Temperature independent shear piezoelectric response in relaxor-PbTiO$_3$ based crystals

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The temperature dependence of the shear piezoelectric responses in relaxor-PbTiO$_3$ based perovskite crystals with rhombohedral, orthorhombic, and tetragonal phases were investigated. Based on thermodynamic analysis, high shear piezoelectric coefficients (d_{24}) and good thermal stability were predicted in orthorhombic crystals, owing to the "*vertical*" orthorhombic-rhombohedral phase boundary. By resonance measurements, shear piezoelectric coefficient d_{24} was found to be on the order of $\sim$2100 pC/N at room temperature, maintaining same value over the temperature range of -50–100 °C. In contrast, the shear piezoelectric coefficients d_{15}, with values of 3300, 3600, and 2000 pC/N at room temperature for rhombohedral, orthorhombic, and tetragonal crystals, respectively, exhibited strong temperature dependent behavior due to their respective ferroelectric-ferroelectric phase transitions. © *2010 American Institute of Physics*. [doi:10.1063/1.3529952]

Relaxor-PbTiO$_3$ (PT) based ferroelectric single crystals, such as $(1-x)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ (PMN-PT) and Pb(In$_{1/2}$Nb$_{1/2}$)O$_3$−Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$−PbTiO$_3$ (PIN-PMN-PT) have attracted much interest due to their superior electromechanical coupling factors ($k_{33}>90\%$) and piezoelectric coefficients ($d_{33}>1500$ pC/N) along the [001] crystallographic direction.[1] The ultrahigh piezoelectric coefficient d_{33} in domain engineered relaxor-PT crystals is believed to be associated with the high level of shear piezoelectric response (d_{15}/d_{24}),[2] being >3000 pC/N (Refs. 3–6) for rhombohedral crystals, and >2000 pC/N for tetragonal crystals.[7] Furthermore, the high shear piezoelectric coefficients make relaxor-PT crystals promising candidates for various applications, such as vector sensors, nondestructive evaluation transducers, and low frequency sonar transducers. For most electromechanical devices that required operation in the temperature range of -50 °C–100 °C, a stable piezoelectric behavior is desired. Thus, it is of particular importance to investigate the temperature dependent shear piezoelectric behavior.

In general, the dielectric and piezoelectric responses of relaxor-PT ferroelectric crystals exhibit relatively large temperature variation,[7–9] owing to multiple ferroelectric-ferroelectric phase transitions lying in or near the temperature range of -50 °C–100 °C. Based on thermodynamic analysis of pervoskite single crystals,[10] the temperature dependence of the shear piezoelectric response is strongly related to the ferroelectric-ferroelectric phase transitions, at which the shear piezoelectric coefficients exhibit maximum values. The aim of this work is to develop a fundamental approach, to explore temperature independent shear response in relaxor-PT crystals over a broad operating temperature range.

The PIN-PMN-PT and PMN-PT crystals were grown using modified Bridgman method. The compositions of studied orthorhombic crystals were marked in Fig. 1 by four-point star. The details of studied rhombohedral and tetragonal PIN-PMN-PT crystals were described in Ref. 9 (part B crystals) and Ref. 7, respectively. Studied crystals were oriented by real-time Laue x-ray. All the samples were electroded by vacuum sputtered gold on the polished side faces, and then poled by applying the dc electric field of 10–15 kV/cm. Subsequently, the electrodes were removed and re-electroded on the large surfaces. The shear electromechanical couplings and piezoelectric coefficients were determined by resonance method, following IEEE standard,[11] using HP4294 impedance analyzer. The samples were put in a specially designed sample holder in furnace, connected to the measurement equipments for the high temperature studies.

A schematic phase diagram for relaxor-PT crystals is shown in Fig. 1.[12,13] The temperature dependence of the shear piezoelectric properties for crystals with various phases, as shown in Fig. 1, is analyzed in the following section. The symmetry of the rhombohedral, orthorhombic, and tetragonal phase are 3 m (only one independent shear coef-
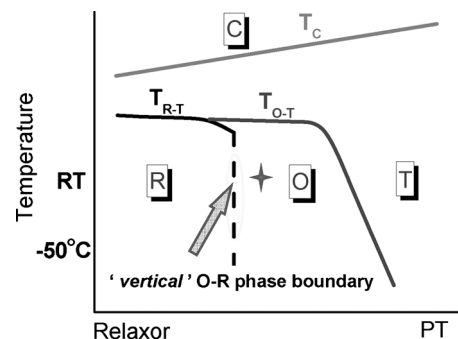

FIG. 1. Schematic phase diagram for relaxor-PT based crystals, where R, O, and T represent rhombohedral, orthorhombic/monoclinic (M_C), and tetragonal phase regions. The monoclinic (M_C) phase was found to be a slightly distorted orthorhombic phase (e.g., see Refs. 12 and 13). Thus, after poled along [011] direction, it was proper to consider the M_C phase as a quasi-orthorhombic phase.
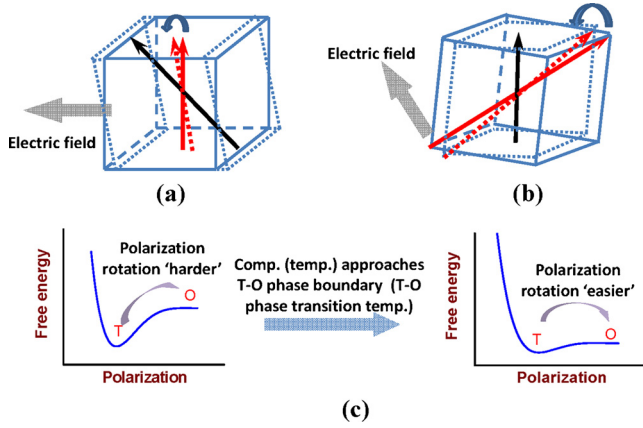
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FIG. 2. (Color online) Polarization rotation and related shear piezoelectric deformation for (a) tetragonal crystals and (b) rhombohedral crystals under electric field perpendicular to spontaneous polarization direction. The solid red arrows represent the spontaneous polarization for rhombohedral and tetragonal phases, respectively. The dotted red arrows represent the spontaneous polarization under perpendicular electric field. The solid black arrows represent the $[011]_C$ and $[001]_C$ directions in (a) and (b), respectively, in order to indicate the polarization rotation path. (c) Free energy profile for tetragonal crystals, where free energy profile is flattened with temperature approaching T-O phase boundary, corresponding to an easier polarization rotation.
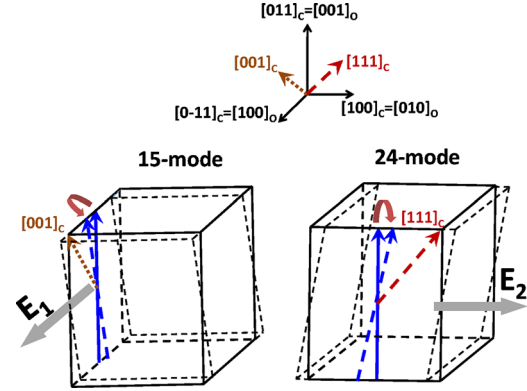

FIG. 3. (Color online) Two independent shear piezoelectric responses (15- and 24-mode) and related polarization rotation paths in orthorhombic crystals, where the solid and dotted blue arrows represent the polarization rotation process under perpendicular electric field. The coordinate system of orthorhombic crystal is presented on the top of the figure. The principle axis of orthorhombic phase are notated as $[001]_O$, $[010]_O$, and $[100]_O$, being equal to $[011]_C$, $[0-11]_C$, and $[100]_C$ cubic axis, respectively.

ficient, $d_{15}=d_{24}$), mm2 (two independent shear coefficients, $d_{15} \neq d_{24}$) and 4 mm (only one independent shear coefficient $d_{15}=d_{24}$), respectively.

According to thermodynamic theory,[14] it is known that the shear piezoelectric coefficient is proportional to the transverse dielectric permittivity, spontaneous polarization, and electrostrictive coefficient, as given in Eq. (1)

$$d_{15} \propto \varepsilon_0 \varepsilon Q P, \qquad (1)$$

where P is the spontaneous polarization, Q the electrostrictive constant, and ε the transverse dielectric permittivity. Regardless of the phase transition(s), the variation of spontaneous polarization and electrostrictive coefficient with temperature can be neglected in contrast to the dielectric permittivity.[10,14,15] Thus, the variation of the piezoelectric coefficient is mainly attributed to the change in dielectric permittivity, as reported in previous investigations.[7–9] For pervoskite ferroelectric single crystals, the transverse dielectric response arises from a polarization rotation process, as depicted in Figs. 2(a) and 2(b). According to the analysis in Ref. 15, an "easier" polarization rotation process corresponds to a "higher" level of transverse dielectric permittivity and thus high shear piezoelectric coefficient.

For tetragonal crystals, as shown in Fig. 2(a), the polarization vector rotates within the path of $[001]_C \rightarrow [011]_C$, as the electric field applied perpendicular to the spontaneous polarization. This rotation process gives rise to crystal symmetry deviating from 4 mm (tetragonal phase) to mm2 (orthorhombic phase). As the crystal composition approaches tetragonal-orthorhombic (T-O) phase boundary from tetragonal side (or the temperature close to T-O phase transition temperature), the polarization rotation process from $[001]_C$ to $[011]_C$ direction becomes easier due to a flatting of the free energy profile.[16] Consequently, the shear piezoelectric response will increase as depicted in Fig. 2(c). Based on the above analysis, the shear piezoelectric response for relaxor-PT based tetragonal crystals will not be temperature independent, owing to the existence of a T-O phase transition

below room temperature. Similarly, for rhombohedral crystals, upon applying the perpendicular electric field, the spontaneous polarization could rotate within the path of $[111]_C \rightarrow [001]_C$, as shown in Fig. 2(b). This rotation process becomes easier as the temperature approaches the rhombohedral-tetragonal (R-T) phase transition temperature (T_{R-T}). As a result, the shear piezoelectric response for rhombohedral crystal is not expected to exhibit good temperature stability, owing to the existence of a R-T phase transition above room temperature.

For the orthorhombic phase, two independent shear piezoelectric coefficient d_{15} and d_{24} are presented in [011] poled crystals. As shown in Fig. 3, the polarization rotation paths of the piezoelectric 15- and 24-modes are $[011]_C \rightarrow [001]_C$ and $[011]_C \rightarrow [111]_C$, respectively. Analogous to the analysis for tetragonal and rhombohedral crystals, the shear piezoelectric coefficient d_{15} should increase as the temperature approaches the orthorhombic-tetragonal (O-T) phase transition temperature (T_{O-T}), while coefficient d_{24} should increase with the temperature close to orthorhombic-rhombohedral (O-R) phase transition temperature. Thus, a temperature independent shear coefficient d_{15} is not expected, due to an O-T phase transition which is above room temperature. Of significant importance to this study, a compositionally *"vertical" O-R phase boundary* exists in relaxor-PT based crystals, as shown in Fig. 1, indicating no O-R phase transition occurs as a function of temperature for orthorhombic crystals. Therefore, a temperature independent d_{24} can be expected in relaxor-PT crystals with orthorhombic phase. Furthermore, the composition of orthorhombic crystals should be selected near O-R phase boundary, in order to achieve relatively high level of shear coefficient d_{24}.

Based on the above hypothesis, the shear piezoelectric properties of relaxor-PT perovskite crystals were studied as a function of phase and temperature. The room temperature properties of PIN-PMN-PT and PMN-PT crystals were listed in Table I. High shear piezoelectric coefficients (>2000 pC/N) and electromechanical coupling factors ($>85\%$) were found for all single domain crystals, including rhombohedral "1R," orthorhombic "1O," and tetragonal crystals "1T," due to the easy polarization rotation in single domain relaxor-PT crystals with MPB compositions.

TABLE I. The room temperature properties of PIN-PMN-PT and PMN-PT single crystals, where 1O, 1R, and 1T represent orthorhombic, rhombohedral, and tetragonal single domain crystals, respectively.

Material	T_c (°C)	$T_{F\text{-}F}$ [a] (°C)	$\varepsilon_{11}^T/\varepsilon_0$	s_{55}^E (pm^2/N)	d_{15} (pC/N)	k_{15}	$\varepsilon_{22}^T/\varepsilon_0$	s_{44}^E (pm^2/N)	d_{24} (pC/N)	k_{24}
PIN-PMN-PT (1R)	165	125	6000	242	3300	0.92	$=\varepsilon_{11}^T/\varepsilon_0$	$=s_{55}^E$	$=d_{15}$	$=k_{15}$
PIN-PMN-PT (1T)	215	−50	13 000	52	2050	0.84	$=\varepsilon_{11}^T/\varepsilon_0$	$=s_{55}^E$	$=d_{15}$	$=k_{15}$
PIN-PMN-PT (1O)	195	105	5600	295	3600	0.94	15 000	46	2050	0.85
PMN-PT (1O)	145	85	5400	280	3450	0.94	18 000	42	2250	0.87

[a]$T_{F\text{-}F}$ presents $T_{R\text{-}T}$ for 1R; $T_{O\text{-}T}$ for 1T and 1O engineered domain configurations, respectively.

As mentioned above, it is the target of this research to explore the temperature stability for these high shear piezoelectric responses. Figure 4(a) showed the temperature dependence of shear piezoelectric coefficients for orthorhombic PIN-PMN-PT and PMN-PT crystals. As expected, the piezoelectric coefficients d_{24} were found to be nearly temperature independent, being on the order of 2000 pC/N for both PIN-PMN-PT and PMN-PT crystals over the temperature range from −50 °C to their respective O-T phase transition temperatures, being 105 and 85 °C. The coefficient d_{15} of orthorhombic PIN-PMN-PT crystals, however, was found to increase significantly with respect to temperature, being in the range of 2300–7000 pC/N upon increasing the temperature from −50 to 100 °C. For comparison, the temperature dependent shear piezoelectric response of rhombohedral and tetragonal PIN-PMN-PT crystals was measured and given in Fig. 4(b). It can be seen that the coefficient d_{15}, though high in the rhombohedral crystal ($\sim$3300 pC/N) and tetragonal crystal ($\sim$2050 pC/N) at room temperature, exhibited strong temperature dependent behaviors. As the temperature increased from −50 to 120 °C, the shear piezoelectric coef-

ficient d_{15} increased from 2600 to 8000 pC/N for rhombohedral PIN-PMN-PT crystals, while decreasing from 2700 to 1500 pC/N for the tetragonal crystals.

In summary, the shear piezoelectric coefficients of relaxor-PT based crystals were investigated as a function of the phase and temperature. Based on thermodynamic analysis and experimental measurements, nearly temperature independent shear piezoelectric response was expected and experimentally confirmed in relaxor-PT orthorhombic crystals, benefiting from the vertical R-O phase boundary. The present results indicated that the relaxor-PT based orthorhombic crystals should be a promising candidate for shear mode electromechanical devices where temperature stability is desired. In addition, an approach to obtain temperature independent piezoelectric response was proposed for pervoskite ferroelectric systems.
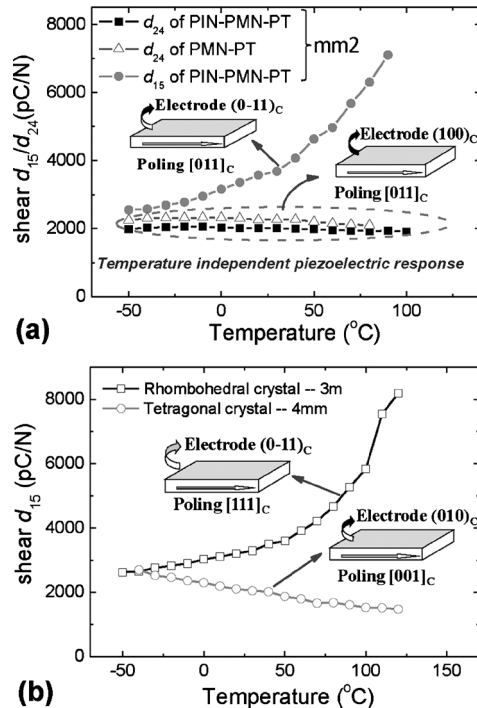
FIG. 4. The temperature dependence of shear piezoelectric coefficients for (a) orthorhombic relaxor-PT based crystals, and (b) rhombohedral and tetragonal PIN-PMN-PT crystals.

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