SAND2000-0278C

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Pressure as a Probe of the Physics of Relaxor Ferroelectrics

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Pressure studies have provided new insights into the physics of compositionally-disordered ABO_3 oxide relaxors. Specifically, results will be presented and discussed on a pressure-induced ferroelectric-to-relaxor crossover phenomenon, the continuous evolution of the energetics and dynamics of the relaxation process, and the interplay between pressure and electric field in determining the dielectric response.

[ferroelectric, relaxor, perovskite, soft mode, polar domains, correlation length]

1. 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 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 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. We have advocated that hydrostatic pressure is a much “cleaner” variable.[3] By applying pressure to a sample of fixed composition, one varies only the interatomic interactions and balance between long- and short-range forces, making it easier to get to the essential physics. This paper illustrates this approach.

We have investigated the influence of pressure on the properties of a number of mixed ABO_3 oxides which include several compositions of La-modified $PbZr_{1-x}Ti_xO_3$ (or PLZT), Ba-modified PZT (or PBZT), $PbMg_{1/3}Nb_{2/3}O_3$ (or PMN); $PbZn_{1/3}Nb_{2/3}O_3$ + 9.5% $PbTiO_3$ (or PZN-9.5 PT) and a number of $KTa_{1-x}Nb_xO_3$ (or KTN) compositions. The various substituents are randomly distributed over the A or B sites and introduce disorder which leads to relaxor behavior. The results show common general features and have revealed the mechanism for relaxor behavior in mixed ABO_3 oxides. Among the most interesting of these results are the observations of (1) a pressure-induced FE-to-R crossover and the stabilization of the R phase, (2) continuous evolution of the energetics and dynamics of the relaxation process, (3) a spontaneous R-to-FE transition (in the absence of a biasing electric field) at $T < T_m$, (4) the vanishing of this transition with pressure at a critical point, and (5) the interplay between pressure and electric field in the FE-R crossover phenomenon. Unfortunately, space limitations do not allow us to deal with all of these results here. Consequently, we restrict the presentation to brief accounts of a few of the common features. The measurements (largely of the real and lossy 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 fluid. The reader is referred to published papers[3,4] for experimental details.

2. Ferroelectric-Relaxor Crossover

We illustrate the pressure-induced FE-to-R crossover for two different materials: a PLZT composition with 65 mol % Zr, 35 mol % Ti and 6 mol % La referred to as PLZT 6/65/35 and a KTN sample with 2.3 at % Nb which also contains 0.055 at % Ca. In the PLZTs the substitutions of La^{3+} for Pb^{2+} introduces A site vacancies and breaks translational symmetry. For low La concentrations the materials exhibit normal FE transitions, but for large concentrations they are relaxors. PLZT 6/65/35 was chosen because it is very close to FE-R boundary. In the absence of relaxor behavior, the expected response at (1 bar) is for this material to transform on cooling from the high T cubic PE phase to the rhombohedral FE phase at ~440 K, and the dielectric response should be essentially independent of frequency. Figure 1 shows the T dependence of ε'. Starting in the PE phase, ε' increases with decreasing T in a Curie-like manner and exhibits a maximum at the expected PE-FE transition temperature, T_m. ε' is independent of frequency in the PE phase, but exhibits very weak frequency dispersion just below T_m, indicating that the sample is on the verge of entering the R phase. On further cooling, FE behavior with rhombohedral symmetry is observed. This response can be understood as follows. On cooling in the PE phase, the

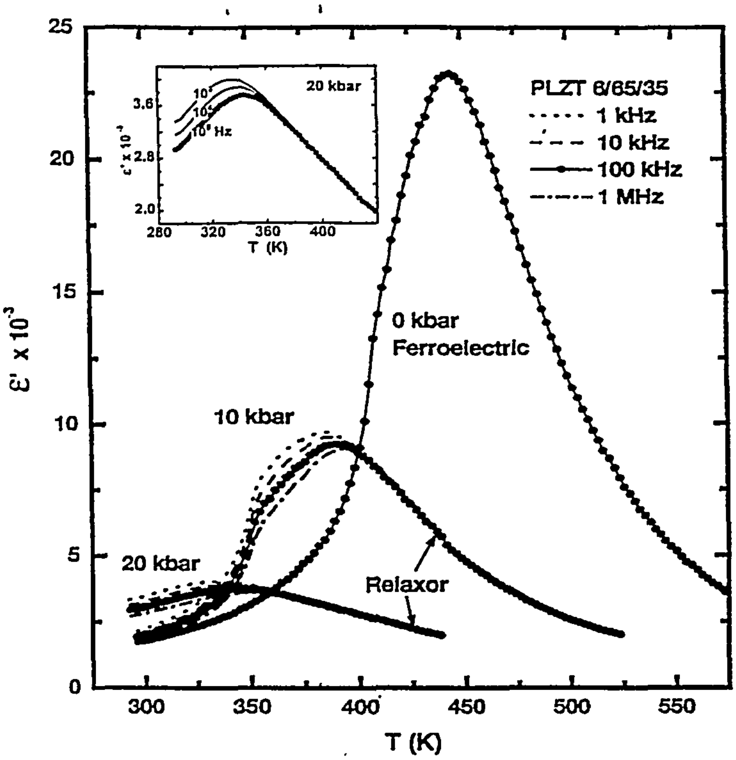

Fig. 1. Pressure-induced FE-R crossover in PLZT 6/65/35.

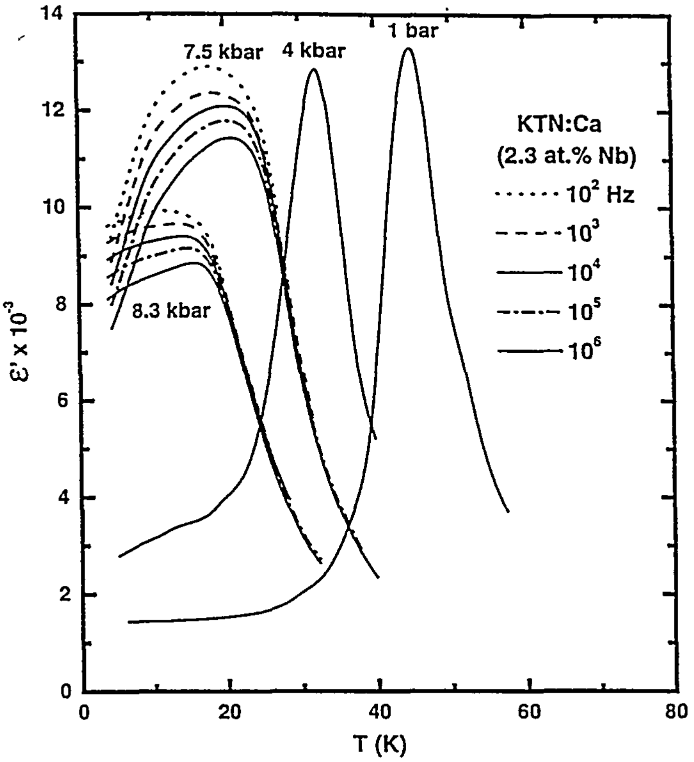

Fig. 2. Pressure-induced FE-R crossover in KTN:Ca.

disorder-induced polar nanodomains grow and become large and nearly static (hence the weak frequency dispersion at $T < T_m$), but not sufficiently large to condense a full FE state at T_m. Continued correlation among the dynamically slowed-down domains due to the high polarizability of the host lattice results in their further growth and condensation into macro-domains and an FE state below T_m.

Pressure causes large decreases in the amplitude for the $\varepsilon'(T)$ anomaly at T_m and in the transition temperatures and induces full relaxor character for the PE-R transition (Fig. 1). The inset in Fig. 1 provides an expanded view of the 20 kbar response and shows the classic dipolar, glass-like relaxor response.

In KTN with small Nb content, the Nb^{5+} ion occupies an off-center position leading to a large dipole moment.[4] Above ~2 at % Nb these materials exhibit normal FE transitions, but below 2 at. % relaxor behavior sets in. Figure 2 shows the $\varepsilon'(T)$ response of our sample. At 1 bar the response is the classic FE signature with ε' essentially independent of frequency. Up to ~6.5 kbar the main influence of pressure is a decrease in T_c as is commonly observed for many soft mode FEs. At ~ 7 kbar there is a qualitative change in the $\varepsilon'(T)$ response signifying an FE-to-R crossover as seen in the 7.7- and 8.5-kbar isobars.

As already noted, we have now observed this pressure-induced FE-to-R crossover in many compositionally-disordered ABO_3 oxides and believe it to be a general phenomenon in soft phonon mode systems. The crossover can be explained in terms of a large decrease in the correlation length, r_c, among polar nanodomains with pressure – a unique property of soft FE mode systems where the soft mode frequency, ω_s, controls the polarizability of the host lattice and, thereby, r_c.[3] Specifically, in the high temperature PE phase $\omega_s(r_c)$ decreases (increases) with decreasing temperature, but increases (decreases) with increasing pressure. The effects are quite large; e.g., for our KTN crystal we estimate that at 44 K r_c decreases by a factor of ~8 between 0 and 8.5 kbar, and the corresponding correlation volume decreases by a factor of over 500.[4]

Physically, we envision each disorder-related dipole inducing polarization (or dipoles) in adjoining unit cells of the highly polarizable host and forming a dynamic "polarization cloud" whose extent is determined by r_c. At high temperatures r_c is small, and the polarization clouds are effectively polar nanodomains. With decreasing T at low pressures, the rapidly increasing r_c couples these nanodomains 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 $T < T_c$. 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) to precipitate a FE transition. Rather, the clusters exhibit dynamic "slowing down" of their fluctuations at $T < T_m$ 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 frequency dispersion and the suppression of the dielectric anomaly (Figs. 1 and 2). It is thus seen that the FE-to-R crossover results simply from the large decrease in r_c with pressure.

3. Dynamics of the Dipolar Freezing Process

The upper inset in Fig. 3 shows the relaxational dielectric response of a typical relaxor (PBZT) below T_m. These results reflect the dynamics of the dipolar freezing process. They define relaxation frequencies, f, corresponding

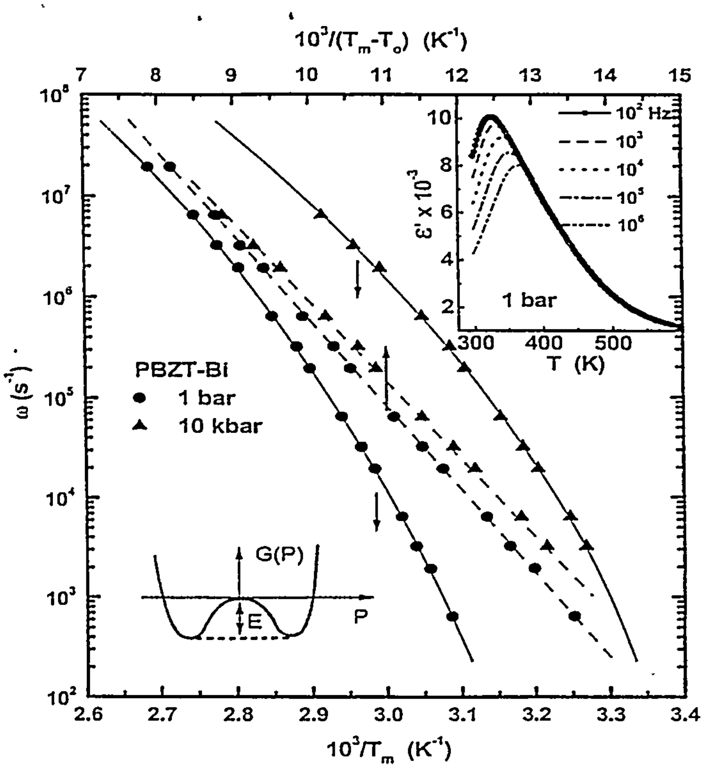

Fig. 3. Non-Arrhenius behavior of the dipolar relaxation time ($\tau = 1/\omega$) for PBZT.

to the peak temperatures, T_m, and characteristic relaxation times, $\tau = 1/\omega$, where $\omega = 2\pi f$ is the angular frequency.

Since relaxation processes are usually thermally activated, it is natural to present relaxation data as Arrehenius plots of ln ω vs. $1/T_m$. Such plots for many relaxors at 1 bar and at the higher pressures reveal the non-Arrehenius character of the response and the large decrease of τ with pressure as shown in Fig. 3 for PBZT. The departure from Arrehenius behavior can be generally satisfactorily described in a variety of ways many of which can be expressed[3] in the form of the Vogel-Fulcher (V-F) equation $\tau^{-1} = \omega = \omega_0 \exp[-E/k(T_m - T_0)]$ which is found to be applicable to many relaxational phemonena. Here ω_0 is the attempt frequency related to the cut-off frequency of the distribution of relaxation times, E is the energy barrier between equivalent dipole directions, and T_0 is a reference temperature where all relaxation times diverge (and where the distribution of τ's becomes infinitely broad). T_0 can be viewed as the "static" dipolar freezing temperature for the relaxation process. Figure 3 shows that the 1 bar and 10 kbar data are well-fit by this Eq., the fitting parameters being E = 0.17 (0.15) eV, T_0 = 250 (230) K and $\omega_0 = 1.0 \times 10^{14}$ (4.4×10^{13})s^{-1} for the 1 bar (10 kbar) data, respectively.

These results agree with expectation: the decrease in E is a manifestation of the decrease in the size of the polar nanodomains with pressure, as noted earlier. Simply stated, smaller domains are easier to reorient than larger domains, hence a lower E. The decrease in T_0 with pressure is the expected response for a perovskite, and it is satisfying to note that dT_0/dP is comparable to $dT_m/dP \simeq -3$ K/kbar.

A physical picture of the energetics of the behavior can be gleamed from examining the free energy of a polar region having two equivalent directions of polarization, P, as shown in the lower inset in Fig. 3. E is the energy barrier separating the two alternative domain states. Because ferroelectricity is a cooperative phenomenon, all energies scale with the volume of the domain, so that E ∝ volume. For a macroscopic domain, E is larger than the thermal activation energy, kT, and the dipolar region will be stable with fixed orientation. However, as the volume of the polar region decreases so does E, and ultimately for small enough volumes kT ≥ E, the dipolar orientation becomes unstable fluctuating within the polar region. At 1 bar the magnitude of E for a given relaxor is determined by temperature and the local chemistry. Pressure, as we have seen, strongly reduces the size of polar domains in ABO_3 relaxors leading to lower Es. It is the magnitude of E which determines the behavior of the polarization, and hence the properties of the R phase.

4. Field-Induced Nano-to-Macro Polar Domain Transition

As already noted, in highly polarizable hosts each dipole induces polarization in a domain whose size is determined by r_c. At T » T_m these domains in relaxors 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, i.e., zero field cooling (ZFC), the reorienting polar nanodomain ultimately freeze into an 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 polar domains and increases their r_c and size, effectively cancelling the influence of the random fields. For sufficiently large 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 can be seen in TEM images and from scattering data.[5]

Here we illustrate some interesting field-induced effects in PLZT 6/65/35. As already noted, this composition is at the FE/R boundary at 1 bar, and the application of even a weak field stabilizes the FE phase. Figure 4 shows the dielectric response at 4 kV/cm. 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 $\varepsilon'(T)$ and tanδ(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 cycle reproduces the first.

Figures 5 (a) and (b) show the influence of 4 kV/cm bias on the $\varepsilon'(T)$ response at 10 kbar. This response is fundamentally different from that at 1 bar. Recall that in the absence of bias, the material exhibits full relaxor character at 10 kbar. On FH at 10 kbar the sample undergoes a very sharp, dispersionless, first-order phase transition followed by the evolution of a relaxor phase and ultimately a transition to the PE phase. The behavior is reversed on FC but with a hysteresis of 7 K for the FE transition. Evidently the field increases r_c just enough at 10 kbar to strengthen the

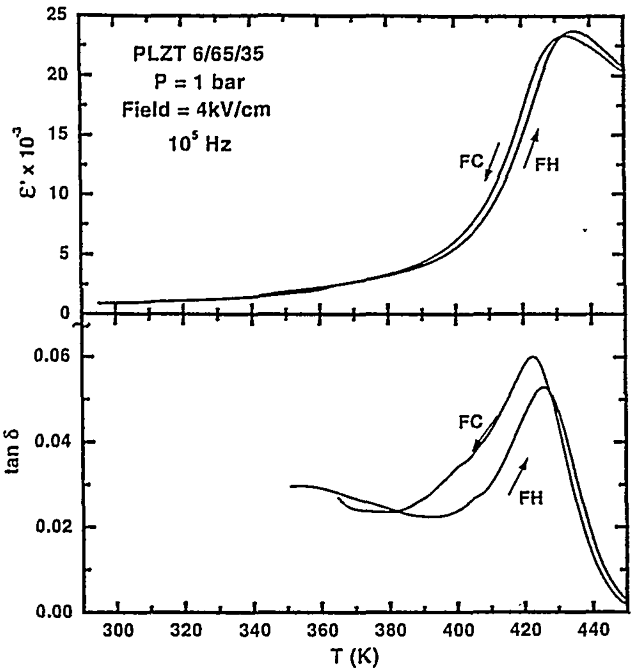

Fig. 4. Influence of a dc field on the dielectric response of PLZT 6/65/35.

collective behavior of the polar domains and stabilize the FE phase. On heating r_C decreases just enough to result in a spontaneous phase 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.

At a still higher pressure (18 kbar, Fig. 5c) the response changes qualitatively. Here 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.

5. Concluding Remarks

All of 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 which controls the polarizability of the host lattice. The interplay between pressure and external electric fields provides further insights into the energetics and dynamics of the FE-R transition.

Acknowledgement

I express appreciation to L. V. Hansen for technical support. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

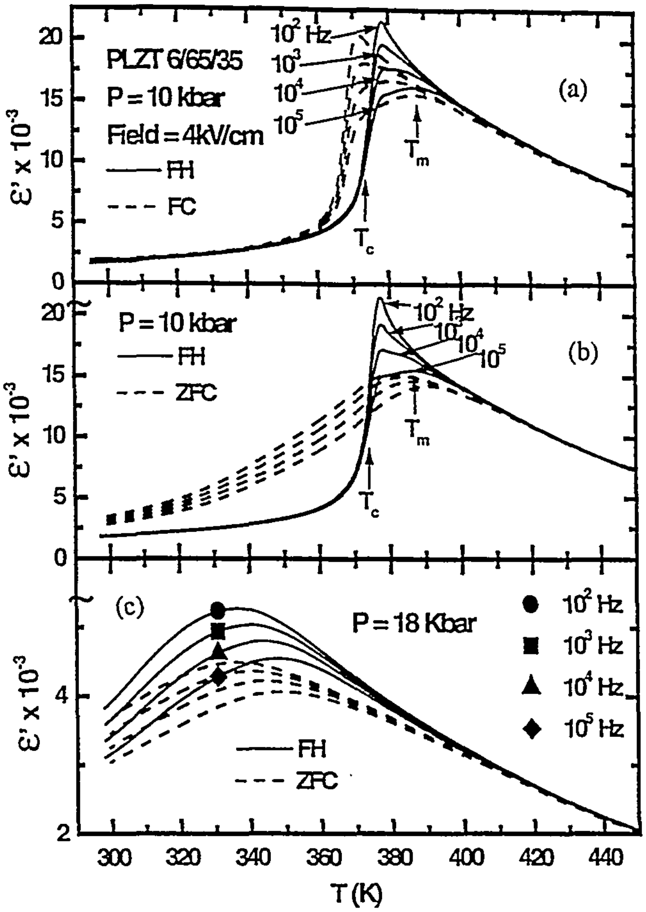

Fig. 5. Influence of a dc field on the dielectric response of PLZT 6/65/35.

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