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Temperature dependence of the direct piezoelectric effect in relaxor-ferroelectric single crystals: Intrinsic and extrinsic contributions

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The direct piezoelectric response d_{33} of $[001]_C$-poled $0.955Pb(Zn_{1/3}Nb_{2/3})O_3-0.045PbTiO_3$ [PZN-4.5PT] and $0.98Pb(Zn_{1/3}Nb_{2/3})O_3-0.08PbTiO_3$ [PZN-8PT] has been investigated as a function of temperature upon heating above 40 °C to the paraelectric phase. Using a Rayleigh-law based analysis, it is shown that both the reversible/intrinsic and irreversible (extrinsic) contributions to the response increase in both compositions as the phase transition to a tetragonal phase is approached. The latter is likely due to an increased domain wall mobility close to the first order transition temperature, which also gives rise to an increased frequency dispersion. Large reversible direct piezoelectric responses $d_{33} > 1600 pm/V$ are observed for both compositions, which increase dramatically close to the transition temperature. Most importantly, the reversible contribution is always much larger than the irreversible part in the low temperature, domain-engineered phase, the latter accounting for around 20% of the response in PZN-8PT, at 40 °C, and 5% in PZN-4.5PT. The importance of this result to the validity of the adaptive phase model is discussed. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2358408]

I. INTRODUCTION

Relaxor-based ferroelectric single crystals, $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN-xPT) and $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PZN-xPT), remain the subject of much scientific interest. Rhombohedral, orthorhombic, or monoclinic[1] crystals of either material oriented and poled along the $[001]_C$ prototypic cubic direction exhibit attractive, anhysteretic, strain-field behaviors and "giant" piezoelectric strain coefficients $d_{33} > 2000 pm/V$.[2] Such converse piezoelectric properties make PZN-xPT and PMN-xPT very promising for next generation sensor and actuator technology.[3]

Directly relevant to the use of such crystals in sensor applications (especially in marine-based devices) is their *direct* piezoelectric response, that is, the generation of electrical charge D under applied stress σ. In an earlier article,[4] we reported measurements of the direct piezoelectric response of $[001]_C$-poled, domain-engineered PMN-32PT and PZN-4.5PT to dynamic stresses (at frequencies between 0.1 and 100 Hz) applied both along and perpendicular to the poling direction; such measurements are referred to as longitudinal d_{33} and transverse d_{31} modes, respectively, as shown in Fig. 1.

Importantly, for small dynamic stresses (<10 MPa) applied perpendicular to the poling direction, the transverse d_{31} response ($D_3 = d_{31}\sigma_1$) was found to be anhysteretic and linear. Such behavior is useful for sensors where hysteresis, meaning the measured response is not a single-valued function of applied pressure, is undesired. In contrast, the longitudinal d_{33} response ($D_3 = d_{33}\sigma_3$) was found to be hysteretic

and nonlinear at all stresses, behavior unexpected from the corresponding anhysteretic converse (strain-field) response[2] of such domain-engineered crystals. Moreover, d_{33} was found to be a quasilogarithmic or power law function of frequency,[5] similar to that observed in ceramic lead zirconate titanate (PZT) and barium titanate[6,7] where it is characteristic of domain wall motion.[6]

Furthermore, the longitudinal response was found to be adherent to the Rayleigh law (see Sec. II). Rayleigh-law behavior is characteristic of *pinned interface motion*; again, it is commonly observed in the direct piezoelectric response of polycrystalline ferroelectrics where ferroelastic switching is expected and these interfaces can be identified as non-180° domain walls.[7,8] However, at least in $[001]_C$-poled, domain-engineered rhombohedral crystals, ferroelastic switching is not expected when stress is applied along the poling direction.[4,9]

The origins of the hysteresis in the direct longitudinal piezoelectric response remain unclear. However, it has been postulated that the differing longitudinal and transverse re-
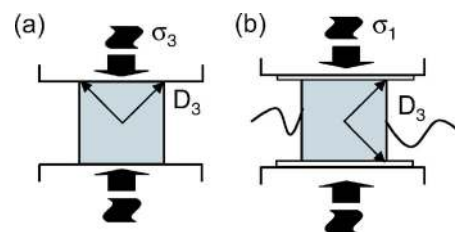

FIG. 1. Schematic drawing of the direct (charge-stress) piezoelectric measurements in (a) longitudinal and (b) transverse modes. The arrows represent the spontaneous polarization vectors of the constituent variants in the domain-engineered structure formed by poling a pseudorhombohedral or pseudo-orthorhombic crystal along $[001]_C$.

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sponses are due to differing directions of polarization rotation, the polar vectors in each domain variant of the polydomain structure rotating *toward* the poling direction in the transverse mode (and likewise in the unipolar converse effect) but *away* from the poling direction in the longitudinal mode.[4] The hysteretic response could also be due to a background stress-induced phase transition to an orthorhombic phase[9,10] as evidenced in static load-unload cycles.[10] Notably, in the transverse mode the crystal will remain domain engineered with respect to the poling direction throughout the change of phase; in the longitudinal mode, the domain-engineered structure is broken. Finally, it might be possible that the motion of other interfaces rather than domain walls, such as two-phase boundaries, is responsible for the behavior.[4]

Besides the hysteresis and nonlinearity discussed above for many applications it is also useful to know the *thermal stability* of a given piezoelectric material, i.e., the variation of its piezoelectric properties with temperature; this will be particularly true for sensor applications. In this article we will present measurements of the direct piezoelectric response of $[001]_C$-poled PZN-4.5PT and PZN-8PT in the longitudinal mode upon heating between 40 °C and the depoling temperature. The "extrinsic"[11] (from the irreversible motion of pinned interfaces) and "intrinsic" (or lattice) contributions to the response are separated quantitatively using a Rayleigh-law based analysis; the evolutions of both contributions through the phase transition to a high temperature tetragonal phase are described. Importantly, it will be shown that the intrinsic part accounts for the majority of the giant piezoelectric response of these crystals under applied stress; domain wall motion plays only a minor role.

To facilitate discussion of the results, $[001]_C$-poled PZN-4.5PT will be described as "pseudorhombohedral";[9,10,12] that is, it is assumed to be either rhombohedral or slightly distorted monoclinic[13] M_A at room temperature under zero applied field (although PZN-4.5PT is generally found to be rhombohedral[14,15]). It thus takes a $4R$ (Ref. [16]) (or $4M_A$) domain-engineered structure containing four degenerate, pseudorhombohedral domain variants, each with polar vectors equally inclined to the $[001]_C$ poling direction.[2] Similarly, $[001]_C$-poled PZN-8PT will be referred to as "psuedo-orthorhombic"[10] at room temperature, meaning either orthorhombic or slightly distorted monoclinic[13] M_C; both phases have been reported under zero field[14,17] and are often difficult to resolve.[1] Therefore, $[001]_C$-poled PZN-8PT is $4O$ (Ref. [16]) (or $4M_C$) domain engineered, again composed of four degenerate domain variants.

II. QUANTITATIVE DESCRIPTIONS OF NONLINEARITY

For piezoelectric materials obeying the Rayleigh law, the D-σ_{dy} charge density versus stress loop can be directly calculated from a simple relationship between d_{33} and the dynamic stress amplitude σ_0, and vice versa:[4,8]

$$d_{33} = d_0 + \alpha\sigma_0, \tag{1}$$

$$D = (d_0 + \alpha\sigma_0)\sigma_{dy} \pm \frac{\alpha}{2}(\sigma_{dy}^2 - \sigma_0^2), \tag{2}$$

where σ_{dy} is the applied (dynamic) stress.

Firstly, Eq. (1) constitutes a linear description of the stress dependence of d_{33}; α is thus a measure of nonlinearity. d_0 is the zero-field piezoelectric coefficient and describes the reversible component of d_{33}; this will include the *intrinsic* piezoelectric effect. Notably, for most ferroelectric materials, any *reversible extrinsic* component (e.g., the field independent contribution from domain wall motion) is small in comparison to the intrinsic component.[18] For the present purposes, therefore, the experimentally determined sum of the reversible extrinsic and intrinsic components d_0 can be considered equal to the intrinsic component. On the other hand, $d_{33} - d_0 = \alpha\sigma_0$ describes the irreversible part and is a purely *extrinsic* contribution.[8]

Secondly, Eq. (2) describes a hysteretic, and therefore lossy, charge-stress loop with a finite width (at $\sigma_{dy} = 0$) of $\Delta D = \alpha\sigma_0^2$.

Finally, the dependence of the piezoelectric coefficient upon the frequency f of the applied dynamic stress can be written as[5,8]

$$d_{33} = d_{33}^{(f=1\ \text{Hz})} - \gamma\log(f). \tag{3}$$

It is defined by two parameters, γ, again a measure of nonlinearity, and $d_{33}^{(f=1\ \text{Hz})}$, the coefficient measured at 1 Hz. Alternative descriptions of the frequency dispersion using a power law have also been discussed.[5]

III. EXPERIMENT

All measurements were made using the dynamic Berlincourt-type method well described elsewhere.[8,19] For all measurements, pressure is applied to the sample between two flat, well-aligned steel plates. Dynamic $[\sigma_{dy} = \sigma_0 \sin(2\pi f t)]$ and static (σ_{st}) pressures are applied to the sample by a PZT actuator and the resultant force on the sample is measured with a quartz sensor. A prestress (P) is first applied by a stepper motor to put the entire system in compression. Further details about the measurements are given in a previous article.[4] Notably, although the dynamic stress is a zero-centered function the system is never allowed to go into tension since the static component of stress ($P + \sigma_{st}$) is always greater than the dynamic one. The measured charge density is shown center shifted as a mathematical convenience.[4] The sample temperature was regulated using a small furnace.

$\langle 001 \rangle_C$-oriented single crystals of PZN-4.5PT and PZN-8PT were obtained from TRS Ceramics (State College, PA, U.S.A.) with nominal dimensions of $3 \times 3 \times 3$ mm^3. These sample dimensions were chosen to give a suitable aspect ratio for longitudinal d_{33} measurements in the press.[4,9,20] Gold electrodes were sputtered onto opposite 3×3 mm^2 surfaces and the crystals were poled by applying a small field (200 V/mm) while cooling from the cubic phase to room temperature. Samples were repoled between subsequent heating runs.
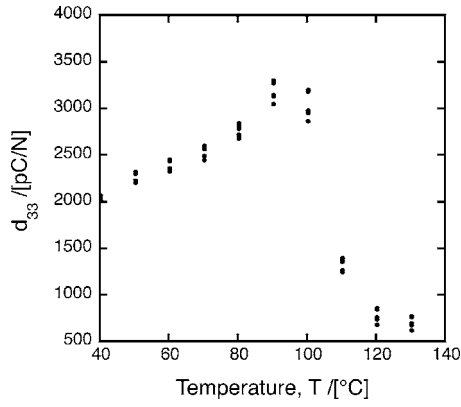
FIG. 2. d_{33} as a function of temperature for $[001]_C$-poled PZN-8PT measured upon heating at four frequencies: 1, 7, 10, and 50 Hz. Higher response is observed at lower frequency $[(P+\sigma_{st})=2$ MPa, $\sigma_0=0.5$ MPa].

Direct measurements similar to those reported previously[4] were made of the longitudinal response at temperatures between 40 and 200 °C, upon heating. The static stresses and dynamic stress amplitudes used for each measurement are marked in the figure captions.

IV. RESULTS AND DISCUSSION

The variation in $d_{33}(f)$ as a function of temperature is shown in Fig. 2 for a sample of $[001]_C$-poled, domain-engineered pseudo-orthorhombic PZN-8PT. Upon heating, PZN-8PT transforms to a tetragonal phase at a temperature (T_{FE-FE}) close to 100 °C.[21,22] Hysteresis loops in both the pseudo-orthorhombic and tetragonal phases, at 40 and 130 °C, respectively, are shown in Fig. 3. Importantly, assuming that the sample remains poled, the sample will be monodomain $1T$,[16] and no longer domain engineered, in the tetragonal phase above T_{FE-FE}. The large hysteresis in the tetragonal phase, as shown in Fig. 3(b), suggests the presence of 90° domains, probably induced by the applied static pressure. This state will thus be referred to as quasimonodomain.

Close to room temperature, at 40 °C, the direct piezoelectric response is already large (>2000 pm/V), as reported previously for $[001]_C$-poled PMN-32PT and PZN-4.5PT.[4]

Notably, there is a clear increase in d_{33} as the temperature is increased towards T_{FE-FE} in the pseudo-orthorhombic phase (Fig. 2). Similar behavior has been shown elsewhere, for example, in $[001]_C$-poled PMN-30PT (Ref. 23) and PZN-9PT,[24] based on (small-field) resonance measurements.

$d_{33}(f)$ is characteristically large (>2000 pC/N) in the $4O$ domain-engineered state, approaching 3500 pm/V at 90 °C before the phase transition. It is much lower (>500 pm/V) above T_{FE-FE} in the quasimonodomain $1T$ state, where the crystal is no longer domain engineered and the direct response is measured along the $[001]_C$ polar axis of the tetragonal phase; in contrast, the direct response is measured away from the polar axes of the constituent domains in $4O$ PZN-8PT. The larger response of the domain-engineered crystal might be expected from *piezoelectric anisotropy*, where the piezoelectric response is known to be greater along nonpolar directions for all ferroelectric perovskites in the vicinity of first order phase transitions between ferroelectric phases.[25,26]

Noticeably, Fig. 2 suggests that the frequency dispersion increases near the ferroelectric-ferroelectric (FE-FE) phase transition to a tetragonal phase. By fitting Eq. (3) to the $d_{33}(f)$ data at each temperature from Fig. 2, as shown in Fig. 4(a), we can plot the variation of nonlinearity γ as a function of temperature. This is shown in Fig. 4(b). Notably, the frequency dispersion quantified by the parameter γ does indeed increase toward the FE-FE phase transition in both pseudo-orthorhombic and tetragonal phases.

Very similar behavior was observed in $4R$, $[001]_C$-poled PZN-4.5PT, as shown in Fig. 5. Pseudorhombohedral PZN-4.5PT also transforms to a tetragonal phase at a temperature (T_{FE-FE}) close to 100 °C.[27] Again, $d_{33}(f)$ is shown to increase in the low temperature pseudorhombohedral phase as the FE-FE phase transition is approached [Fig. 5(a)] from around 2000 pm/V at 40 °C to around 5000 pm/V just before the phase transition. Again, the frequency dispersion, quantified by γ, is maximum very close to T_{FE-FE} [Fig. 5(b)]. Notably, there is no qualitative difference between the behaviors of $4O$ PZN-8PT and $4R$ PZN-4.5PT, both of which are domain
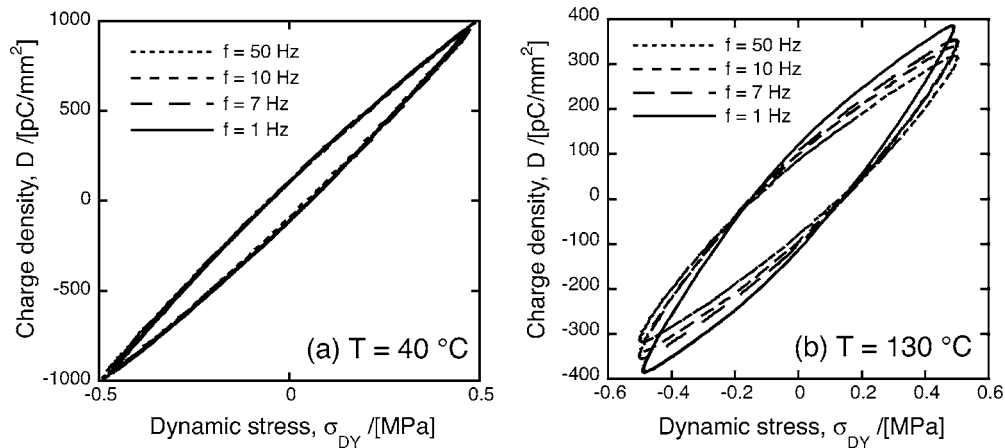

FIG. 3. Charge-stress loops for $[001]_C$-poled PZN-8PT at two different temperatures and various frequencies: (a) at 40 °C in the pseudo-orthorhombic phase and (b) at 130 °C in the tetragonal phase $[(P+\sigma_{st})=2$ MPa, $\sigma_0=0.5$ MPa].
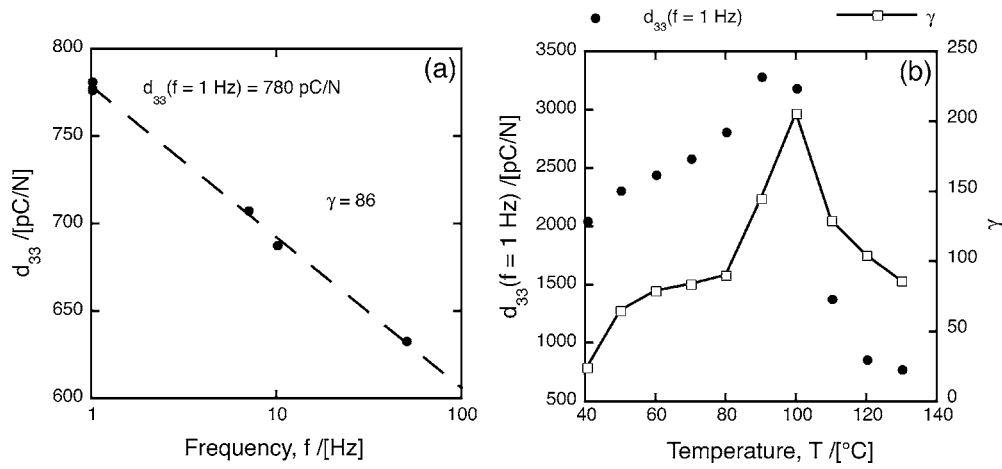
FIG. 4. (a) Logarithmic dependence of d_{33} on frequency for $[001]_C$-poled PZN-8PT at 130 °C. (b) Variation of the low frequency (1 Hz) piezoelectric coefficient and the coefficient of nonlinearity γ defined by Eq. (3) with temperature upon heating.

engineered at room temperature and undergo a temperature-induced phase transition to a non-domain-engineered tetragonal phase.

As noted in the Introduction, quasilogarithmic frequency dependence of $d_{33}(f)$, as observed in various ferroelectric ceramics, is characteristic of irreversible domain wall motion.[6,8] As shown above, frequency dispersion in the longitudinal, direct response of $[001]_C$-poled PZN-4.5PT and PZN-8PT increases to a maximum at the transition temperature T_{FE-FE}. If the frequency dispersion is indeed due to the motion of pinned domain walls then it seems that the extent of this motion is maximal near FE-FE phase transitions.[28]

As shown elsewhere, the dielectric loss tangent (tan δ) also peaks at both T_{FE-FE} and the depoling temperature T_d in $[001]_C$-poled, $4R$ and $4O$ PMN-xPT and PZN-xPT.[9,22] Importantly, the peak in dielectric loss (tan δ) and the minimum in mechanical quality factor Q that occurs just below the depoling temperature (or Curie temperature T_C) in ferroelectrics and ferroelastics are commonly attributed to domain wall motion.[29] Upon increasing temperature towards T_C there is a decrease in order parameter, or polarization in the case of ferroelectrics. For tetragonal barium titanate and lead titanate, for example, this corresponds to a decrease in

tetragonality.[30] Accordingly, the domain wall energy is reduced near T_C, which leads to an increase in domain wall mobility.[29] This is manifest in a peak in loss tangent at the Curie temperature followed by a sharp decrease in the paraelectric phase; above T_C, all extrinsic contributions from domain walls vanish as they do.

The situation at transitions *between* ferroelectric phases at T_{FE-FE} is less clear. However, in both barium titanate and potassium niobate, the orthorhombic distortion does decrease with increasing temperature before the FE-FE transition to a tetragonal phase.[30] Notably, the coercive (electric) field E_C also falls.[30] Similar behavior is observed close to the morphotropic phase boundary[1] (MPB) in PZT ceramics which constitutes a chemically induced, first order phase transition.[25] In the tetragonal phase, there is a very marked decrease in tetragonality with decreasing lead titanate towards the MPB;[30] this is accompanied by a strong decrease in coercive field.[31]

We might postulate, therefore, that the increase in frequency dispersion $d_{33}(f)$ at T_{FE-FE} evidenced in Figs. 4 and 5 and the related increase in dielectric loss evidenced elsewhere[21,22] have the same origin: they are both related to
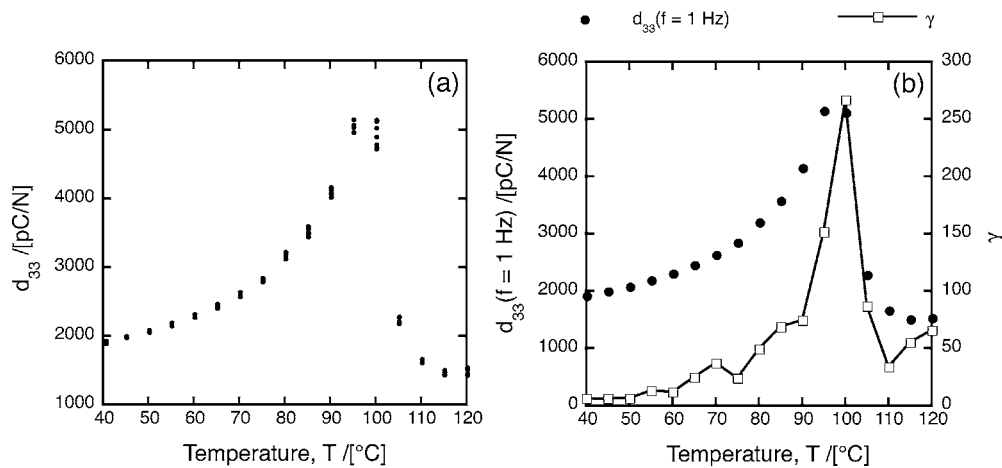

FIG. 5. (a) Temperature dependent piezoelectric coefficient and (b) its frequency dispersion in $[001]_C$-poled PZN-4.5PT. Measurements were made at 1, 7, 10, and 50 Hz. $[(P+\sigma_{st})=2$ MPa, $\sigma_0=0.5$ MPa$]$.
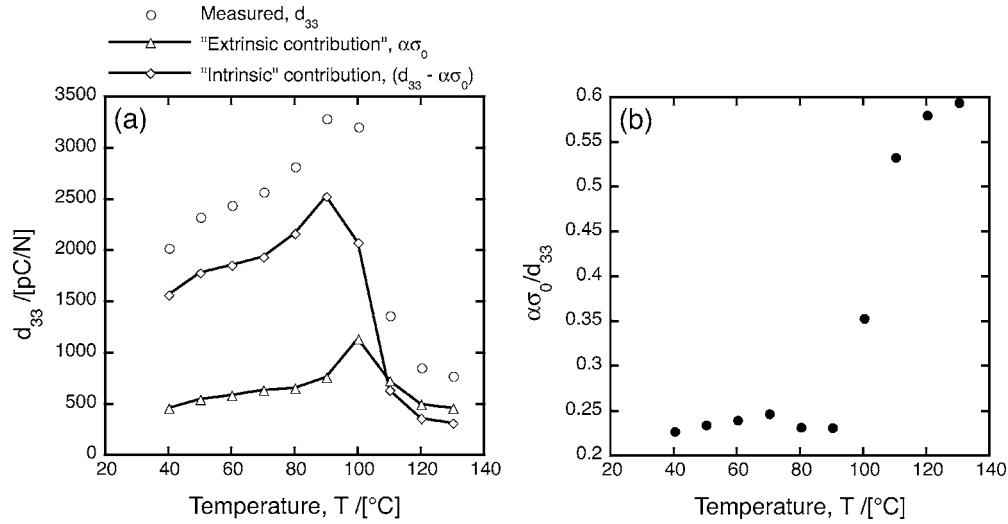
FIG. 6. (a) Intrinsic and extrinsic contributions to d_{33} assuming Rayleigh behavior in the direct piezoelectric response of $[001]_C$-poled PZN-8PT ($f = 1$ Hz). (b) Proportion of the extrinsic contribution to the total measured response.

an increased domain wall mobility close to the first order phase transition between ferroelectric phases.

As noted in Sec. II, according to the Rayleigh law, the charge-stress hysteresis loop width at the origin ($\sigma_{dy} = 0$) is given by $\Delta D = \alpha \sigma_0^2$. This can be taken from experimental charge-stress loops, for a given frequency, and used to calculate the irreversible (or extrinsic) contribution to the piezoelectric response: that is, $\alpha \sigma_0$ in Eq. (1). The reversible (intrinsic) part d_0 can be quite simply calculated from the measured piezoelectric coefficient d_{33} by subtracting $\alpha \sigma_0$. This has been done for the data taken from $[001]_C$-poled PZN-8PT and PZN-4.5PT; the results are shown in Figs. 6 and 7.

Figure 6 shows the intrinsic (reversible) and extrinsic (irreversible) contributions to d_{33} (at 1 Hz) as a function of temperature for $[001]_C$-poled, $4O$ PZN-8PT, assuming Rayleigh-law behavior. Notably, both the intrinsic and extrinsic contributions are shown to peak near T_{FE-FE} [Fig.

6(a)]. Interestingly, the extrinsic contribution ($\alpha \sigma_0$) peaks 10 °C after both the intrinsic contribution (d_0) and the total measured response (d_{33}).

Importantly, in the low temperature, domain-engineered, pseudo-orthorhombic phase, the intrinsic contribution is always much larger than the extrinsic contribution. However, this is not true in the quasimonodomain, $1T$ tetragonal state where the reversible contribution is smaller than the irreversible one. The relative importance of the irreversible contribution is more clearly shown in Fig. 6(b), where it is plotted as a proportion of the total response ($\alpha \sigma_0 / d_{33}$). In the $4O$ domain-engineered state, the irreversible contribution is never more than 25% of the total. In contrast, it reaches around 60% of the total response in the quasimonodomain $1T$ state.

The behavior of $4R$, $[001]_C$-poled PZN-4.5PT was found to be similar, as shown in Fig. 7, except that here the reversible contribution was always larger than the irreversible con-

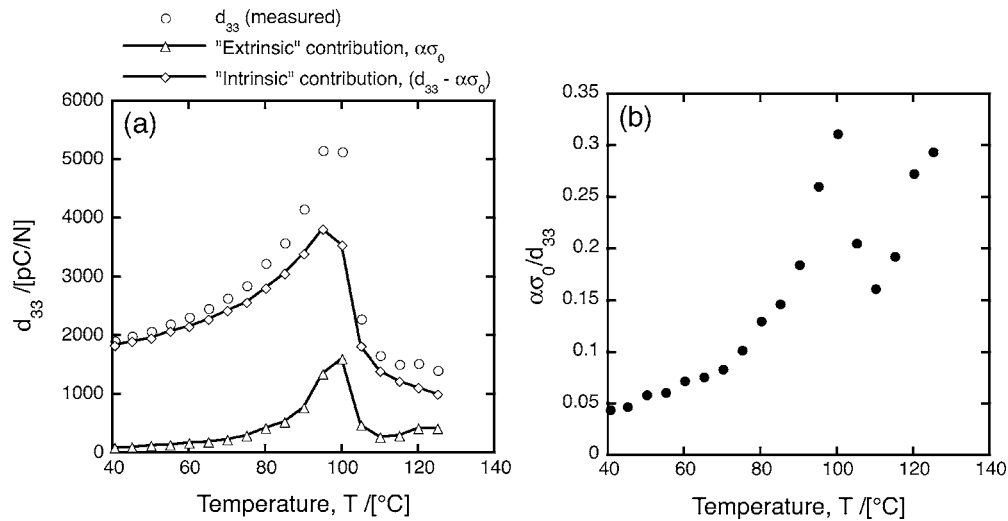

FIG. 7. (a) Intrinsic and extrinsic contributions to d_{33} assuming Rayleigh behavior in the direct piezoelectric response of $[001]_C$-poled PZN-4.5PT ($f = 1$ Hz). (b) Proportion of the extrinsic contribution to the total measured response.

tribution, even in the tetragonal phase. However, the relative size of the irreversible component was again larger in the $1T$ tetragonal phase being $>15\%$ compared to 5% at 40 °C in the $4R$ domain-engineered state. The second peak in the irreversible response upon heating near 120 °C is perhaps due to the proximity of the depoling temperature ($T_d \approx 140$ °C in PZN-4.5PT) and the increased mobility of domain walls discussed above.

The peaks in the irreversible contribution for each material will likely have the same origin as the increased frequency dispersion (coefficient γ), that is, in an increased domain wall mobility. As discussed in the Introduction, although ferroelastic switching is not expected, at least in the $4R$ domain-engineered structure, it could be driven by a background stress-induced phase transition.[9,10]

Importantly, in both domain-engineered $4R$ PZN-4.5PT and $4O$ PZN-8PT the reversible contribution is always much larger than the (purely extrinsic) irreversible contribution. Pinned interface motion, for example, accounts for less than 25% of the response in $[001]_C$-poled PZN-8PT [Fig. 6(b)] and less than 5% of the response of $[001]_C$-poled PZN-4.5PT [Fig. 7(b)], at room temperature, for the range of stresses applied. In PZN-4.5PT the reversible response is around 1800 pm/V at 40 °C and rises to more than 5000 pm/V close to the FE-FE phase transition [Fig. 7(a)]. Similarly, the reversible response of PZN-8PT is around 1600 pm/V at 40 °C and rises to nearly 3000 pm/V close to $T_{\text{FE-FE}}$ at 90 °C [Fig. 6(a)].

Calculations have shown that at least 80% of the giant piezoelectric response of $[001]_C$-poled, domain-engineered PMN-33PT (>2000 pm/V) can be accounted for by the intrinsic piezoelectric anisotropy of the constituent domains.[32,33] Similar calculations have shown that intrinsic piezoelectric anisotropy accounts for at least 50% of the piezoelectric response of $[001]_C$-poled, domain-engineered PZN-9PT.[34] Thus, a majority intrinsic contribution to the direct piezoelectric response of $[001]_C$-poled PZN-4.5PT and PZN-8PT might be expected. Moreover, the intrinsic contribution, as measured along the non polar $[001]_C$ poling direction of each domain-engineered crystal, is also expected to increase as the first order ferroelectric-ferroelectric phase transition is approached.[25]

There is significant evidence that the presence, rather than motion, of domain walls in domain-engineered barium titanate and potassium niobate leads to an increase piezoelectric response,[35–39] especially when the domain structure becomes very fine [<10 μm (Ref. 38 and 39)]. In the Rayleigh model, this contribution would appear in the reversible part, d_0. At very low lead titanate contents, relaxor-ferroelectric PMN-xPT (Ref. 40) and PZN-xPT (Ref. 41) are well known to exhibit fine domain structures due to a low domain wall energy.[42] However, crystals with compositions close to the MPB, such as PZN-8PT,[41,43] exhibit (ferroelastic) domain sizes larger than 50 μm in such compositions, the intrinsic (lattice) contribution might be expected to dominate.

Another possible explanation for the giant piezoelectric response of PMN-xPT and PZN-xPT is the "adaptive phase"[44] model recently proposed by Jin et al.,[42] Viehland,[45]

and Wang.[46] Noting the similarities[47] between relaxor-ferroelectrics and martensites the authors propose a model based on the fine-scale *twinning* of tetragonal (or rhombohedral) domains. In their model, the lattice parameters of the observed monoclinic and orthorhombic phases, derived from x-ray diffraction measurements with a finite beam size, are actually the volume-averaged parameters of the finely twinned tetragonal (or rhombohedral) phase. Upon application of an electric field, the progressive switching of more and more domains leads to a rotation of the *volume-averaged polarization*, rather than the intrinsic polar vector, and thus the observation of increased monoclinic distortion in diffraction experiments. Such a model is indeed in agreement with the experimental evolution of the lattice parameters as a function of electric field and temperature, which satisfy the required "invariance conditions."[45,46]

Importantly, in the adaptive phase model, the piezoelectric response when a stress or electric field is applied along a nonpolar direction is inherently coupled to local ferroelastic domain wall motion, albeit on a very fine scale. That is, it will be irreversible wherever domain walls are *pinned* and Rayleigh-law hysteresis will be expected as a result. However, from the above it is clear that the majority of the (direct) piezoelectric response of $[001]_C$-poled PZN-4.5PT and PZN-8PT is reversible. The reversibility of the microvariant switching proposed by the adaptive phase model should be addressed further.

V. CONCLUSIONS

The dynamic, direct piezoelectric response of $[001]_C$-poled PZN-4.5PT and PZN-8PT has been investigated as a function of temperature. For both compositions, and for the loading conditions used here, d_{33} is shown to increase dramatically towards the phase transition to a tetragonal phase; such information will be useful for the application of such crystals as sensors. Qualitative differences have been evidenced between the behavior in the low temperature, domain-engineered $4R$ and $4O$ structures of PZN-4.5PT and PZN-8PT, respectively, and the high temperature, quasimonodomain tetragonal phase.

Reversible and irreversible (extrinsic) contributions to the response have been quantified over the temperature range. Both the irreversible contribution and the quasilogarithmic frequency dispersion $d_{33}(f)$ peak close to the ferroelectric-ferroelectric phase transition to a tetragonal phase. Both likely have their origin in the pinned motion of non-180° domain walls.

Finally, for the temperatures and loading conditions considered here, the reversible contribution to the piezoelectric response of $4R$ and $4O$ domain-engineered crystals is always greater than the irreversible (extrinsic) contribution; the maximum irreversible contribution observed is around 30% in $[001]_C$-poled $4R$ PZN-4.5PT close to $T_{\text{FE-FE}}$. The reversible (intrinsic) contribution to the response rises from around 1600 pm/V at 40 °C to 2500 pm/V at 90 °C in PZN-8PT; in PZN-4.5PT, it rises from around 2000 to over 5000 pm/V in the same temperature range. This increase can be expected from intrinsic piezoelectric anisotropy.[25] Importantly, the

contribution from domain wall motion is minor; this result might have consequences for the validity of the adaptive phase model.

ACKNOWLEDGMENT

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