Pressure-Induced Crossover from Long- to Short-Range Order in Compositionally Disordered Soft Mode Ferroelectrics

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Results on a lanthanum-modified, lead zirconate-titanate have revealed (1) pressure-induced crossover from normal ferroelectric- (nFE-) to-relaxor (R) behavior; (2) the continuous evolution of the dynamics of the relaxation process; (3) a spontaneous R-to-nFE transition at a temperature well below the dynamic glass temperature of the R phase; and (4) the vanishing of this transition with pressure at a critical point. These results can be understood in terms of a large decrease in the correlation radius among polar nanodomains—a unique property of soft ferroelectric phonon mode systems. [S0031-9007(96)00638-2]

Motivated by the strong interest in developing an understanding of the relaxational properties of highly disordered ferroelectrics, we have investigated the dielectric properties of a lanthanum-modified, lead zirconate-titanate (or PLZT) material. The key results summarized in the abstract provide new insights into the physics of disordered soft mode ferroelectrics.

In ferroelectrics, relaxor behavior results from either frustration- or compositionally induced disorder [1–3]. The latter type of disorder and related random fields are believed to be responsible for the relaxor properties of mixed perovskite oxides such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (or PMN) [2], $KTa_{1-x}Nb_xO_3$ (or KTN) [3], $K_{1-x}Li_xTaO_3$ (or KLT) [1], $Pb(Sc_{0.5}Ta_{0.5})O_3$ (or PST) [4], and La-modified $PbZr_{1-x}Ti_xO_3$ (or PLZT) [5]. The parent compounds of these materials are the prototypical soft ferroelectric (TO) mode systems. A newly discovered feature in the response of some of these materials is the observation of a spontaneous, first-order relaxor- (R-) to-normal ferroelectric (nFE) transition on cooling *in the absence of a poling electric field*. Specifically, this transition has been observed in: (1) disordered PST, where it vanishes with the introduction of vacancies [4], (2) KLT, where it is observed above a critical (2.2 at.%) Li concentration [6]; and PLZT $x/40/60$, where it is observed over a narrow range of La concentration x (namely around 12 at.%) [5].

The physics of the relaxor behavior and R-nFE transition is not well understood. The usual manner of studying these properties has been to vary the composition and degree of disorder in order to induce relaxor behavior. However, these approaches introduce complications such as added randomness, compositional fluctuations, lattice defects, and changed interatomic forces. Consequently, there is always considerable vagueness in interpretation. We suggest that hydrostatic pressure is a much "cleaner" variable for studying such systems. 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 simpler to get to the essential physics. This paper demonstrates the value of this approach.

For the present study we selected a PLZT composition near the ferroelectric-relaxor boundary. The substitution of La^{3+} for Pb^{2+} on the A sites in lead zirconate-titanate (PZT) leads to a well-known family of ceramics having the chemical formula $(Pb_{1-3x/2}La_x)(Zr_{1-y}Ti_y)O_3$, or PLZT, with unusual dielectric and electro-optic properties [7]. The La^{3+} ions and accompanying vacancies (one vacancy for every two La^{3+} ions), which are randomly distributed on the A sites, represent a type of disorder which significantly modifies the properties of these materials. One manifestation of this disorder is the condensation of local dipolar nanodomains leading to local, randomly oriented polarization at a temperature much higher than the ferroelectric transition temperature (T_c) [8]. These polar nanodomains increase in size with decreasing temperature and, for relatively low La concentration, ultimately result in the formation of macroscopic ferroelectric domains with long-range FE order. The peak in the dielectric constant at T_c is relatively sharp and independent of frequency below the GHz range. For higher La concentrations, the disorder hinders the onset of long-range order, and the polar nanodomains condense below the freezing temperature (T_m) of the polarization fluctuations [9] into a glasslike, or *relaxor*, state with no macroscopic phase (symmetry) change. For the particular system La-modified $PbZr_{.65}Ti_{.35}O_3$ (PZT 65/35), relaxor behavior in the dielectric response becomes experimentally discernible [9] for La concentrations above ~6 at.%.

Thus for the present study we chose a composition with 6 at.% La or PLZT 6/65/35. It was prepared by conventional mixed oxide synthesis and processing [7]. The sample used was a thin plate whose large faces were sputter coated by Cr followed by Au. Information about the phase transitions and relaxational

properties was obtained from dielectric constant (ϵ') and dissipation ($\tan\delta$) measurements. These measurements were performed *without a dc biasing field* as functions of frequency ($10^2 - 10^6$ Hz), temperature (290–600 K) and hydrostatic pressure (0–20 kbar) [10].

In the absence of relaxor behavior, the expected response of PLZT 6/65/35 at 1 bar is for it to transform on cooling from the high temperature cubic paraelectric (PE) phase to a rhombohedral nFE phase at ~440 K [9]. Figure 1 shows the temperature dependences of ϵ' and $\tan\delta$ at 1 bar at different frequencies. Starting in the PE phase, ϵ' increases with decreasing temperature in a Curie-like manner and exhibits a maximum at the expected PE-FE transition temperature, which we denote by T_m. ϵ' is frequency independent in the PE phase, and its magnitude ϵ_{max} at T_m is also essentially independent of frequency. T_m exhibits weak dispersion having a value of 442 K at 10^2 Hz and increasing to 447 K at 10^6 Hz with most of this increase occurring above 10^4 Hz. On further cooling below T_m, there is some dispersion in the magnitude of ϵ', primarily above 10^4 Hz. This dispersion becomes considerably smaller below a spontaneous R-to-nFE transition denoted by T_x in Fig. 1 and manifested by a sharper drop in $\epsilon'(T)$ and a sharp frequency-independent peak in the $\tan\delta(T)$ response. These anomalies are the signature of this type of transition as seen earlier in PST [4], KLT [6], and PLZT 12/40/60 [5].
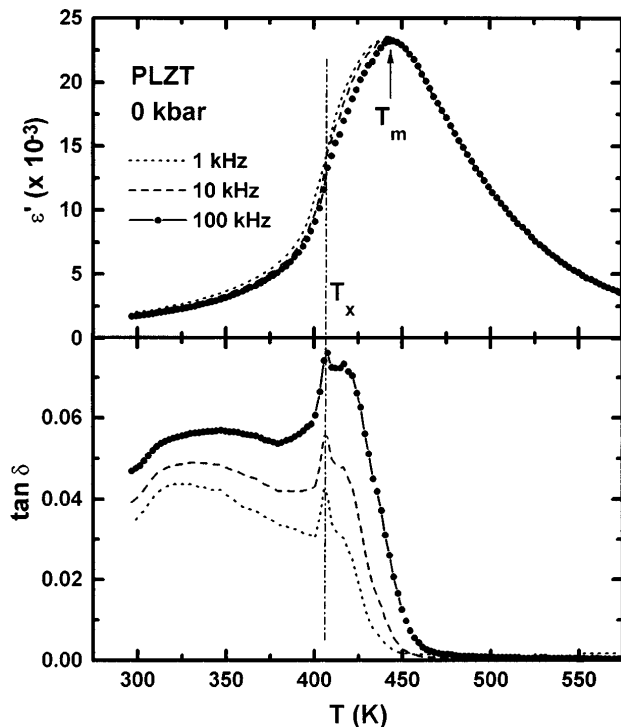
Pressure causes large decreases in the amplitude of the $\epsilon'(T)$ anomaly at T_m and in the transition temperatures and induces full relaxor character for the PE-R transition by 5 kbar. Figure 2 shows that at 15 kbar there is still no frequency dispersion in T_x, but there is increased dispersion in ϵ' at $T \leq T_x$ compared with the response at lower pressures. Taking the difference, ΔT, in T_m between 10^6 and 10^2 Hz as a measure of the dispersion in T_m, the inset in Fig. 2 shows the change in ΔT with pressure. Clearly, this dispersion evolves for reasons which will become clear later. Figure 3 shows the response at 20 kbar which is the classic dipolar, glasslike response of a relaxor ferroelectric, with strong dispersion continuing to lower temperatures as discussed below.

A key feature of the response at 20 kbar is the apparent vanishing of the R-nFE transition at T_x. Figure 4 shows the shifts in T_m and T_x with pressure measured at 10^5 Hz. Within experimental uncertainty, T_m and T_x have the same slope, namely, $dT_{m,x}/dP = -5.2 \pm 0.2$ °C/kbar, a value comparable to that for many perovskite ferroelectrics which can be understood in terms of soft mode theory [11]. Note that the difference $T_m - T_x$, 38 K, is essentially independent of pressure up to 15 kbar. If this trend were to continue to higher pressures, then at 20 kbar T_x would be 305 K. Reference to Fig. 3 shows that there is no evidence for this transition in either the $\epsilon'(T)$ or the $\tan\delta(T)$ data down to 290 K. The transition is, however,
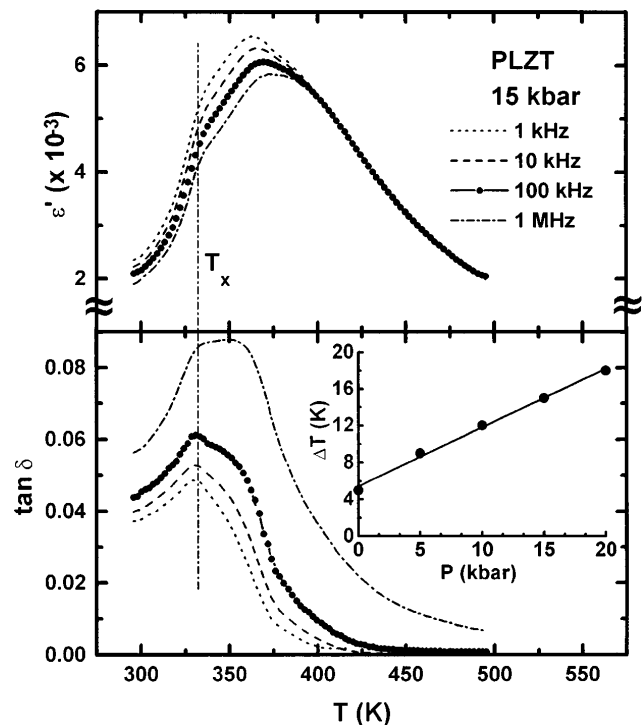

FIG. 1. Temperature and frequency dependences of the dielectric constant (ϵ') and the dissipation ($\tan\delta$) for PLZT 6/65/35 at 1 bar (0 kbar).

FIG. 2. Temperature and frequency dependences of ϵ' and $\tan\delta$ for PLZT 6/65/35 at 15 kbar. The inset shows the increase in the frequency dispersion in T_m with pressure.

clearly evident for $P \leq 15$ kbar as marked by T_x in Figs. 1 and 2. Thus the transition vanishes between 15 and 20 kbar. Support for this assertion is provided by the $\tan\delta(T)$ data in Figs. 1 and 2 which show that the $\tan\delta(T)$ peak associated with T_x broadens considerably with increasing pressure with indication that it may vanish.

Results as in Figs. 2 and 3 define relaxation frequencies f corresponding to the peak temperatures T_m and characteristic relaxation times $\tau = 1/\nu$, where ν is the angular frequency $(= 2\pi f)$. Since relaxation processes are usually thermally activated, it is natural to present relaxation data as Arrhenius plots of $\ln\nu$ vs $1/T_m$. Such plots for the present data at the higher pressures reveal the non-Arrhenius character of the response as has been observed for other systems [3,9]. This departure from Arrhenius behavior can be satisfactorily described in a variety of ways, many of which can be expressed [3] in the form of the Vogel-Fulcher (VF) equation $\tau^{-1} = \nu = \nu_0 \exp[-E/k(T - T_0)]$, which is found to be applicable to many relaxational phenomena [3]. The parameters in this equation can be given the following physical interpretations [12]: ν_0 is the attempt frequency related to the cutoff frequency of the distribution of relaxors, E is an activation energy, 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. The inset in Fig. 3 shows a VF plot

at 20 kbar. This fit yields $\nu_0 = 6.6 \times 10^{13}$ s^{-1}, $E = 740$ K ($= 54$ meV), and $T_0 = 303$ K. For the 15 kbar data, $E = 1210$ K and $T_0 = 330$ K. These results show the expected large decrease of E with pressure and, satisfyingly, they yield $dT_0/dP \approx -5$ K/kbar, which is of the same magnitude as dT_m/dP. An important manifestation of the results is a large decrease in the relaxation time with pressure. This is a consequence of the large decrease in the correlation length or radius r_c among nanopolar domains with pressure as discussed below.

In earlier work on KTaO$_3$ with dilute dipolar Nb substitution for Ta, we observed pressure-induced relaxor behavior which was interpreted in terms of a novel, pressure-induced crossover phenomenon from long-range FE order to dipolar glass behavior [3]. We believe that this phenomenon is a general feature of soft mode ferroelectrics with dipolar impurities, or polar nanodomains, and is a consequence of the unique pressure dependence of the soft mode frequency ω_s, which controls the polarizability of the host lattice. Since ω_s decreases and tends to zero as $T \to T_c$, the polarizability of the lattice, and thereby r_c for polar fluctuations, which are inversely related to ω_s, increase rapidly as $T \to T_c$. Because ω_s is determined by a delicate balance between long- and short-range interactions, it is very strongly pressure (or volume, V) dependent [3]. A measure of this dependence is the soft mode Grüneisen parameter γ, $\equiv -(\partial \ln\omega_s/\partial \ln V)_T = \frac{1}{2}(\partial \ln\epsilon'/\partial \ln V)_T$, which is simply the ratio of the fractional change in ω_s to the fraction change in V. For ordinary dielectrics, γ for transverse optic (TO) phonons is on the order of 1–2 and very
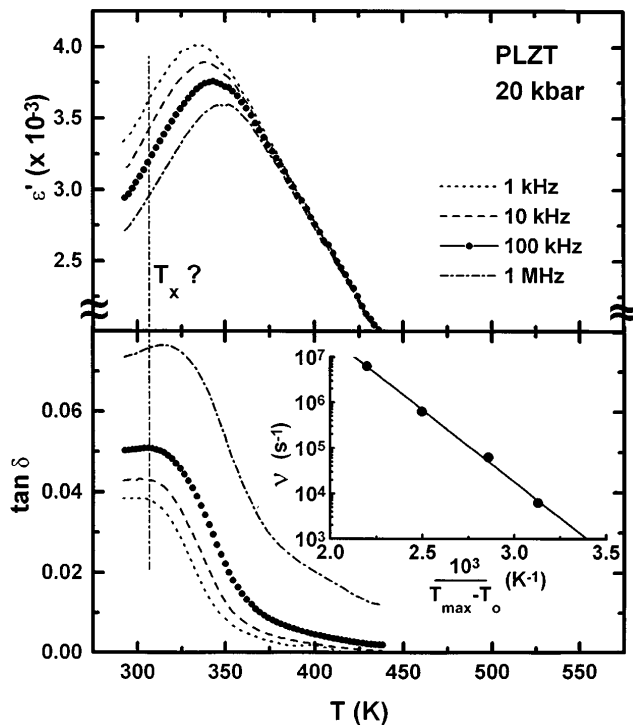

FIG. 3. Temperature and frequency dependences of ϵ' and $\tan\delta$ for PLZT 6/65/35 at 20 kbar. The inset shows a Vogel-Fulcher plot for the relaxational process.
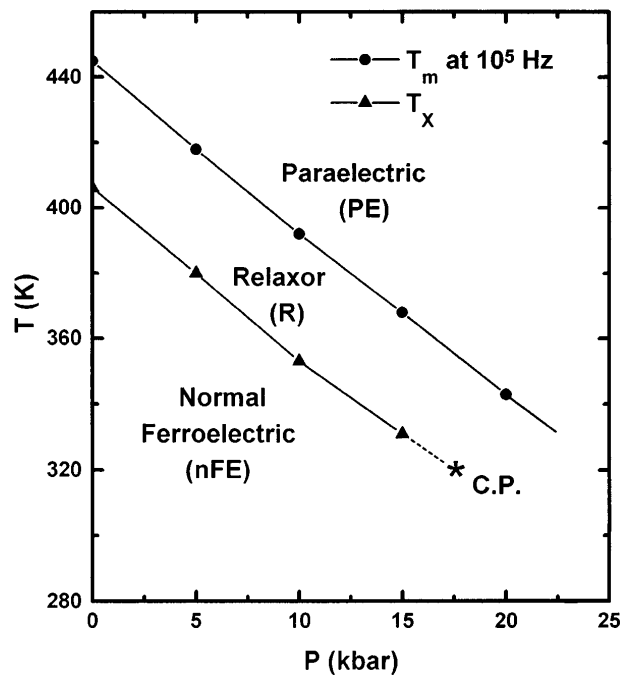

FIG. 4. Phase diagram of PLZT 6/65/35.

weakly temperature dependent. However, for soft TO mode hosts like PZT 65/35 and other perovskites, γ is very large and increases with decreasing temperature approaching values of several hundred as $T \rightarrow T_c$. The large γ translates to a large increase (decrease) in ω_s (r_c) with pressure. The decrease of r_c with pressure is nonlinear and largest at T_m where we estimate it to be about 10^3 larger than the decrease in the lattice constant of the host [3]. For the present case we estimate that r_c decreases by a factor of ~ 2.5 between 0 and 20 kbar.

On the basis of the above discussion, the present results can be understood as follows. With decreasing T in the PE phase, the rapidly increasing r_c for polar fluctuations couples the nanodomains, increasing their size and coulombic interactions; however, thermal fluctuations prevent the formation of an ordered state. The weak frequency dispersion in T_m at 1 bar indicates that the domains have become large at this temperature (to be nearly static), but not sufficiently large to permeate most of the sample (i.e., the grains in this ceramic) and condense into a nFE state below T_m. Rather, at T_m dynamic (relaxor) slowing down of the fluctuations of these domains occurs resulting in a glasslike state with short-range order. Thus at 1 bar the present sample is very close to the boundary between long-range and short-range order, but slightly favors the latter. On further cooling, there is evidently some continued correlation among the dynamically slowed-down glassy domains resulting ultimately in their growth and condensation into macrodomains and a nFE state at $\leq T_x$, i.e., a R-to-nFE transition. It should be noted here that this transition can be induced by a poling field [9]. Because PLZT 6/65/35 is close in composition to the normal-to-relaxor FE boundary, a small decrease in r_c is sufficient to induce full relaxor behavior. Indeed, as already noted, we observe such behavior by 5 kbar. Because r_c decreases continuously with pressure, the increasingly weaker correlations cause the polar domains to become smaller—a fact that accounts for the observed increase in frequency dispersion with pressure. The decrease in r_c and associated size of the polar domains is also responsible for the vanishing of the spontaneous R-to-nFE transition at T_x above 15 kbar. Stated simply, as r_c becomes sufficiently small, there is not sufficient correlation among polar domains to result in a long-range ordered state, i.e., the FE state vanishes, and the material becomes glasslike at all temperatures.

The above results lead to a better understanding of PLZTs and other perovskite relaxors at 1 bar. As already noted, relaxor behavior sets in above a certain La concentration in PLZT [5,9]. The explanation is straightforward. The incorporation of La and associated A-site vacancies into the lattice introduces disorder which disrupts the correlations among polar nanodomains, effectively reducing r_c. Consequently, above a certain La concentration the polar domains never grow to be large

enough to permeate (or percolate) most of the sample, and relaxor behavior sets in at and below T_m. In this concentration regime, the higher the La concentration, the smaller the effective r_c and the stronger the frequency dispersion, as observed [5,9]. There is thus an analogy between increasing pressure and increasing La concentration in PLZT, but it is the pressure results that clarify the physics. We believe that this physics is applicable to other perovskite relaxors.

Finally, the vanishing of the R-nFE transition above 15 kbar represents a novel feature in the phase diagram of PLZT 6/65/35. Specifically, the R-nFE phase boundary in Fig. 4 terminates in a critical point (CP)—a point that should thermodynamically be equivalent to the liquid-gas critical point in fluids. For a solid, a CP can exist only if the two phases separated by the phase boundary have the same internal symmetry [13]. In PLZT, the R phase, as determined by x rays, is macroscopically cubic, whereas the nFE phase is rhombohedral. So how can a CP exist for this material? The likely explanation is that whereas the macroscopic symmetry of the R phase is cubic, at the polar nanodomain level the symmetry is rhombohedral making a CP possible.

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