

Piezoelectric activity of relaxor-PbTiO₃ based single crystals and polycrystalline ceramics at cryogenic temperatures: Intrinsic and extrinsic contributions

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(Received 3 April 2010; accepted 24 April 2010; published online 13 May 2010)

The piezoelectric activity in [001] poled Pb(In_{1/2}Nb_{1/2})O₃-Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ crystals was investigated as a function of composition and temperature. The level of intrinsic and/or extrinsic contribution to the total piezoelectric activity was analyzed using Rayleigh method. The results revealed that though 95% of the observed piezoelectric activity in rhombohedral crystals was intrinsic (lattice), the properties decreased significantly with decreasing temperature. At -150 °C, the piezoelectric response decreased by 40%–55% for the compositions close to a morphotropic phase boundary (rhombohedral-monoclinic or monoclinic-tetragonal), while decreasing only 20%–30% for the compositions in the rhombohedral region. The piezoelectric properties of Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ polycrystalline ceramics were found to decrease by 75%, showing both intrinsic and extrinsic contributions play important role in the reduction in piezoelectricity at cryogenic temperatures for ceramics. © 2010 American Institute of Physics.

[doi:10.1063/1.3430059]

Relaxor-PbTiO₃ (PT) based crystals, such as (1-x)Pb(Zn_{1/3}Nb_{2/3})O₃-xPbTiO₃ and (1-x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃ (PMN-PT), have attracted significant attention owing to their high piezoelectric activity ($d_{33} > 1500$ pC/N) along the [001] crystallographic direction.¹ In addition to high piezoelectric activity, rhombohedral ternary Pb(In_{1/2}Nb_{1/2})O₃-Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PIN-PMN-PT) crystals have been studied,^{2–4} offering expanded temperature usage range, >30 °C higher than that of commercial PMN-PT binary crystals. The ultrahigh piezoelectric activity in domain engineered relaxor-based crystals is believed to be primarily intrinsic (lattice) in nature. Two underlying intrinsic mechanisms, including “polarization rotation” (Ref. 5) and “high piezoelectric anisotropy ($d_{15}/d_{33} \gg 1$)”,⁶ have been proposed as the origin of the high piezoelectric activity. Actually, an “easy” polarization rotation is directly related to the high piezoelectric anisotropy.⁷ Investigations of polycrystalline ceramics and single crystals at cryogenic temperatures^{8–13} revealed a high reduction in piezoelectric response, being attributed to the clamping of domain wall motion and/or mobility,^{8,9} reflecting a high level of extrinsic contribution in ceramics/crystals. However, based on a recent investigation,¹⁴ the extrinsic contribution was found to be less than 10% of the total piezoelectric response across the compositional range of $0.25 < x < 0.35$ in (1-x)PMN-xPT crystals, owing to the stable domain engineered structure. Thus, it was deemed important to further investigate the intrinsic and extrinsic contributions to the piezoelectric response in relaxor-PT based crystals as a function of decreasing temperature.

Rayleigh law has been used to study the degree of intrinsic/extrinsic contribution to dielectric and piezoelectric

activity in ferroelectric crystals and ceramics.^{15,16} In the present study, the Rayleigh analysis was used to delineate the level of the intrinsic and extrinsic contributions to piezoelectric activity in PIN-PMN-PT crystals from room temperature to -150 °C. To provide a contrast to crystals, a relaxor-PT based polycrystalline ceramic was also investigated.

PIN-PMN-PT single crystals investigated in this study were grown along their crystallographic [001] direction using the modified Bridgman technique. Analogous to the binary systems (1-x)PMN-xPT and (1-x)PZN-xPT,¹⁷ a schematic phase diagram of the ternary composition PIN-PMN-PT system studied in this work is depicted in Fig. 1, where C, R, M, and T represent cubic, rhombohedral, monoclinic, and tetragonal phases, respectively. At room temperature, the PT content of the R-M and M-T phase boundaries were found to be 0.31 and 0.35, respectively. The composition and phase of the studied crystals were inferred by temperature-dependent-dielectric and electric-field-induced-strain behavior, and symbolized as R-I, R-II, R-III, and M-IV.

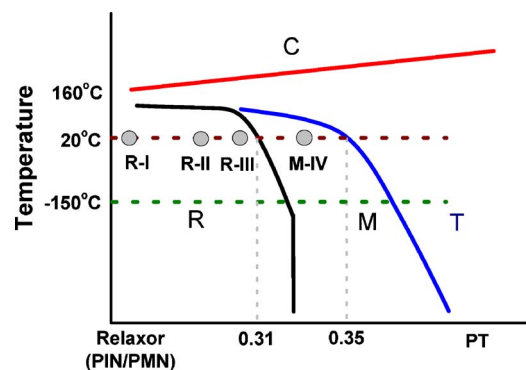


FIG. 1. (Color online) Schematic phase diagram for PIN-PMN-PT crystals, compositions studied in this work were labeled as R-I, R-II, R-III, and M-IV.

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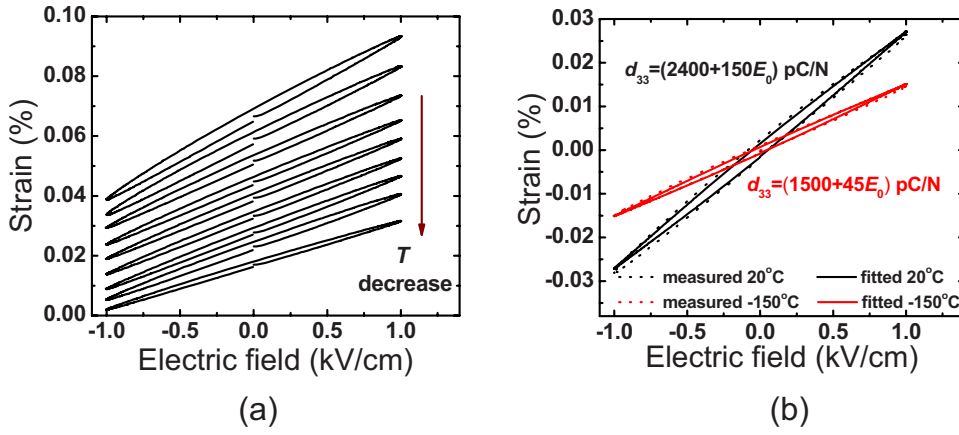


FIG. 2. (Color online) (a) Strain vs electric field loops for PIN-PMN-PT crystals with composition R-III, at various temperatures (20, 0, -20, -40, -60, -80, -100, -130, and -150 °C); (b) the fitted results at 20 °C and -150 °C, respectively.

M-IV. The crystals were oriented by real-time Laue and cut to obtain longitudinal rods with dimensions of $2 \times 2 \times 8$ mm³ for Rayleigh analysis. All the crystal samples were poled by applying a dc electric field of 15 kV/cm at room temperature, while PMN-PT polycrystalline ceramic samples were poled at 25 kV/cm. The electric-field-induced strain was measured at 1 kV/cm and 1 Hz frequency, using a linear variable differential transducer driven by a lock-in amplifier (Stanford Research system, Model SR830), connected to a temperature chamber (Delta Design 2300).

For the case of the converse piezoelectric response, the Rayleigh law can be expressed using the following formulae:¹⁸

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

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

where $S(E)$ is the electric-field-induced strain and E_0 is the level of applied electric field. The coefficient “ d_{init} ” describes the reversible piezoelectric response, including intrinsic contribution and the contribution from reversible displacement of internal interfaces.^{15,18} The latter one was related to the reversible domain wall motion in ferroelectric ceramics. However, in [001] poled domain engineered crystals, the contribution of domain wall motion is minimal due to the four energetically equivalent domains and stable domain configuration. In this investigation, therefore, the measured coefficient d_{init} is considered to arise from an intrinsic contribution. The coefficient “ α ” is the irreversible Rayleigh parameter, resulting from the irreversible motion of internal interfaces (e.g., domain wall, phase boundaries), and αE_0 represents the extrinsic contribution to the total piezoelectric response. Equation (1) describes the Rayleigh hysteresis, where the signs “+” and “-” correspond to decreasing and

increasing electric fields, respectively. The Rayleigh parameters d_{init} and α can be obtained by fitting Eq. (1).

As an example, Fig. 2(a) shows the strain versus electric field (S-E) loops at temperatures from 20 to -150 °C for the [001] poled crystals with composition R-III. Using the Rayleigh law, Fig. 2(b) exhibits the good fitted results to the experimental data measured at room temperature and cryogenic temperature of -150 °C.

Table I presents a summary of the piezoelectric activity of PIN-PMN-PT crystals and PMN-PT ceramics at 20 and -150 °C. At room temperature, the maximum intrinsic piezoelectric response was found in PIN-PMN-PT crystals with composition R-III. In the rhombohedral phase region, the intrinsic piezoelectric response decreased for compositions being relative far from the R-M phase boundary. As expected, the parameter α was relatively small for crystals with compositions R-I (55 cm/kV) and R-II (67 cm/kV) when compared to PMN-PT ceramics (~ 280 cm/kV), due to a lack of domain wall motion in the stable domain engineered configuration (“4R”). The value of α in PIN-PMN-PT crystals was found to be relatively high for the compositions R-III (~ 150 cm/kV) and M-IV (~ 280 cm/kV), lying close to the morphotropic phase boundaries (R-M/M-T). The high level of α at compositions close to the phase boundaries is a consequence of phase boundary motion. Phases at morphotropic phase boundaries (MPB) are energetically similar and easy to transform into one another when an electric/stress field is applied, subsequently contributing to the extrinsic piezoelectric activity αE_0 .

The temperature dependent d_{init} and α values obtained for PIN-PMN-PT crystals and PMN-PT ceramics are summarized in Fig. 3(a). As expected, both parameters d_{init} and α decreased with decreasing temperature for all compositions.

TABLE I. The phase transition temperature and piezoelectric response of studied crystals and polycrystalline ceramics.

Material	T_c (°C)	$T_{R(M)-T}$ (°C)	d_{init}		α (cm/kV)		$\alpha E_0 + d_{\text{init}}$		$d_{\text{init}}/(\alpha E_0 + d_{\text{init}})$	
			20 °C	-150 °C	20 °C	-150 °C	20 °C	-150 °C	20 °C	-150 °C
R-I	155	125	1080	860	55	25	1135	885	95	97
R-II	180	115	1700	1250	67	32	1767	1282	96	97.5
R-III	185	100	2400	1520	150	45	2550	1565	94	97
M-IV	195	55	1500	800	280	40	1780	840	85	95
Ceramic	165	...	750	220	285	42	1035	262	65	85

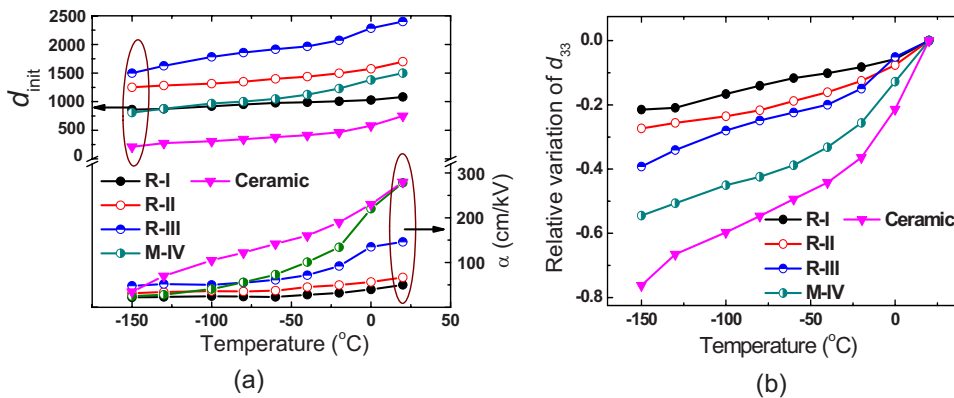


FIG. 3. (Color online) (a) The temperature dependent Rayleigh parameters; (b) relative variation in d_{33} as a function of temperature for [001] poled PIN-PMN-PT crystals and PMN-PT ceramics.

Based on thermodynamic analysis, the shear piezoelectric response (d_{15} or d_{24}) of rhombohedral/monoclinic single domain state will decrease as the testing temperature moves away from the ferroelectric-ferroelectric phase transition temperature ($T_{\text{F-F}}$).^{19,20} The reduction in shear piezoelectric response corresponds to an effective “hardening” of the polarization rotation process.⁷ Thus, the less polarization rotation contribution to the intrinsic piezoelectric activity in domain engineered crystals results in reduced piezoelectricity as the temperature shifts downward from $T_{\text{F-F}}$. The extrinsic contribution αE_0 in domain engineered crystals is believed to be related to an electric field induced phase transition (phase boundary motion).¹⁴ Therefore, as the temperature shifts downward from $T_{\text{F-F}}$, the motion of phase boundary becomes “frozen,” leading to a decrease in the extrinsic parameter α . For PMN-PT ceramics, the parameter α drastically decreased from 280 to 40 cm/kV as the temperature decreased from 20 to -150°C , a result of domain wall motion clamping.^{8,9} Of particular interest is that the α values for both crystals and ceramics were found to be on the same order at -150°C , revealing minimal extrinsic contribution, which can be confirmed by the high intrinsic contribution, $d_{\text{init}}/(\alpha E_0 + d_{\text{init}})$, being on the order of 85%–97%, as listed in Table I.

Figure 3(b) shows the relative variation in piezoelectric response, $[d_{33}(T) - d_{33}(20^{\circ}\text{C})]/d_{33}(20^{\circ}\text{C})$, as a function of temperature. At -150°C , the piezoelectric response was found to decrease by 20%, 30%, 40%, and 55% for PIN-PMN-PT crystals with compositions R-I, R-II, R-III, and M-IV, respectively. The PMN-PT ceramic exhibited the largest decrease, $\sim 75\%$ of the original value. For the rhombohedral PIN-PMN-PT crystals, as the composition approached the R-M phase boundary, the crystals became “softer” and the piezoelectric activity increase, and subsequently the temperature instability also increased.

In summary, the piezoelectric activity of relaxor-PT based crystals and ceramics was investigated from room temperature to -150°C using the Rayleigh analysis. For [001] poled PIN-PMN-PT crystals, the decrease in piezoelectric activity at cryogenic temperatures was observed for rhombohedral to monoclinic compositions. The decrease in piezoelectric activity was mainly attributed to the reduction of the intrinsic piezoelectric response as the temperature moves away from the $T_{\text{F-F}}$. For PMN-PT ceramics, the decreased piezoelectric activity observed at cryogenic temperature, was related both intrinsic (lattice) and extrinsic (domain clamping

effects) contributions. From an application viewpoint, PIN-PMN-PT crystals with compositions far away from the R-M phase boundary (R-I and R-II) offer excellent potential applications at cryogenic temperatures, with high temperature stability and yet high piezoelectric activity at -150°C , being four to five times larger than that of PMN-PT ceramics.

The authors from Xi’an Jiaotong University acknowledged the National basic research program of China under Grant No. 2009CB623306 and the National Natural Science foundation of China under Grant Nos. 50632030 and 10976022. The work supported by NIH under Grant No. P41-EB21820 and ONR under Grant Nos. N00014-09-1-01456 and N-00014-07-C-0858.

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