nm, three times of the value for crystals with domain sizes of $\sim 50 \mu\text{m}$. Thus, the ϵ_{33}^T calculated from Eq. (6) was 10 900 for samples with domain size of 500 nm; which was far below the experimental measured data, being $\sim 13\,800$. In general, non-180° domains contribute to the dielectric and piezoelectric response, while only the 180° domains contribute to the dielectric response.^{20,21} Base on this fact, the

FIG. 5. Unipolar strain for [111]-oriented tetragonal PIN-PMN-PT crystals with domain sizes of 50 μm , 5 μm , and 500 nm.

enhanced dielectric permittivity may be partially induced by the 180° domain walls motion, though there was no evidence of 180° domain wall variation, as observed in Fig. 1.

From previous work, increased 90° ferroelectric/ferroelastic domain wall density was considered to be the main factor for the enhanced piezoelectric property in domain wall engineered BaTiO₃ single crystals.² The simulation in the framework of Ginzburg-Landau-Devonshire theory also suggested that the high density of 90° twin domain boundaries account for the improved piezoelectric coefficients.²² In present work, both 180° and non- 180° domain walls were thought to contribute to the enhanced dielectric property, while non- 180° domain walls were associated with the enhanced piezoelectric property.

D. Domain size stability

Field and temperature stabilities are important for practical transducer applications, thus it is interesting to understand the domain stability in the crystals with fine domain structure. The field stability of the engineered domain wall in tetragonal PIN-PMN-PT crystals was further investigated by observing the domain structure and measuring electrical properties as a function of the pulse-field/cycle. For samples with domain size of $50\ \mu\text{m}$, no domain variation was observed after 7×10^5 pulse cycles with amplitudes of 4 kV/cm and 8 kV/cm, respectively, as summarized in Table II. For samples with domain size of $5\ \mu\text{m}$, there was no difference in the domain size, after 7×10^5 and 1.5×10^6 pulse cycles with amplitudes of 8 kV/cm. For samples with domain size $< 500\ \text{nm}$, no noticeable change in domain size was observed after 3.5×10^5 pulse cycles with amplitude of 4 kV/cm, while slightly increase to $1\ \mu\text{m}$ after 7×10^5 pulse cycles, as shown in Fig. 7(a). Fig. 7(b) shows the change of domain size with pulse at higher electric field of 8 kV/cm, where the domain size increased to $3\sim 5\ \mu\text{m}$. The domain size further increased to $10\sim 20\ \mu\text{m}$, with cycles up to 1.5×10^6 , as shown in Fig. 7(c), indicating that the 180° domains were reversed with some of the non- 180° domain walls disappeared, due to the nucleation and growth of new domains with increasing the number of pulses at electric field of 8 kV/cm ($\sim E_C$).

The temperature stability of dielectric permittivity $\epsilon_{33}^T/\epsilon_0$, electromechanical coupling factor (k_{33}), and piezoelectric coefficient ($d_{33(\text{cal.})}$) for the domain wall engineered

TABLE II. Domain size as a function of pulse field and number of pulse cycles in domain wall engineered [111]-oriented tetragonal PIN-PMN-PT crystals (the pulse duration is 5 ns).

Engineered domain size -before pulsing (μm)	Pulse-field (kV/cm)	Pulse cycles	Domain size-after pulsing (μm)
50	4	7.0×10^5	50
50	8	7.0×10^5	50
5	8	7.0×10^5	5
5	8	1.5×10^6	5
0.5	4	3.5×10^5	0.5
0.5	4	7.0×10^5	~ 1
0.5	8	7.0×10^5	$3\sim 5$
0.5	8	1.5×10^6	$10\sim 20$

FIG. 7. Domain structure of PIN-PMN-PT crystals observed under various pulse conditions: (a) at 4 kV/cm after 7×10^5 cycles, (b) at 8 kV/cm after 7×10^5 cycles, and (c) at 8 kV/cm after 1.5×10^6 cycles.

tetragonal PIN-PMN-PT crystals, with domain sizes of $50\ \mu\text{m}$, $5\ \mu\text{m}$, and $500\ \text{nm}$ are shown in Fig. 8. For samples with domain size of $50\ \mu\text{m}$, the values of $\epsilon_{33}^T/\epsilon_0$ and k_{33} were found to maintain the same orders with increasing temperature, as shown in Figs. 8(a) and 8(b), while the $d_{33(\text{cal.})}$ value increased slightly to 610 pC/N at 105°C , as shown in Fig. 8(c). The same phenomena were also observed for samples with domain size of $5\ \mu\text{m}$, but with much higher properties. For samples with smaller domain size $< 500\ \text{nm}$, however, the $\epsilon_{33}^T/\epsilon_0$, k_{33} , and $d_{33(\text{cal.})}$ were found to decrease drastically with temperature above 55°C , due to the increased domain size at

FIG. 8. The temperature dependent (a) dielectric permittivity (ϵ_{33}^T), (b) electromechanical coupling factor (k_{33}), and (c) piezoelectric coefficient ($d_{33(\text{cal.})}$) in domain engineered PIN-PMN-PT crystals with domain sizes of 50 μm , 5 μm , and 500 nm.

elevated temperature. Thus, the engineered domain structures with fine domain size of less than 500 nm show instable characteristics with electric field and temperature, while samples with domain size being on the order of $\geq 5 \mu\text{m}$ exhibit high stability associated with the drive field and temperature, which may relate to the free energy of the domain wall, further investigations on the mechanism of the evolution of domain wall under various external conditions are underway by high resolution X-ray analysis.

IV. CONCLUSION

The effect of domain size in domain wall engineered [111]-oriented tetragonal PIN-PMN-PT crystal was investigated. It was found that the piezoelectric coefficient ($d_{33(\text{meter})}$) and dielectric permittivity ($\epsilon_{33}^T/\epsilon_0$) increased significantly from 450 pC/N and 3000 to 1630 pC/N and 13 800, as the domain size decreased from 50 μm to 500 nm, respectively. Rayleigh analysis revealed that the irreversible domain wall motion (extrinsic contribution) plays an important role in the enhancement of the dielectric and piezoelectric properties.

The fine domain size ($\sim 500 \text{ nm}$) was found to increase under pulse field and thermal tests, giving rise to the deteriorated dielectric and piezoelectric properties, while samples with domain size being on the order of $\geq 5 \mu\text{m}$ showing improved field and thermal stabilities, with yet high dielectric and piezoelectric properties.

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