

Pressure as a Probe of the Physics of ABO_3 Relaxor Ferroelectrics

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Abstract. Results on a variety of mixed ABO_3 oxides have revealed a pressure-induced ferroelectric-to-relaxor crossover and the continuous evolution of the energetics and dynamics of the relaxation process with increasing pressure. These common features have suggested a mechanism for the crossover phenomenon in terms of a large decrease in the correlation length for dipolar interactions with pressure – a unique property of soft mode or highly polarizable host lattices. The pressure effects as well as the interplay between pressure and dc biasing fields are illustrated for some recent results on PZN – 9.5 PT, PMN and PLZT 6/65/35.

INTRODUCTION

Much of the recent interest in the field of ferroelectricity has centered on relaxor ferroelectrics (or relaxors).¹ On cooling, these structurally/chemically-disordered crystalline solids exhibit slowing down of the relaxation of their orientational polarization, ultimately resulting in a frozen-in, glass-like state that lacks long-range order. A universal signature of such solids is a broad, frequency-dependent peak in the temperature (T) - dependent susceptibility. The peak defines a dynamic freezing or glass transition temperature, T_m . Contrasted with normal ferroelectrics (FEs), relaxors are also characterized by negligibly small remanent polarization and, generally, the absence of macroscopic phase (symmetry) change at the transition. However, there is symmetry breaking at the nanometer scale leading to the formation of polar nanodomains which exist well above T_m and increase in size on cooling, but never become large enough to precipitate a long-range-ordered FE state at low temperatures.

Compositionally-induced disorder and related random fields are believed to be responsible for the relaxor properties of the most studied and useful relaxors, the mixed ABO_3 perovskites. The parent compounds of these mixed oxides are the prototypical soft mode FEs whose dielectric properties and phase transitions are well understood in terms of lattice dynamical theory.² The physics of relaxors on the other hand is not well understood. The usual approach of studying the properties of many relaxors has been to vary the composition and degree of disorder to induce relaxor behavior. However, this approach introduces complications such as added randomness, lattice defects, lattice strains, and changed interatomic forces. Consequently, there is always considerable vagueness in the interpretation and understanding of experimental results. Illuminating new insight into the physics of systems of this type has recently come from high pressure experiments on La-

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modified $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (or PLZT) samples.³ Starting with compositions that exhibit normal FE behavior at 1 bar, we demonstrated that hydrostatic pressure induces a crossover to a relaxor phase. Since pressure clearly does not induce increased compositional fluctuations and disorder in samples of fixed compositions, pressure is a much "cleaner" variable than chemical composition for studying relaxor phenomena. In contrast to changing the composition at 1 bar, the application of pressure changes only the interatomic interactions and thereby balance between long- and short-range forces making it easier to get to the essential physics.

We have now investigated the influence of pressure on the properties of a number of mixed ABO_3 oxides which include several PLZT compositions³, Ba-modified PZT (or PBZT), $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (or PMN); $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3 + 9.5\% \text{ PbTiO}_3$ (or PZN-9.5 PT)⁴ and a number of $\text{KTa}_{1-x}\text{Nb}_x\text{O}_3$ (or KTN) compositions.⁵ The substituents in the various materials are randomly distributed over the appropriate A or B sites and introduce disorder which leads to relaxor behavior. The results have revealed common general features and suggested a mechanism for relaxor (R) behavior in mixed ABO_3 oxides. Among the most interesting of the results, in addition to the pressure-induced FE-to-R crossover and the stabilization of the R phase at high pressure, are the continuous evolution of the energetics and dynamics of the relaxation process, a spontaneous R-to-FE transition (in the absence of a biasing electric field) at $T < T_m$, the vanishing of this transition with pressure at a critical point, the interplay between pressure and electric field in the FE-R crossover phenomenon, and the vanishing of the R phase at 0 K and high pressure. Unfortunately, space limitations do not allow us to deal with all of these observations here. Consequently, we restrict the presentation to brief accounts of a few of the most recent results. The measurements (largely of the real, ϵ' , and lossy, $\tan\delta$ or ϵ'' , parts of the dielectric function as functions of temperature, pressure and frequency) were performed under hydrostatic pressure using either He gas or a mixture of pentanes as pressure fluids. The reader is referred to published papers^{3,5} for experimental details.

PRESSURE DEPENDENCE OF THE DIELECTRIC RESPONSE – THE FERROELECTRIC-RELAXOR CROSSOVER

We illustrate the influence of pressure on the dielectric response for two mixed ABO_3 crystals: PZN-9.5PT and PMN.

Crystals in the (1-x) PZN-xPT (or PZN-x PT for short) family have been attracting a great deal of recent interest⁶ because ultrahigh piezoelectric ($d_{33} > 2000 \text{ pC/N}$) and electromechanical coupling ($k_{33} \approx 92\%$) coefficients have been achieved for compositions near the morphotropic phase boundary, MPB ($x \approx 0.09-0.095$).^{6,7} PZN is a classic relaxor akin to PMN.^{6,8,9} It exhibits a broad, frequency-dependent $\epsilon'(T)$ peak at $T_m = (\sim 410 \text{ K})$. As in the case of PMN, symmetry breaking compositional and structural disorder brought about by differences in valence (5+ vs. 2+) and ionic radii (0.64 Å vs. 0.74 Å) between the Nb^{5+} and Zn^{2+} ions on the B site of the ABO_3 lattice is believed to be responsible for the relaxor character of PZN. The symmetry breaking (rhombohedral) occurs at the nanometer scale leading to the formation of polar nanodomains which exist well above T_m and increase in size on cooling, but never

become large enough to precipitate a long-range-ordered FE state at T_m .^{9,10} Rather, critical slowing down of the polarization fluctuations sets in below T_m . Unlike PMN which retains macroscopic cubic symmetry down to cryogenic temperatures, PZN acquires rhombohedral symmetry (R3m) at room temperature.⁶

PT, on the other hand, is the classic soft FE mode ferroelectric which transforms on cooling from the cubic paraelectric (PE) phase to a tetragonal (P4mm) FE phase at ~ 760 K.² Its addition to PZN, even at the $0.05 \leq x \leq 0.15$ level, imparts FE character to the mixed crystals.⁷ On cooling such crystals transform from the cubic PE phase to a tetragonal FE phase and then to a rhombohedral FE phase.⁷

Figure 1 shows that the 1-bar dielectric response of our PZN-9.5PT crystal in the unpoled, thermally annealed state is a characteristic FE response.⁴ Scans of $\epsilon'(T)$ and $\tan\delta(T)$ for zero-field heating (ZFH) and zero-field cooling (ZFC) measured along the pseudocubic (100) direction are shown across the tetragonal-cubic FE transition. The value of the transition temperature ($T_c = 460$ K on heating), the sharpness of the transition, and the 5 K thermal hysteresis agree with earlier observations.^{7,11} The relatively weak frequency dispersion in $\epsilon'(T)$ at and above the peak is characteristic of many mixed ferroelectrics. The signature of the rhombohedral-tetragonal transition in zero field is a broad shoulder in $\epsilon'(T)$ centered at ~ 340 K (not shown). The diffuseness of this transition is not unexpected because the sample is essentially at the MPB of the PZN-xPT system, and below T_c the crystal should consist of a mixture of tetragonal and rhombohedral domains. Indeed, a mixture of such domains has been observed in samples of comparable composition.¹²

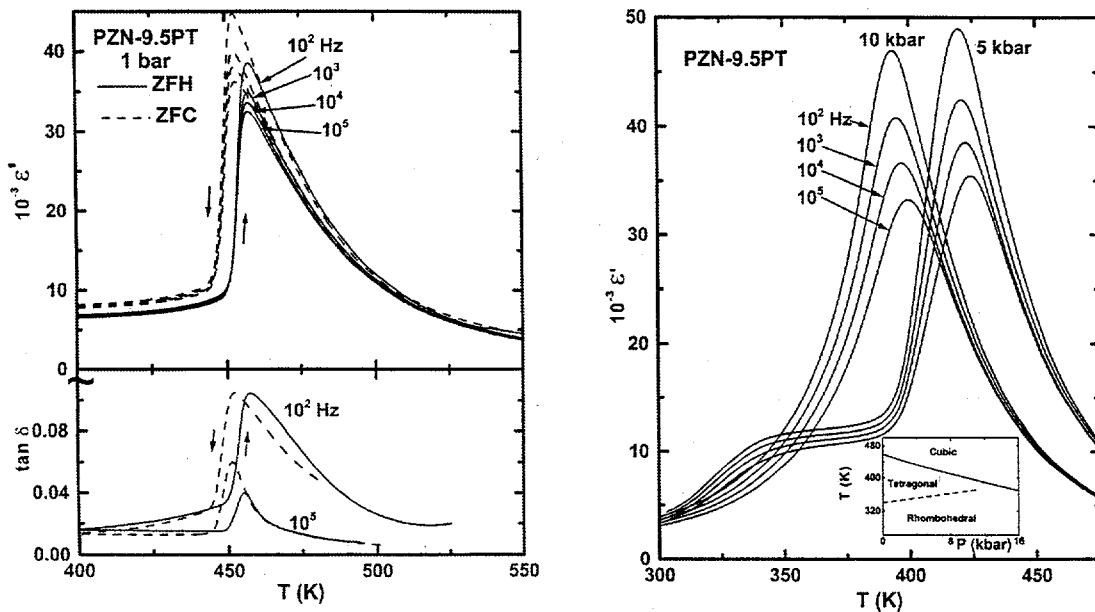


FIGURE 1. (left) Temperature dependences of the dielectric constant (ϵ') and dielectric loss ($\tan\delta$) of PZN - 9.5% PT at 1 bar. Results for both zero field heating (ZFH) and zero field cooling (ZFC) are shown.

FIGURE 2. (right) Temperature dependence of the dielectric constant (ϵ') of PZN - 9.5% PT on ZFC at 5 and 10 kbar. The inset shows a tentative Pressure-Temperature phase diagram.

Modest pressure has a strong influence on the dielectric response and phase transitions of PZN-9.5 PT. Specifically, pressure shifts T_c to lower temperature and induces a FE-to-R crossover in the dielectric response. The crossover evolves with pressure, but is well-established by ~5 kbar in the absence of a biasing field.⁴ Modest fields can, however, re-stabilize the FE phase, as we shall see later. Figure 2 shows some ZFC results at 5 and 10 kbar. The broad $\epsilon'(T)$ peaks and strong frequency dispersion on the low-temperature side at the two pressures shown are the hallmarks of a relaxor phase. These characteristics are seen more clearly in Fig. 3 which shows the response at 15 kbar. This response is the classic relaxor response. Note that there is no thermal hysteresis in T_m .

Figure 2 also shows the $\epsilon'(T)$ anomaly associated with the rhombohedral-tetragonal transition (on cooling at 5 kbar). The anomaly is not observed above 10 kbar, and thus, all vestiges of the "tetragonal phase" vanish above this pressure. The inset in Fig. 2 shows the Pressure-Temperature phase diagram for PZN-9.5% PT.

In the case of PMN, the disorder responsible for the relaxor response is brought about by differences in valence (5+ vs. 2+), ionic radii (0.64 Å vs 0.72 Å) and electronegativities (1.6 vs. 1.2 on the Pauling scale) between the Nb^{5+} and Mg^{2+} ions, respectively. We have chosen PMN for our pressure studies because it is the classic relaxor, and its results offer contrast with the other mixed ABO_3 oxides studied. The sample used was a high quality, dense (96.4%) ceramic containing 0.6 mol % Cu fabricated from chemically-prepared PMN powders. We also investigated small PMN single crystals with similar results.

Figure 4 shows the temperature dependences of ϵ' and ϵ'' of our PMN sample at 1 bar and different frequencies. These relaxor responses are very comparable in terms of magnitudes of ϵ' , ϵ'' and peak temperatures with some of the best single crystals.¹⁰ Also in the figure are the responses at 8 kbar. It is seen that pressure suppresses the magnitudes of ϵ' and ϵ'' in the high temperature phase (and thereby the peaks) and shifts the peaks (T_m) to lower temperatures. This is the expected behavior for ABO_3 oxides and is well understood.² We note that the suppression of $\epsilon''(T)$ in Fig. 4 is mostly due to the suppression of $\epsilon'(T)$. Contrasted with the behavior of PZN-9.5 PT discussed above, pressure in the case of PMN strengthens the relaxor character. This is a feature that is common to all the mixed ABO_3 materials investigated in their relaxor phase.

As already noted, we have now observed the pressure-induced crossover in a variety of different mixed ABO_3 perovskites, and, thus, it appears to be a general phenomenon. Clearly for the pressure case, the crossover is not due to increased compositional fluctuations and disorder. Important questions thus are: what is the cause of this phenomenon? and does it shed any light on the mechanism for relaxor behavior in these materials? Answers for both questions are provided below.

In reflecting on the occurrence of relaxor behavior in perovskites, there appear to be three essential ingredients: (1) the existence of lattice disorder, (2) evidence for the existence of polar nanodomains at temperatures much higher than T_m ¹³ and (3) these domains exist as islands in a highly polarizable (soft mode) host lattice. We believe that the last of these ingredients is the key to understanding the pressure-induced crossover as well as the mechanism for relaxor behavior. We associate the pressure-

induced FE-R crossover with the unique pressure dependence of the soft mode frequency, ω_s , or the polarizability of the lattice, as we now demonstrate.

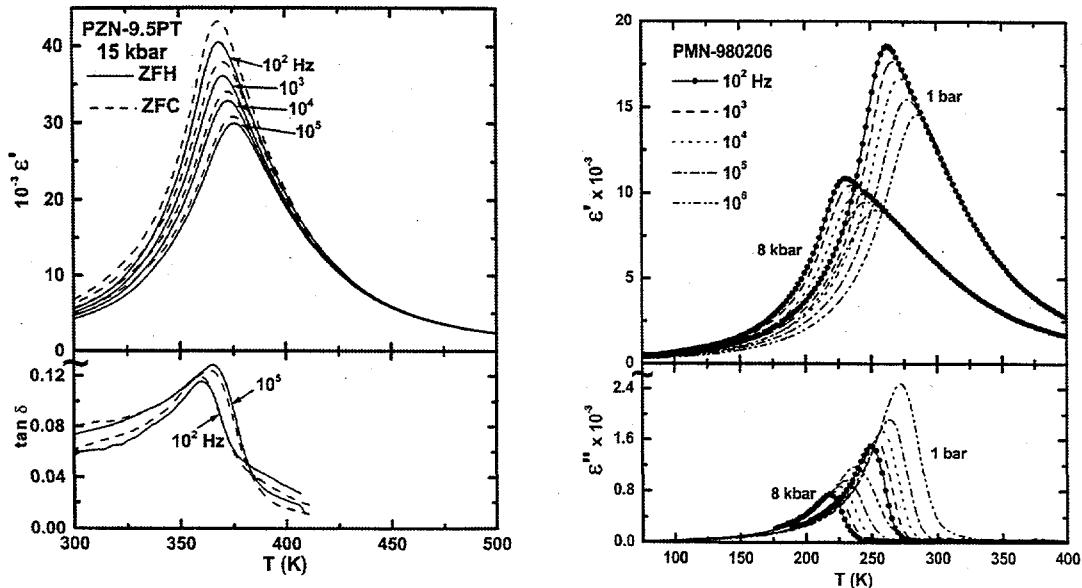


FIGURE 3. (left) Temperature dependences of the dielectric constant (ϵ') and dielectric loss ($\tan \delta$) of PZN – 9.5% PT at 15 kbar for both ZFH and ZFC.

FIGURE 4. (right) Temperature dependences of the real (ϵ') and imaginary (ϵ'') parts of the dielectric function of PMN on ZFH showing the influence of pressure.

The decrease of ω_s with decreasing T in the PE phase causes the polarizability of the lattice and, thereby, the correlation length (r_c) for polar fluctuations (which is inversely related to ω_s) to increase rapidly as $T \rightarrow T_c$. Because ω_s is determined by a delicate balance between long-range and short-range interactions, it is very strongly pressure (or volume V) dependent.² A measure of this dependence is the soft mode Grüneisen parameter, $\gamma \equiv -(\partial \ln \omega_s / \partial \ln V)_T$. For ordinary dielectrics, γ for transverse optic (TO) phonons is on the order of 1-2 and is very weakly temperature dependent. However, for soft ferroelectric (TO) mode systems, like KTaO_3 , PZTs, and other perovskites, γ is very large and strongly temperature dependent – approaching values of several hundred near T_c .² The large value of γ translates to a large increase (decrease) in ω_s (r_c) with pressure. The decrease of r_c with pressure is nonlinear and is largest near T_c where it is estimated to be about 10^3 larger than the decrease in the lattice constant of the host.^{2,14} Thus, modest pressures cause large decreases in r_c and the corresponding correlation volume, as we have demonstrated for several materials.^{3,5,13}

The above results and discussion point to the explanation for the crossover phenomenon. For PZN-PT, PMN and other related mixed ABO_3 perovskites, it is clear that chemical substitution and lattice defects introduce dipolar entities into the lattice. We envision that each such entity will induce polarization (or dipoles) in adjoining unit cells, forming a dynamic polarization “cloud” whose extent is determined by the correlation length for dipolar fluctuations, r_c . At high temperatures

r_c is small and the polarization clouds are effectively polar (FE) nano-domains. With decreasing T at low pressures (i.e., below the pressure needed for inducing the R phase), the rapidly increasing r_c couples these nano-domains into rapidly growing polar clusters and increases their Coulombic interactions. Ultimately, these clusters percolate (or permeate) the whole sample and precipitate a static, cooperative long-range ordered FE state at $T \leq T_c$. At sufficiently high pressure, on the other hand, the clusters increase in size on decreasing T in the PE phase, but do not become large enough to permeate the whole sample (or grains) and precipitate a FE transition. Rather, the clusters exhibit a dynamic "slowing down" of their fluctuations at $T \leq T_m$ leading to the observed relaxor behavior. Because r_c decreases continuously with increasing pressure, the polar clusters become smaller with increasing pressure – a fact that accounts for the observed increase in the frequency dispersion and suppression of the dielectric anomaly. This is what happens in PMN. Pressure reduces the size of its polar nano-domains and strengthens its relaxor character. It is thus seen that the FE-to-R crossover results simply from the large decrease in r_c with pressure – a unique property of soft FE mode or highly polarizable host lattices.

The dipolar entities in relaxors, of course, create random electric fields in the host lattices. The lattice strains x_{ij} associated with these entities also couple to the polarization via terms of the form $x_{ij}P_kP_l$ setting up additional random fields or enhancing their presence. There has been much interest in the influence of random fields on long-range order. Quite sometime ago it was shown theoretically^{15,16} that when the order parameter has continuous symmetry, the ordered state of a large system of less than $d = 4$ dimensions is unstable against an arbitrarily weak random field, i.e., a field much weaker than the interactions which favor the ordered state. Instead of a long-range ordered state, it becomes energetically favorable for such a system to break up on cooling into sufficiently large domains to form a so-called low-temperature domain state. The size of the domains is determined by a balance between the domain wall energy and the statistics of the random field.¹⁵

For systems with uniaxial or cubic anisotropy, long-range order for $d = 3$ can exist in equilibrium, if the width of the random field distribution, δ , does not exceed a critical value, δ_c . A quantitative estimate of δ_c was obtained by Schneider and Pytte¹⁷ for an Ising spin model with infinite-ranged interaction with statistically independent site fields with a gaussian distribution. More recently, Vugmeister¹⁸ examined the existence of long-range (or ferroelectric) order in random-site dipole systems with electric dipole moments possessing cubic anisotropy. He showed that in disordered random-site systems, the critical concentration for the appearance of long-range order is determined by a balance between two competing effects: (i) the interaction energy of the dipolar entities separated by a mean distance, r , and (ii) the width of the static random field distribution. Using an Ising model Hamiltonian with random fields

Vugmeister calculated the phase diagram for the system in terms of the quantity nr_c^{*3} , where n is the density of dipoles and r_c^* is the critical separation needed for the onset of long-range order. In the dilute limit, the system considered by Vugmeister¹⁸ produces a dipolar glass-like phase, and the long-range-ordered state appears only after exceeding a certain critical concentration of dipoles which determines the critical separation r_c^* . Interpreted in terms of this model, the concentration of dipoles or

dipolar nanodomains, n , e.g., for some of the samples we investigated (KTN, KTN:Ca)^{4,5} exceeds the critical concentration at 1 bar or low pressure, and the crystals exhibit a long-range-ordered FE state at low temperatures. With increasing pressure, n scales with the density – a very small effect, i.e., n is essentially constant, but r_c^* decreases rapidly, ultimately falling below the critical value at sufficiently high pressure. Consequently, the dipolar system can no longer achieve long-range order and thus forms a relaxor phase at low-temperatures. This is effectively the argument we advanced above. Here we take r_c^* to be essentially equivalent to the correlation length r_c .

There has been considerable effort aimed at seeking evidence for the existence of a domain state in mixed perovskites. However, there appears to be no unique dielectric signature for such a state, and the issue remains unsettled. The issue is certainly relevant to PMN in particular and to relaxors in general. For these systems an open question has been whether the relaxor state is either (1) a dipolar glass with randomly interacting polar nanodomains in the presence of random fields or (2) an FE state broken up into nanodomains under the constraint of quenched random fields.¹⁹ A recent study¹⁹ of PMN has shed some new light on this question. The authors used 2D ⁹³Nb NMR to determine the temperature dependence of the local polarization distribution function, $W(\bar{p})$, and of the Edwards-Anderson order parameter, q_{EA} . The NMR spectrum was found to consist of a relatively broad and temperature independent component which was attributed to the presence of randomly-oriented, pinned nanodomains, and a relatively narrow and temperature-dependent component, which was attributed to reorientable Nb⁵⁺ nanodomains. This two-phase behavior was described in terms of a “spherical random bond-random field” model for relaxors. For our present purposes the confirmation of the reorientable dipolar nanodomains is a key feature. It relates directly to the arguments advanced above.

FIELD-INDUCED NANO-TO-MACRO DOMAIN TRANSITION

As already noted, in relaxors domain size is determined by r_c . At $T \gg T_m$ domains are on the order of few nm in size, and they grow with decreasing T reaching sizes of 10-100 nm below T_m . The application of a dc biasing electric field can provide much insight into the kinetics and energetics of domain reorientation as well as about the growth of polar domains. On cooling in the absence of a biasing field, the polar nanodomains ultimately freeze into a generally isotropic phase devoid of long-range order, i.e., with random orientations. Cooling in the presence of a biasing field (FC), on the other hand, aligns the domains and increases their r_c and size, effectively canceling the influence of the random fields. For sufficiently large biasing fields the domains become large (~microns in size) and lead to the onset of long-range order and ferroelectricity. This is a field-induced nano-to-macro domain transition. Evidence for such a transition in relaxors can be inferred from the dielectric response and can often be seen in TEM images and from scattering data.²⁰

Here we illustrate some interesting field-induced effects in PLZT 6/65/35 and PZN-9.5 PT. This PLZT composition is at the FE/R boundary at 1 bar, and the

application of even a weak field stabilizes the FE phase. Figure 5 shows the dielectric response at 4 kV/cm at 1 bar. The field was applied at 295 K and it stabilizes the rhombohedral FE phase. On heating under bias (FH), the sample undergoes a FE-to-PE phase transition as seen in the characteristic $\epsilon'(T)$ and $\tan\delta(T)$ signatures shown. The broad peaks are characteristic of polycrystalline ceramic samples. Subsequent cooling from the PE phase under bias (FC) reveals the reverse PE-to-FE transition, but with a 3 K thermal hysteresis indicating a first-order transition. The dielectric response is essentially frequency independent for both FH and FC cycles as is typical of normal FEs. A second FH and FC cycle reproduces the first. The figure also shows zero field cooling (ZFC) results after FH into the PE phase. Both the $\epsilon'(T)$ and $\tan\delta(T)$ responses are characteristic of the R state.

Figures 6 (a) and (b) show the influence of 4 kV/cm bias on the $\epsilon'(T)$ response at 10 kbar. This response is fundamentally different from that at 1 bar. In the absence of bias, the material exhibits full relaxor character at 10 kbar.³ As in the 1 bar case, application of a 4 kV/cm bias at 295K stabilizes the rhombohedral phase. However, on FH at 10 kbar the sample undergoes a sharp, dispersionless, first-order FE phase transition. Immediately thereafter the sample "remembers" that its ground state at 10 kbar is a relaxor state, and it exhibits the evolution of such a state before it enters the PE phase at high temperatures. The behavior is reversed on FC but with a hysteresis of 7 K for the FE transition and no hysteresis for the relaxor phase. Evidently the biasing field increases r_c just enough at 10 kbar to strengthen the collective behavior of the polar domains increasing their size and stabilizing the FE phase at low temperatures. On heating, r_c decreases just enough to result in a spontaneous phase

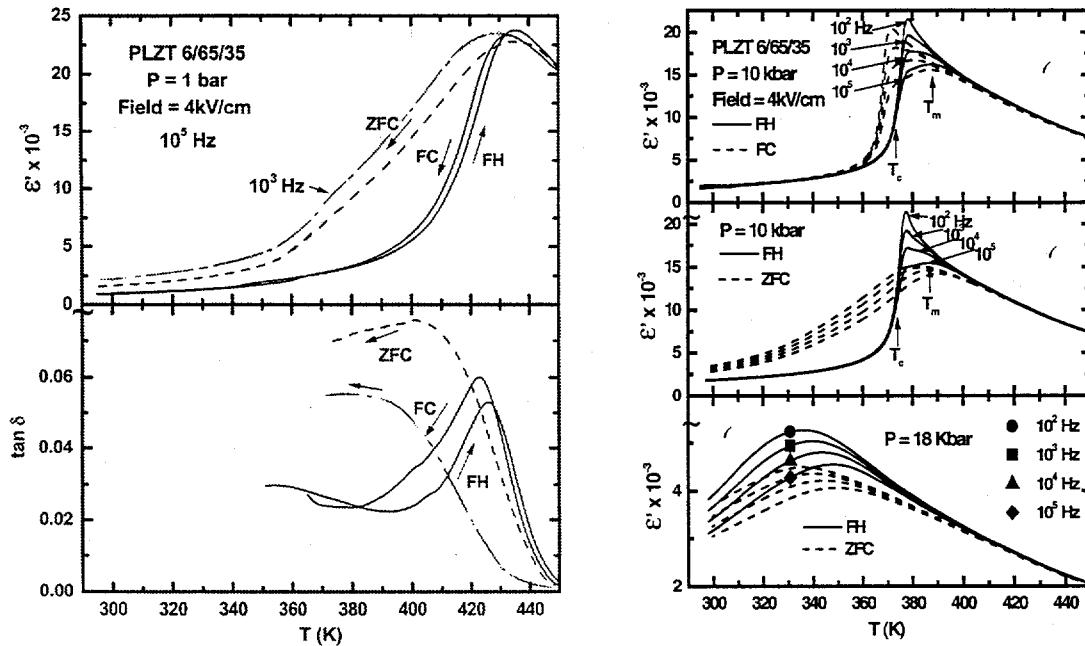


FIGURE 5. (left) Influence of a dc field on the dielectric response of PLZT 6/65/35. All data are at 10^5 Hz except as noted.

FIGURE 6. (right) Influence of a dc field on the dielectric response of PLZT 6/65/35.

transition at T_c following which r_c becomes too short to sustain long-range order and results in an R phase, which on continued heating transforms to the PE phase. The sequence is reversed on field cooling. However, on ZFC at 10 kbar the sample reveals its full relaxor ground state (Fig. 6b).

At a still higher pressure (18 kbar, Fig. 6c) the response changes qualitatively. At this pressure r_c and the polar domains are too small for a 4 kV/cm field to overcome the random freezing of the domains. Consequently, only the R phase is observed under FC and FH conditions as well as in the absence of a bias.

In the case of PZN-9.5 PT, a 4 kV/cm biasing field restabilizes the FE phase at pressures \leq 15 kbar; however, unlike the response of PLZT in Figs. 6(a) and (b), the dielectric signature of the FE transition is a frequency-independent diffuse peak in ϵ' (T). Results on FC from 530 K to 300 K followed by FH from 300 K to 530 K at 15 kbar are shown in Fig. 7. There is no frequency dispersion and practically no thermal hysteresis in T_c at this pressure. Comparison with the results in Fig. 3 shows that T_c is considerably higher than T_m in the absence of bias at the same pressure. Other results suggest that the 4 kV/cm field is just barely capable of reestablishing the FE phase at 15 kbar, and we expect the relaxor state to remain as the ground state of the crystal at higher pressures at this field.

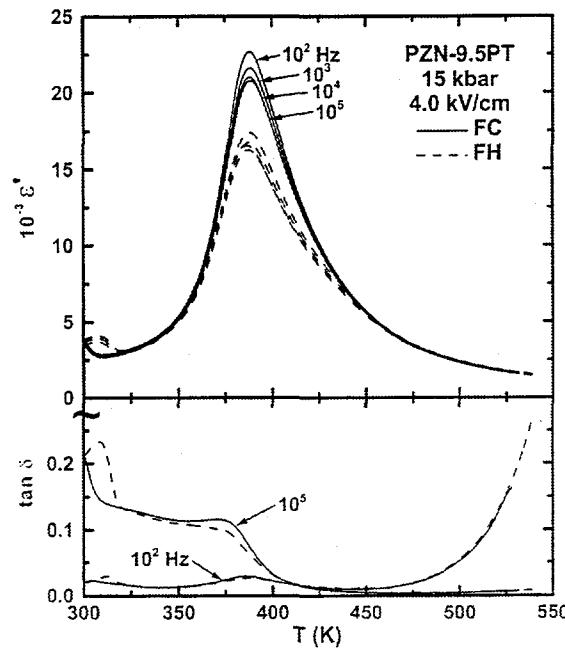


FIGURE 7. Temperature dependences of the dielectric constant and $\tan \delta$ of PZN – 9.5 PT at 15 kbar and 4 kV/cm

The above results are characteristic of other ABO_3 relaxors, and thus reveal general trends which can be understood in terms of the large and unique pressure dependence of the soft mode frequency or the polarizability of the host lattice. The results also point to an analogy between increasing pressure and increasing the degree of disorder by chemical substitution on the onset and evolution of the R phase. In both cases it is

the decrease in correlations among polar domains that leads to the onset of R behavior, but it is the pressure results that clarify the physics.³ The interplay between pressure and external electric fields provides further insights into the energetics and dynamics of the FE-R transition.

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