

Mechanical stability of polar defects in ferroelectric perovskites

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Abstract

The influence of uniaxial compressive stress on the small signal direct piezoelectric coefficient of hard and soft $\text{Pb}(\text{Zr,Ti})\text{O}_3$ at the morphotropic phase boundary was investigated as a function of temperature from 25 °C to 450 °C. The stress- and temperature-dependent piezoelectric data indicate that stress is capable of either directly or indirectly modifying the orientation of polar defects in the crystal lattice. At higher temperatures, the mobility of polar defects was found to increase, corresponding to a two-step decrease in the direct piezoelectric coefficient and a decrease in the frequency dispersion. Quenching experiments were used to elucidate the role of the internal bias field on the stress-dependent piezoelectric response.

1. Introduction

Perovskite oxides are an increasingly important material class due to their numerous functional properties, which include ferroelectricity, [1] colossal magnetoresistance, [2] mixed ionic/electronic conductivity, [3] and more recently high-efficiency photovoltaics. [4] One of the central advantages of the simple ABO_3 structure is the ability to significantly alter the functional properties with relatively small amounts of aliovalent and isovalent substitutions. Often, in the case of ferroelectric materials, aliovalent transition metals or rare-earth ions are selected that occupy either an A- or B-site, resulting in the formation or elimination of oxygen vacancies for charge compensation. Acceptor-doping with lower valence ions leads to the formation of oxygen vacancies ($V_o^{\bullet\bullet}$), which has been shown to electrically “harden” the ferroelectric, [1] i.e., increase the electrical poling field and decrease the piezoelectric response, and result in aging. [5] These effects correspond closely to the development of an apparent internal bias electric field that depends on the concentration content as well as the thermoelectrical history of the sample. [6, 7] Studies on acceptor-doped (Fe^{3+}) $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ($\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})_{0.99}\text{Fe}_{0.01}\text{O}_3$) have also demonstrated the formation of nanodomains and increasing rhombohedral content in comparison to undoped materials. [8] Although donor-doped ferroelectrics are less understood, it is generally agreed that the observed enhancement in electromechanical properties and decreased electric poling fields may empirically be correlated with the decreased oxygen vacancy content, the formation of A-site vacancies, and changes in B-site valance. [1] This facilitates increased domain wall motion and, therefore, increased extrinsic contributions to the electromechanical properties.

Although the exact mechanism responsible for aging behavior remains under debate, it is understood that dopant-generated oxygen vacancies are the principal cause. [6] The primary differences are in the location of the point defects, i.e., at the bulk, domain walls, or grain boundaries. According to the model of domain wall pinning by polar defects (*bulk model*), the transition metal dopants typically substitute the B-site in acceptor-doped ferroelectrics, which can become associated with a compensating oxygen vacancy to form a polar defect complex, [5, 9] which is in some literature referred to as “defect dipoles”. Alternatively, lone charged defects within polar lattice can act as pinning centers, [10] although their pinning strength was shown to be lower compared to defect associates. [11] These polar defects or their associates remain in the bulk and lie along one of the $\langle 001 \rangle$ crystallographic directions, acting to stabilize the domain structure. Polar defects and internal bias fields have been observed in numerous acceptor-doped ferroelectrics, e.g., Mn^{2+} -doped

BaTiO₃, [5] Ni²⁺-doped BaTiO₃, [7] Cu²⁺-doped PbTiO₃, [12] and Fe³⁺-doped Pb(Zr_{0.58}Ti_{0.42})O₃. [13] The local spontaneous polarization (P_s) of the surrounding domain reduces the energy for a polar defect oriented parallel or close to P_s. The resulting polar defects thereby hinder domain wall motion. Investigations on aged single crystal BaTiO₃ with a 0.02 at% Fe³⁺ impurity concentration have shown that the net internal bias field can also be an indicative value of the restoring force for reversible ferroelectric domain switching, significantly enhancing the unipolar strain. [14] Similar results have also been shown for Mn-doped single crystal BaTiO₃ and polycrystalline (Ba,Sr)TiO₃. [15, 16]

Importantly, the macroscopic hysteretic behavior is strongly dependent on the thermal and electrical history of the material as well as the dopant (oxidation state, ionic radius, etc) and its concentration. [6, 7, 17, 18] After initially cooling from the annealing temperature (over the Curie point, T_c) the bipolar polarization (P)-electric field (E) hysteresis has a *pinched* characteristic, due to the defect ordering stabilizing the initial domain structure. [6, 17] Electron paramagnetic resonance investigations on Fe³⁺- and Mn²⁺-doped BaTiO₃ have revealed that the initially randomly distributed point defects can be aligned in a way that positive and negative charges adopt the direction of an external electric field through the motion of oxygen vacancies. [18, 19] In contrast, the repeated bipolar electrical cycling above the coercive electric field can randomize the polar defects in respect to the domain structure, i.e., the polar defects do not necessarily align with the local spontaneous polarization direction. This results in the appearance of a more-square P-E loop, signified by a loss of pinching. [6, 17] This process is, however, dependent on time and temperature as well as electric field magnitude and frequency. Carl and Härdtl have, for example, shown that the internal bias field increases with both time and temperature, indicating a thermally activated temporal evolution of the polar defects. [6]

Despite the importance of perovskite ferroelectrics and the number of investigations, there has been little work on the mechanical stability of polar defects. Understanding the role of mechanical fields on acceptor-doped ferroelectrics is important, as many applications apply mechanical loads during operation. Arlt and Neumann have proposed the existence of both an electric dipole as well as an elastic dipole, formed by elastic strains in the lattice found at a polar defect. [7, 20] It is suggested that elastic dipoles could contribute to the aging process if a mechanical stress was capable of reorienting them. This corresponds well with simulations that demonstrate the large elastic anisotropy of an oxygen vacancy in SrTiO₃. [21] There is, unfortunately, little experimental data available on the influence of mechanical stress on acceptor-doped perovskite ferroelectrics. Previous characterization of the macroscopic electromechanical and stress-strain behavior has shown that uniaxial compressive stress can result in ferroelastic switching [22, 23] as well as field-induced phase transitions in polycrystalline PZT. [24] Therefore, the primary aim of this work is to investigate role of stress on donor and acceptor-doped Pb(Zr,Ti)O₃ through the characterization of the stress- and temperature-dependent direct piezoelectric response.

2. Experimental Methodology

Materials

The samples used in this study are widely used, industrial important and commercially available *soft* and *hard* PZT, which are both near the morphotropic phase boundary on the tetragonal side. These terms *soft* and *hard* are loosely used here and only exemplify the observed constitutive behavior; both materials are substituted with multiple cations, some of which can act as an acceptor or donor depending on the site location and oxidation state. Replacing Ti/Zr with lower valence ions on B-site is most often referred to as acceptor doping although this is more correctly described as chemical substitution. The soft PZT material (PIC151, PI Ceramic GmbH, Lederhose, Germany) has the following composition: Pb_{0.99}[Zr_{0.45}Ti_{0.47}(Ni_{0.33}Sb_{0.67})_{0.08}]_{1.00}O₃. Nickel is typically found in a 2+ oxidation state (Ni²⁺), although Ni³⁺ is possible. The oxidation state decreases the ionic radius from 69 pm to 56 pm (low spin) or 60 pm (high spin) with an increase from Ni²⁺ to Ni³⁺ in the six-fold coordination state. Nickel is understood to be a B-site dopant, which is due to the similar ionic radii of Zr⁴⁺

(72 pm) and Ti^{4+} (60.5 pm); Pb^{2+} has a much larger radius of 149 pm in the twelve-fold coordination state. [25] The influence of antimony, however, is not as clear. The primary oxidation state is Sb^{3+} , with an ionic radius of (76 pm), although Sb^{5+} can be also observed with an ionic radius of 60 pm. [25] This indicates that Sb should occupy a B-site, which has been previously suggested for Sb-doped $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$. [26] Choi *et al.* [26] determined that the primary oxidation state was Sb^{3+} using X-ray photoelectron spectroscopy and argued that the B-site was more likely than A-site due to the tolerance factor closer to unity. Macroscopic measurements, however, show a clearly soft PZT material with a large piezoelectric coefficient (~ 520 pC/N) and a relatively low coercive field (0.95 kV/mm). [27] Sb-doping has also been observed to decrease the coercive field significantly. [28] This indicates that Sb might be in the Sb^{5+} oxidation state or Sb^{3+} may also partially occupy the A-site and, therefore, act as a donor dopant. The primary reason for doping PZT with Sb appears to be the increased Curie point and the improved fatigue behavior. [28] The hard PZT (PIC181, PI Ceramic GmbH, Lederhose, Germany) has the following composition $\text{Pb}_{1.00}[\text{Zr}_{0.47}\text{Ti}_{0.48}(\text{Mn}_{0.33}\text{Sb}_{0.32}\text{Nb}_{0.33})_{0.05}]_{1.00}\text{O}_3$. Mn^{2+} acts as an acceptor-dopant on the B-site, whereas Nb^{5+} is a donor dopant. Previous characterization of the macroscopic electromechanical behavior shows an increase in the coercive field (1.8 kV/mm) and a decrease in the piezoelectric coefficient (~ 270 pC/N) over the soft PZT, which is understood to be due to an increased oxygen vacancy concentration. [23] This demonstrates that the behavior is primarily controlled by acceptor dopants and the presence of polar defects.

Experimental Procedure

Cylindrical samples of 5.8 mm diameter and 6 mm height were produced by core drilling and grinding from an as-sintered block of material. After machining, the samples were electroded with a sputtered thin layer of platinum. Prior to testing, all samples were annealed at 450 °C for 30 min to remove stresses and domain orientations induced by the machining process. Measurement of the temperature- and stress-dependent longitudinal direct piezoelectric coefficient d_{33} was performed on a screw-driven load frame (Z030, Zwick GmbH & Co.KG, Ulm, Germany) fitted with a heating chamber (SV800, Thermal Technology GmbH, Bayreuth, Germany) and custom-built equipment capable of applying small mechanical impulses at various frequencies. A detailed description of the load frame and heating chamber is available elsewhere. [22] The load frame applied the global bias uniaxial compressive stress, while an integrated piezoelectric stack actuator (P-025.80, PI Ceramic GmbH, Lederhose, Germany), positioned in series with the sample and controlled by a LabVIEW program, partially unloaded the sample with a sinusoidal mechanical signal. During testing a load amplitude of ± 0.5 MPa was used. At each bias stress level the load amplitude was corrected to account for stress-dependent changes in the elastic compliance. [22, 29] The small signal direct piezoelectric coefficient was calculated from the measured amplitudes of stress and polarization in a frequency range between 50 mHz and 240 Hz with an accuracy of better than ± 0.2 pC/N. The Sawyer-Tower circuit, including the cables extending into the heating chamber, was shielded against external parasitic electric fields. The temperature was measured during characterization with a K-type thermocouple. During temperature-dependent measurements, a heating rate of 1 K/min was used.

3. Results and Discussion

The direct piezoelectric coefficient of the soft and hard compositions was determined during uniaxial compressive loading and unloading in the frequency range between 50 mHz – 240 Hz (Fig. 1). The arrows indicate the direction from lower frequencies to higher frequencies. Prior to testing each sample was poled at 150 °C for 5 min with an electric field of 3 kV/mm. Following poling, the temperature of the oil bath was reduced to ~ 30 °C with the field remaining applied. This is referred to as *field cooling* during the subsequent discussion. The soft material displays a significantly larger d_{33} value (550 to 600 pC/N, depending on frequency) in the poled state without applied stress. In contrast, the hard PZT composition has a d_{33} of 250 to 280 pC/N over the same frequency range. The lower piezoelectric

response of hard PZT is due to the decrease in domain wall mobility and a subsequent decrease in the intrinsic contribution. [30]

With an increasing compressive stress, the piezoelectric response of the soft PZT is found to monotonically decrease above approximately -25 MPa, which is related to the first deviation from the linear elastic behavior (Fig. 1a). This point is where ferroelastic domain reorientation begins and is defined as the onset stress (σ_o). As the external compressive stress reorients domains parallel to polarization direction, the average piezoelectric response of the polycrystal decreases. This effect continues until saturation, where no additional domains are available to be switched. The saturation stress was found to be at approximately -300 MPa in the soft PZT, which naturally corresponds to a d_{33} of nearly zero. A d_{33} of ~ 8 pC/N remains even at the highest compressive stress tested because of the inability to completely ferroelastically switch all domains. To ensure that this small d_{33} value wasn't caused by experimental error, a polycrystalline Al_2O_3 sample was also tested and the resulting d_{33} was measured to be 0 ± 0.1 pC/N, indicating that the observed high stress behavior is not a measurement artifact. The overall trend is similar to that observed in other perovskite ferroelectrics. [31] Upon unloading, the piezoelectric response does not fully recover. There is, however, a minor increase to 62 pC/N, which is due to the domain backswitching effect and a reduction in the mechanical clamping of domain walls.

In comparison, the hard PZT displays a considerably different response to the applied compressive stress (Fig. 1b); namely, an initial increase in d_{33} until -75 MPa, followed by a decrease and subsequent saturation. A similar increase in d_{33} with compressive stress in Fe^{3+} -doped PZT has been previously observed, although this study only applied bias stresses up to -80 MPa and, therefore, did not observe the subsequent decrease. [32] The initial increase is proposed to be due to the presence of an internal bias field, created by the high temperature poling procedure. At elevated temperature, the mobility of polar defects increases, [18] which allows for their orientation in the polarization direction. Upon field cooling, the polar defects remain in the oriented state (aligned in the direction of applied electric field) and are frozen in at room temperature, where their mobility is significantly decreased. Warren *et al.* have shown that the reorientation time with a bias electric field decreases nearly 4 orders of magnitude between 24 °C and 110 °C in Fe^{3+} -doped BaTiO_3 . [18] The oriented polar defects result in an offset of polarization hysteresis loop with an apparent internal bias field, [6] which acts antagonistically against the compressive stress. Similar increases in the stress-dependent electric field-induced unipolar strain have also been observed in other ferroelectric materials [33-35] and have been rationalized as a balance between applied electric and mechanical fields. When a compressive stress is applied, the number of domains oriented perpendicular to the electric field increases, which results in an increased ferroelectric switching strain. Eventually, however, the applied mechanical load is too large and clamps the domains, meaning that the electric field is no longer large enough to reorient domains in the direction of polarization. This results in a subsequent decrease in unipolar strain. A similar effect is found here, although the role of electrical field is played by the apparent internal bias field generated by the oriented polar defects. During characterization, the small mechanical impulse moves domain walls that are stabilized in the polarization direction by the internal bias field. As the applied bias stress increases, the electrostatic and mechanical forces work antagonistically and result in an increase in the piezoelectric response through enhanced domain wall motion. Further increases in the mechanical load see a shifting of this balance and a mechanical clamping of domains. It is expected that with larger mechanical impulse amplitudes or an increase in the polar defect orientation along the polarization direction, the observed peak would shift to higher compressive stress levels.

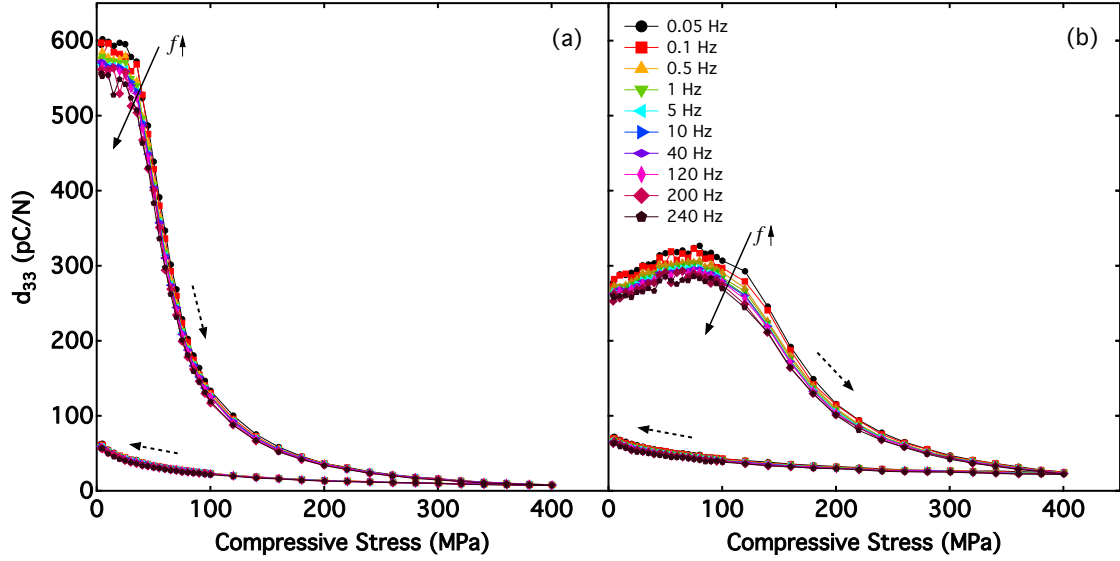


Figure 1. Frequency dependent piezoelectric coefficient during uniaxial compressive loading in soft (a) and hard (b) PZT. The solid arrows indicate the direction of increasing measurement frequency, which was varied from 50 mHz to 240 Hz. The dashed arrows illustrate the loading direction.

The piezoelectric coefficient is irreversibly decreased when the applied compressive stress is over a material specific value. The path of d_{33} versus stress during unloading from the maximum compressive stress is relatively flat in both soft and hard PZT. Upon further unloading there is an apparent nonlinear increase in the d_{33} of both compositions, which is likely due to the domain backswitching effect. Within the polycrystalline material there are internal electrical and mechanical fields generated by local inhomogeneities and defects. These local fields can be of sufficient magnitude to switch the surrounding domains back to their original orientations when the external field is decreased below a critical value. Interestingly, however, although it is anticipated that the presence of a stable internal bias field in the hard PZT would result in a much larger backswitching effect, this was not observed. Hard PZT was found to increase from 25 pC/N at -400 MPa to approximately 70 pC/N at -5 MPa, while soft PZT increased from 8 pC/N at -400 MPa to approximately 62 pC/N at -5 MPa. The only clue to the effect of polar defects is the slight frequency dependence during unloading observed in hard PZT, although this is relatively minor. These results indicate that the internal bias field of hard PZT has been decreased by the application of an external compressive stress. It should be noted, however, that the remanent d_{33} value of hard PZT represents 26 % of the initial value and only 10 % for the soft PZT. These experimental data correspond well with previous investigations that showed a significant decrease in the asymmetry of bipolar $P(E)$ hysteresis of poled hard PZT by the application of uniaxial compressive stress for up to 20 hr. [36] Unpoled hard PZT experienced no discernable change in the $P(E)$ hysteresis from mechanical loading.

The frequency dependence of the piezoelectric response has been plotted for several selected bias stress levels (-5, -100, -200, -300, and -400 MPa) in Figure 2. These results correspond well to previous measurements of the frequency-dependent d_{33} [37], which showed a logarithmic decrease with increasing frequency. This is due to the relaxation nature of domain wall motion in ferroelectrics and can be described by the following relation [38]

$$d_{33}(f) = d_0 + \beta \ln(f) \quad (1)$$

where d_0 and β are material parameters that describe the intrinsic piezoelectric coefficient at zero frequency and the slope of the d_{33} -frequency (f) curve, respectively.

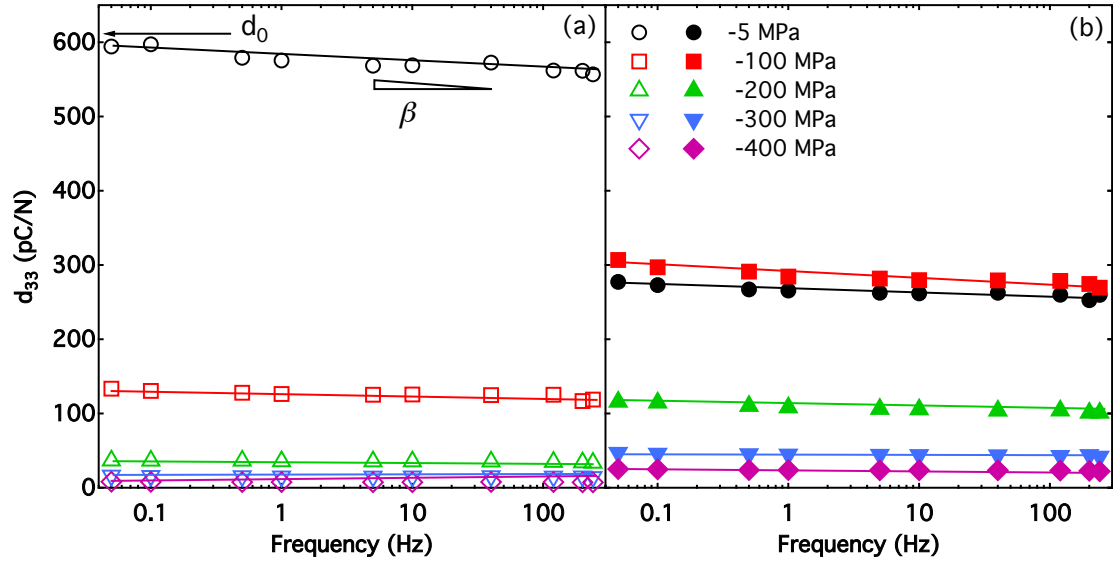


Figure 2. The direct piezoelectric coefficient at -5, -100, -200, -300, and -400 MPa as a function of frequency for soft (a) and hard (b) PZT.

In analogy to the Rayleigh coefficient, the β constant is a measure of the frequency dependence of irreversible domain wall motion, whereas d_0 represents the frequency independent contribution to the piezoelectric response. Both parameters were determined as a function of compressive stress and are shown in Figure 3. With an increasing compressive stress there is an apparent nonlinear change in β , with a peak observed at -34 MPa for soft PZT and -84 MPa for hard PZT. This means that the irreversibility of the domain wall movement is initially increasing under a compressive stress. In both materials the critical stress at peak β corresponds to the compressive stress where d_{33} first begins to decrease. These results indicate that the compressive stress initially relieves local, internal stress, which facilitates domain wall motion and increases the irreversibility. Above this material specific parameter, however, the compressive stress monotonically decreases β , indicating that the applied stress clamps domain walls and reduces their movement. In contrast, d_0 was found to display a similar behavior to that observed in Figure 1 namely a monotonic decrease in soft PZT and a peak and subsequent decrease in hard PZT.

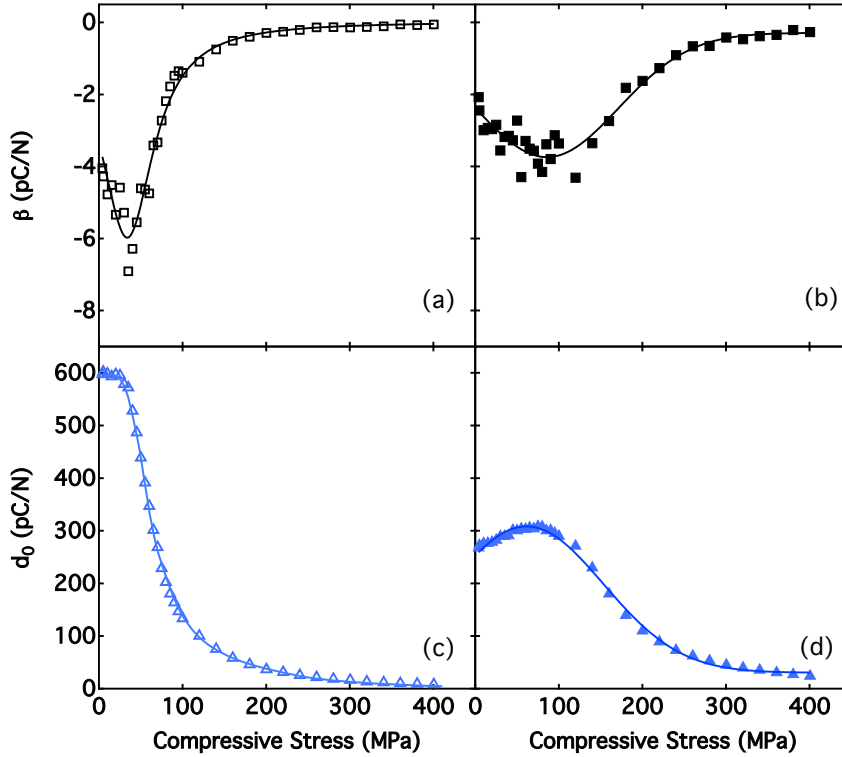


Figure 3. The material parameters β and d_0 as a function of compressive stress in soft (a, c) and hard (b, d) PZT. The lines are meant only to guide the eye.

To elucidate the role of the internal fields developed during the poling process, quenching experiments were performed on both soft and hard PZT. Here, two samples were cooled at a rate of 1 °C/min from an anneal temperature of 450 °C (above T_C), while two other samples were removed directly from the oven at 450 °C and quenched in air. From these four samples, one slow-cooled and one quenched sample were poled at 25 °C with 3 kV/mm, which was held constant for 5 min. The remaining two samples were heated to 150 °C, poled with 3 kV/mm for 5 min, and field cooled to room temperature. Following the poling processes, the stress-dependent d_{33} of all four samples was characterized with a load amplitude of ± 0.5 MPa at 10 Hz (Fig. 4). There is no significant change in the behavior of soft PZT with different poling procedures or thermal treatments. At low stress levels the samples poled at 150 °C show a slightly more stable d_{33} than those poled at room temperature. As previously noted, the oxidation state of the substitutions can result in a softening or hardening, which has likely resulted in the presence of polar defects that affect the macroscopic response. Overall, however, the effect is relatively small and it is expected that the concentration of polar defects is minor. In contrast, the hard PZT displays significant changes in the stress-dependent d_{33} with the poling procedure and thermal treatment. When the samples were poled at room temperature, there was an observed decrease in the piezoelectric constant compared to the samples poled at 150 °C, which corresponded with a loss of the d_{33} maximum, i.e., only a monotonic decrease with stress was found. Here, the quenched sample poled at 25 °C had a d_{33} nearly twice as large as that of the sample cooled slowly. Interestingly, both samples poled at 150 °C displayed the same behavior; namely, a maximum d_{33} and a subsequent decrease with compressive stress. This suggests that a poling field of 3 kV/mm at 150 °C is enough to reorient polar defects, which most likely is due to reconfiguration of oxygen vacancies to lattice positions in favor of the external field. This finding corresponds well with temperature dependent macroscopic polarization-electric field behavior on 1 at% Fe-doped PZT that shows an opening of the hysteresis loop, i.e., a loss of a pinched hysteresis at 125 °C, indicating polar defect relaxation. [17]

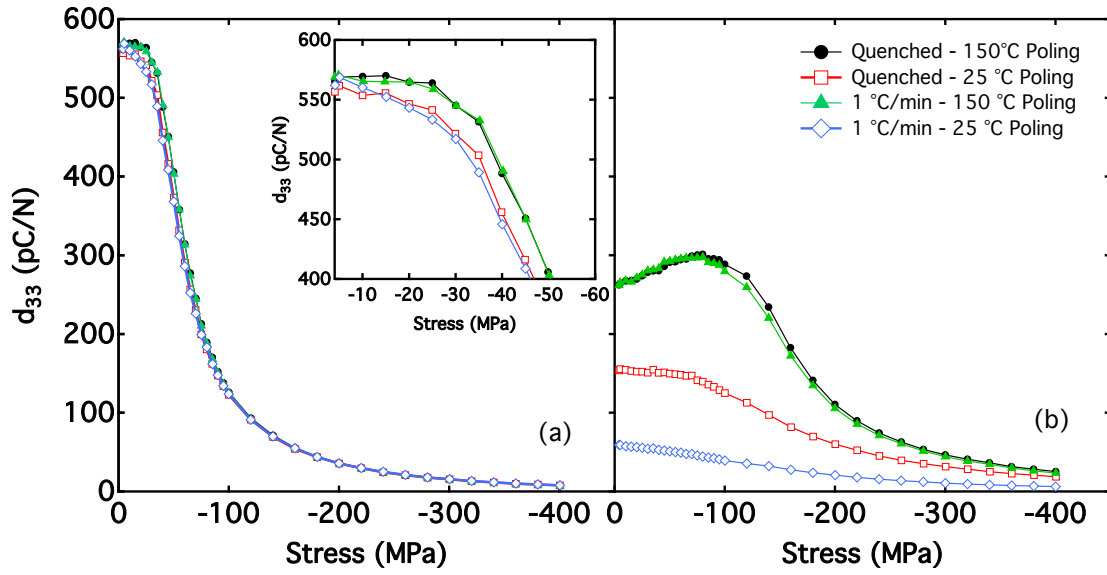


Figure 4. The stress-dependent direct piezoelectric coefficient (10 Hz) of air quenched and slowly cooled (1 K/min) soft (a) and hard (b) PZT, both poled at either 25 °C (open symbols) or 150 °C (closed symbols).

The difference in the piezoelectric response of the hard PZT material is suggested to be due to the relative orientation of the polar defects in relation to the local domain structure. Previous work has suggested that variations in this behavior can influence the energy profile of a domain wall. [20] At high temperatures, the polar defects are mobile and can be reoriented by internal and external fields. During slow cooling from above the Curie point, domains are formed that have a local spontaneous polarization direction that acts to reorient the polar defects, shown in Figure 5a. With further decreasing temperatures the defects become less mobile and act to hinder changes to this domain structure, which results in reduced piezoelectric response due to a lower extrinsic contribution and a lower poling efficiency. In the quenched sample, however, the polar defects are not allowed sufficient time to fully align with local domain structure, meaning that some polar defects are aligned in a crystallographic orientation different than the local spontaneous polarization (Fig. 5b). In this case, domain wall motion is less hindered than the slowly cooled material, as some polar defects might actually favor a different polarization direction, resulting in a larger piezoelectric response. In both the slowly cooled and quenched samples poled at room temperature, a maximum in d_{33} is not observed. This indicates the lack of an apparent internal electric field. In the final case, the polar defects have been reoriented due to the externally applied electrical field and temperature and display a net internal field that results in a maximum in d_{33} during compressive stress loading. It is expected that the internal electric field increases the number of domains aligned with the applied compressive stress and, therefore, enhances the piezoelectric response (Fig. 5c). Similar behavior was found in previous experimental investigations of the electric field-dependent indirect d_{33} of aged Fe-doped PZT, which showed an increase of the piezoelectric coefficient with increasing applied electric field. [39] This effect was discussed in terms of the clamping of domain walls by polar defects and the increasing extrinsic contributions at higher field levels.

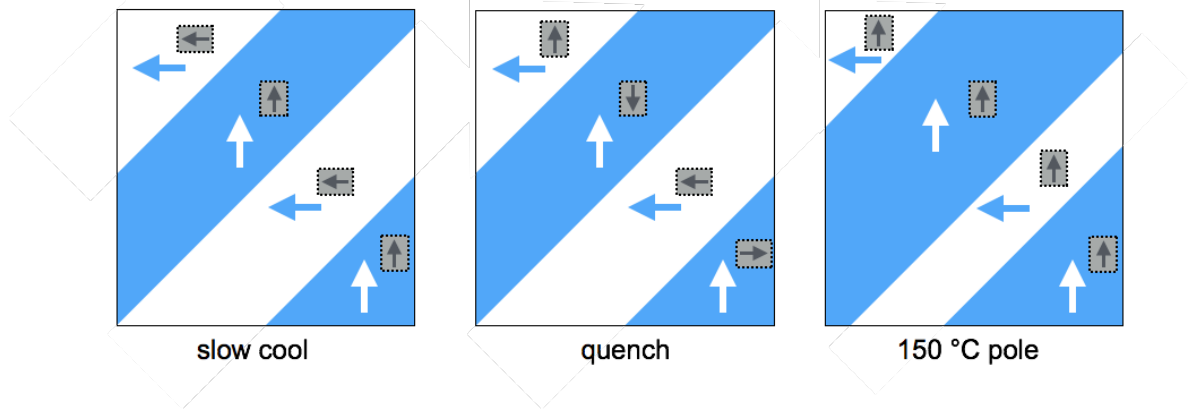


Figure 5. Schematic of the domain structure in relation to the orientation of the polar defects for slowly cooled samples (a), quenched sample (b) and samples poled at 150 °C (c).

It is understood that polar defects become increasingly mobile at elevated temperatures. The most likely candidate for mobile charged point defects is oxygen vacancies. There is considerable indirect evidence supporting this, including that the loop pinning-depinning activation energy and the activation energy of hopping conductivity nearly coincide with the activation energy of oxygen vacancy diffusion in the same material. [13] To determine the influence of temperature on d_{33} , soft and hard PZT samples poled at 150 °C where characterized from 25 °C to 350 °C and 25 °C to 450 °C, respectively, at various frequencies between 1 Hz and 240 Hz. Measurements were done under preload (-5 MPa) and -100 MPa compressive stress. The experimental data are shown in Figure 6. Here, it can be clearly observed that both soft and hard PZT display an increase in d_{33} in the preload case, followed by a sharp decrease. The peak was found to be at approximately 233 pC/N and 305 pC/N for soft and hard PZT, respectively. The temperature dependent piezoelectric behavior is understood to be due to the increasing dielectric permittivity and the decreasing spontaneous polarization:

$$d_{33} = 2Q_{11}P_0\varepsilon'_{33}\varepsilon_0$$

where Q_{11} is the electrostrictive coefficient, P_0 is the spontaneous polarization, ε'_{33} is the relative dielectric permittivity, and ε_0 is the permittivity of free space. In addition, hard PZT showed considerably more significant frequency dispersion at higher temperatures than soft PZT. This is likely due to the increasing mobility of the polar defects. Lower frequencies show higher d_{33} values, which is likely due to their increased ability to follow the applied mechanical stress signal. In such a case, the increased in-phase movement of ferroelastic domain walls along with the surrounding polar defects would naturally imply weakening of the pinning activity. At higher frequencies the polar defects cannot follow and hinder the motion of the domain walls. The higher the temperature, the more pronounced are these effects. This frequency dispersion, however, peaks at the maximum d_{33} and then decreases with increasing temperature.

The stress-dependent experimental results (Fig. 1) indicate that compressive stress can reduce the apparent internal bias that is caused by the ordered orientation of polar defects. Through the increase in temperature, the influence of stress on the polar defect should increase with the increasing thermally activated mobility of such defects. Figure 6b and 6d show the temperature and frequency dependence of d_{33} with a constant bias stress of -100 MPa for hard and soft PZT, respectively. Soft PZT displays a reduced d_{33} value at room temperature, consistent with stress-dependent measurements (Fig. 4), and a gradual decrease with increasing temperature. There was little frequency dispersion observed, which is likely due to the clamping of domain wall motion by the stress. Hard PZT, however, clearly shows a two-step switching process with the first decrease occurring at ~40 °C. Importantly for

applications, this limits the thermal operating range of such materials when a compressive stress is applied. Above approximately 150 °C, the rate of decrease in d_{33} drops and the subsequent $d_{33}(T)$ behavior matches well that observed in soft PZT. In addition, the high temperature frequency dispersion is also reduced with a bias stress of -100 MPa. This two-step switching step is proposed to be due to the reorientation of the polar defects with the application of a bias stress. At lower temperatures, the mobility of the polar defects is low enough that they are not significantly influenced by the stress. However, as the temperature and the mobility increase, they can reorient, which is the origin of the first step. Because they are mechanically clamped, the frequency dispersion at higher temperatures also decreases. Eventually, the material loses the spontaneous polarization and the d_{33} reduces to zero.

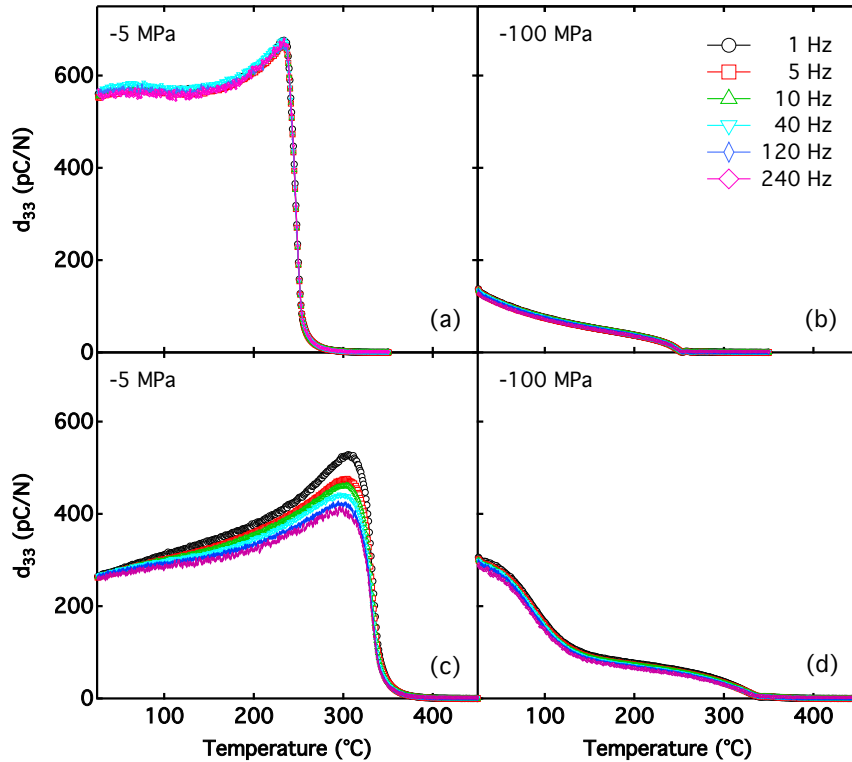


Figure 6. Temperature-dependent direct piezoelectric coefficient for soft (a), (b) and hard (c), (d) PZT with a bias compressive stress of -5 MPa and -100 MPa.

Previous work has referred to such defect structures in crystalline materials as “elastic dipoles”, which is due to point defects. [40-42] In analogy to an electric dipole, which is defined by a dipole moment and the relative crystallographic orientation, an “elastic dipole” possesses a local, anisotropic strain field that has an orientation along specific crystal axes. In acceptor doped tetragonal PZT the elastic dipole is most likely parallel to the electric dipole. It has been suggested, primarily based on metallic crystals, that an externally applied stress can result in a macroscopic anelastic strain due to the stress-induced ordering of “elastic dipoles”. Although isotropic strain fields are possible for a substitutional atom or a vacancy in a cubic crystal, a point defect cluster may cause an anisotropic strain. [7] It is important to note, however, that these experimental data cannot directly separate the direct stress-induced ordering of polar defects from the indirect ordering. In the direct case, the elastic dipoles have a strain field that can be directly ordered by an applied mechanical field. In the indirect case, the surrounding domain is first ferroelastically switched, generating a local electric field that causes the polar defect to reorient. Previous stress-strain measurements on the same hard PZT composition showed a coercive stress at 25 °C and 100 °C of approximately -140 MPa and -130 MPa respectively, [23] although ferroelastic switching below these values is likely. It is, therefore, unclear to what extent the domain wall motion influenced the polar defect

orientation. Such questions could be addressed with stress-dependent electron magnetic resonance measurements on acceptor-doped perovskites in the cubic phase to eliminate the influence of local spontaneous polarization.

Conclusions

The stress-dependent piezoelectric response of hard and soft PZT was characterized as a function of frequency and temperature to elucidate the role of mechanical fields on the domain wall pinning capability by charged point defects. The present findings indicate that compressive stress reduces the intrinsic forces generated by electrostatic ordering of charged defect population. This resulted in the presence of a two-step switching in hard PZT with increasing temperature that was rationalized to be due to the increasing mobility of the charged point defects, most likely oxygen vacancies. These data, however, cannot directly determine whether the observed behavior is due to the direct influence of stress on the polar defects or the indirect reorientation of ferroelastic domains. Further stress-dependent electron paramagnetic resonance measurements are required in order to directly address this.

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