SAND97-1683C

# PRESSURE AS A PROBE OF THE GLASSY STATE OF FERROELECTRICS WITH RANDOM SITE DISORDER

SAND--97-1683C

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CONF-971201--

## ABSTRACT

Results on lanthanum-modified lead zirconate-titanates (PLZTs) have revealed a pressure-induced crossover from a normal ferroelectric to a relaxor state and the continuous evolution of the dynamics and energetics of the relaxation process. This crossover appears to be a general feature of soft mode ferroelectrics with random site dipolar impurities or polar nanodomains and results from a large decrease in the correlation radius among polar nanodomains - a unique property of soft mode ferroelectrics.

## INTRODUCTION

The study of the dynamic and static properties of systems in which randomly competing interactions cause the formation of a glass-like state has been an active research area.[1,2] These systems include disordered magnetic materials such as spin glasses and structurally-disordered crystalline solids of which so-called relaxor ferroelectrics is a subclass.[3] On cooling, such systems exhibit a slowing down of the relaxation of their orientational degrees of freedom, ultimately resulting in a collectively frozen-in multipole state without long-range order. A universal signature of such disordered solids is a broad, frequency-dependent peak in the temperature-dependent susceptibility. The peak defines a dynamic freezing, or glass transition temperature ($T_m$). Despite the fairly general character of the phenomena associated with the orientational freezing process, many questions remain concerning the nature of the transition.

In ferroelectrics, relaxor (R) behavior results from either frustration- or compositionally-induced disorder.[3,4] 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), $Pb(Sc_{0.5}Ta_{0.5})O_3$ (or PST) and La-modified $PbZr_{1-x}Ti_xO_3$ (or PLZT)[2-7]. A newly-recognized feature in the response of some of these materials is the observation of a spontaneous, first-order R-to-normal ferroelectric (nFE) transition in the absence of a poling electric field. Specifically, this transition has been observed in: disordered PST, where it vanishes with the introduction of vacancies;[5] and PLZT x/40/60 and PLZT x/65/35 where it is observed over a narrow range of La concentrations, x, namely x $\approx 12$ and $\approx$ 6-7, respectively.[6,7] The parent compounds of these materials are the prototypical soft ferroelectric (TO) mode systems.[8]

The physics of the relaxor behavior and R-nFE transition in these systems is not well understood. The usual way to study the properties has been to vary the composition and degree of disorder 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 the interpretation and understanding of experimental results. We have advocated that hydrostatic pressure is a much "cleaner" variable.[4] 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 demonstrates the power of this approach.

For the present study we selected PLZT compositions near the ferroelectric-relaxor boundary. The substitution of $La^{3+}$ for $Pb^{2+}$ on the A sites in lead zirconate-titanate (PZT) is known to lead 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.[9] 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 transition temperature of the sample.[10] These polar nanodomains increase in size with decreasing temperature, but for relatively low La concentrations the disorder is not sufficient to prevent the formation of a macroscopic ferroelectric state. The peak in the dielectric constant at $T_c$ is relatively sharp and independent of frequency below the GHz range. For higher La concentrations, on the other hand, the increased fluctuations in La content and disorder broaden the transition and induce a relaxor state. For the particular system La-modified $PbZr_{.65}Ti_{.35}O_3$ (PZT 65/35), relaxor behavior becomes experimentally discernible[7] for La concentrations above ~6-7 at %. Thus, for the present study we chose compositions with 6 and 8 at % La, or PLZT 6/65/35 and PLZT 8/65/35. We also chose a composition $x \approx 12$ at % La in PLZT x/40/60, where it is known [6] that relaxor behavior sets in at about this composition.

## EXPERIMENTAL DETAILS

The samples were prepared by conventional mixed oxide synthesis followed by hot-press annealing.[9] They were thin plates whose large faces were sputter coated by Cr followed by Au. Information about the phase transitions and relaxational properties were obtained from dielectric constant ($\epsilon'$) and dissipation (tan $\delta$) measurements. These measurements were performed without a dc biasing field as functions of frequency ($10^2$ - $10^6$Hz), temperature (290-600K) and hydrostatic pressure (0-20 kbar). A 50/50 mixture of normal- and iso-pentanes served as the pressure transmitting fluid.

## RESULTS AND DISCUSSION

Space limitations do not allow us to discuss all of the results on the three PLZT compositions. Thus, we restrict the presentation to a summary of the highlights of the work with the objective of emphasizing the generality of the pressure-induced effects which get to the heart of the physics. We begin with PLZT 6/65/35 which is very close to the nFE-R boundary for PLZT x/65/35. In the absence of relaxor behavior, the expected response at 1 bar is for the material to transform on cooling from the high temperature cubic PE phase to a rhombohedral nFE phase at ~440 K, and the dielectric response should be essentially independent of frequency below ~1 GHz. Figure 1 shows the temperature dependence of $\epsilon'$ at 1 bar. Starting in the PE phase, $\epsilon'$ increases with decreasing temperature in a Curie-like manner and exhibits a maximum at the expected PE-FE transition temperature, which we denote by $T_m$. $\epsilon'$ is independent of frequency in the PE phase, but weak frequency dispersion is observed in $T_m$ and in $\epsilon'$ below $T_m$.[7]

These results indicate that the sample is indeed very close to the nFE-R boundary, but exhibits the onset of relaxor behavior. On further cooling, there is a phase transition denoted by $T_c$ and manifested by a sharper drop in $\epsilon'(T)$ and a frequency-independent peak in tan $\delta$ (T) as shown for the $10^3$Hz response in Fig. 1. These anomalies in $\epsilon'(T)$ and tan $\delta$ (T) are the

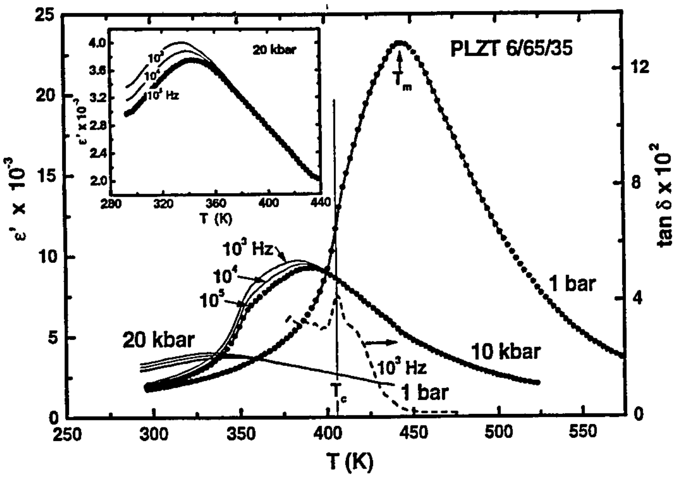

Figure 1. Influence of pressure on the dielectric response.

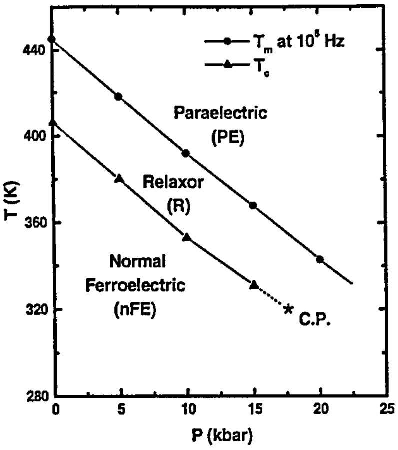

Figure 2. Shifts of the dynamic glass transition temperature, $T_m$, (at $10^5$Hz) and nFE-R transition temperature, $T_c$ with pressure.

signatures of the R-to-nFE transition seen in other disordered perovskites[5-7]. The overall response at 1 bar can then be understood as follows. On cooling from the PE phase, the local, La-induced polar nanodomains grow and become large and nearly static (hence the weak frequency dispersion) at $T_m$, but not sufficiently large to condense a nFE state below $T_m$. Rather, critical slowing down of the fluctuation of these domains occurs at $T_m$ resulting in the onset of relaxor behavior (i.e., short-range order). On further cooling, 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 a nFE state at $T \leq T_c$.

Figure 1 shows that pressure causes large decreases in the amplitude for the $\epsilon'(T)$ anomaly at $T_m$ and in the transition temperatures and induces full relaxor character for the PE-R transition. Taking the difference, $\Delta T$, in $T_m$ between $10^6$ Hz and $10^2$ Hz as a measure of the dispersion in $T_m$, we note that $\Delta T$ increases from 5 at 1 bar to 18K at 20 kbar indicating that this dispersion evolves with pressure for reasons which will become clear later. $T_c$ remains frequency independent. The inset in Fig. 1 provides an expanded view of the response at 20 kbar , the highest pressure reached in the present work. This is the classic dipolar, glass-like response of a relaxor ferroeledtric. A key feature of the response at 20 kbar is the apparent vanishing of the R-nFE transition at $T_c$ as discussed elsewhere.[7] The data indicates that this transition vanishes between 15 and 20 kbar, a finding that represents an important feature in the phase diagram of PLZT 6/65/35. Specifically, the R-nFE phase boundary terminates in a critical point (C.P.) – a point that should be thermodynamically equivalent to the liquid-gas critical point in fluids. The results are shown in Fig. 2. For a solid, it is generally believed that a C.P. can exist only if the two phases separated by the phase boundary have the same internal symmetry.[11] In PLZT, the R phase, as determined by x-rays, is macroscopically cubic, whereas the nFE phase is rhombohedral. So how can a C.P. exist for this material? The likely explanation is that, whereas the macroscopic symmetry of the R phase is cubic, at the nanodomain level the symmetry is rhombohedral making a C. P. possible. Figure 2 also shows the pressure dependence of $T_m$ at one frequency. $T_m$ is of course frequency dependent, but its pressure derivative is only weakly dependent on frequency.

Figure 3 shows the influence of pressure on the dielectric properties of PLZT 8/65/35. In this case, the higher La content causes a higher level of lattice disorder and induces full

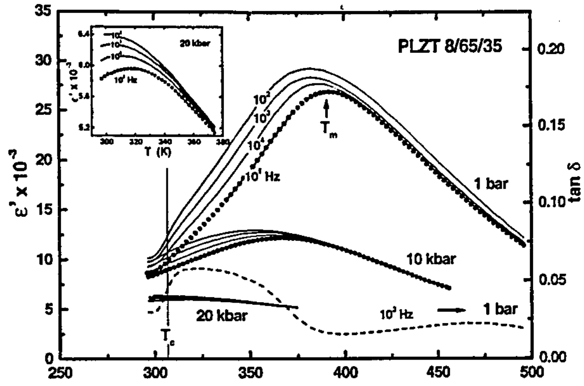

Figure 3. Influence of pressure on the dielectric response.

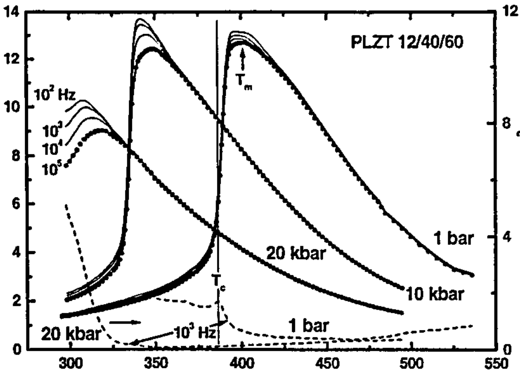

Figure 4. Influence of pressure on the dielectric response.

relaxor behavior even at 1 bar. Otherwise, the effects of pressure are qualitatively similar to those on PLZT 6/65/35, namely large pressure-induced suppression of the magnitude of $\in'$ at $T_m$, a broadening of the $\in'$ (T) response and an increase in the frequency dispersion in $T_m$. The inset in Fig. 3 shows, in an expanded view, the classic relaxor charator of the 20-kbar data. Another feature in the PLZT 8/65/35 data that is also analogous to the behavior of PLZT 6/65/35 is seen in the 1-bar results in Fig. 3. This is the weak anomaly (a shoulder) in $\in'$ (T) between 300 and 305K. This anomaly, which is better manifested by a step in the tan δ (T) response (shown only at $10^3$Hz), corresponds to the R-nFE transition. As in the case of PLZT 6/65/35, this transition exhibits thermal hysteresis and is first order. Its temperature, $T_c$, decreases with pressure; however, because of its proximity to room temperature and our inability to cool the massive pressure apparatus used, we did not study the pressure dependence of $T_c$. Nonetheless, here again we expect $T_c$ to vanish with pressure as is also suggested by the PLZT 12/40/60 data described below.

The results on PLZT 12/40/60 are shown in Fig. 4. As noted earlier, this composition demarks the PE-R boundary for PLZT x/40/60. At 1 bar the dielectric response exhibits on cooling a peak with weak frequency dispersion at $T_m$, consistent with the onset of relaxor behavior, followed by a first-order R-to-nFE transition at $T_c$. The thermal hysteresis for this transition is 17K and decreases to 5K at 18 kbar (not shown).[12] The transition is accompanied by a peak in tan δ (T) as depicted by the $10^3$ Hz data. The influence of pressure on this sample is qualitatively similar to those on the two PLZT x/65/35 samples presented above, the main effects being: large decreases in $T_m$ and $T_c$, evolution of the relaxor behavior, and a suggestion in the data[12] that the R-nFE transition should vanish at a pressure somewhat >20 kbar.

The above results point to an important analogy between pressure and La content in determining the dielectric properties of the x/65/35 and x/12/40 PLZT families. In both cases increasing pressure has the same qualitative influence as increasing La content, namely a crossover from nFE to a relaxor state accompanied by suppression and broadening of the $\in'$(T) anomaly. The conventional wisdom has been (the Smolenski model) that relaxor behavior and the associated diffuse phase transitions in perovskite ferroelectrics at 1 bar are induced by increased compositional fluctuations or disorder at both the A and B sites leading to large fluctuations in transition (Curie) temperatures.[3] Clearly pressure does not induce increased fluctuations in a sample of fixed composition, and thus the mechanism for the nFE-R crossover has remained an open question. We believe that the pressure results hold the key to the essential physics, as we now demonstrate.

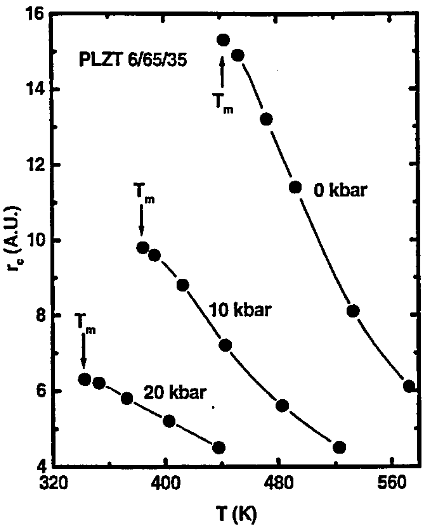

Figure 5. The temperature and pressure dependences of the correlation radius, $r_c$, for the interaction of polar nanodomains in the cubic PE phase of PLZT 6/65/35.

First we note that the parent compositions PZT 65/35 and 40/60 and PLZT compositions with La contents below the critical values exhibit nFE transitions that can be understood in terms of soft mode theory[8]. Specifically, the frequency, $\omega_s$, of the soft FE mode in the cubic PE phase decreases with decreasing T accounting for the Curie-Weiss $\epsilon'(T)$ response, since $\omega_s$ and $\epsilon'$ are related by a Lyddane-Sachs-Teller relationship such that $\omega_s^2\epsilon' =$ constant[8]. $\omega_s$ becomes sufficiently small (or vanishes for a second-order transition) at $T_c$ precipitating a nFE (i.e., long-range ordered) phase.

In earlier work on perovskite oxides with both A-site disorder (PLZT 6/65/35) and B-site disorder ($KTa0_3$ with dilute Nb substitution for Ta) we observed pressure-induced relaxor behavior which was interpreted in terms of a novel, pressure-induced crossover phenomenon from normal long-range FE order to dipolar glass behavior.[4,7] 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 which controls the polarizability of the host lattice. Here we summarize the physics.

The decrease of $\omega_s$ with decreasing T in the PE phase causes the polarizability of the lattice, and thereby the correlation length (or radius, $r_c$) for polar fluctuations, which is inversely related to $\omega_s$, to increase rapidly as $T \rightarrow T_c$. Because $\omega_s$ is determined by a delicate balance between long-range and short-range interactions, it is very strongly pressure (or volume V) dependent.[8] A measure of this dependence is the soft mode Grüneisen parameter $\gamma$,

$$\gamma \equiv -(\partial \ln \omega_s / \partial \ln V)_T = \frac{1}{2}(\partial \ln \epsilon' / \partial \ln V)_T ,$$

which is simply the ratio of the fractional change in $\omega_s$ to the fractional change in volume. For ordinary dielectrics $\gamma$ for transverse optic (TO) phonons is on the order of 1-2 and very weakly temperature dependent. However, for soft TO mode systems, like the PZTs and other perovskites, $\gamma$ is very large and strongly temperature dependent, approaching values of several hundred[8] near $T_c$.

The large $\gamma$ translates to a large increase (decrease) in $\omega_s$ ($r_c$) with pressure. Figure 5 shows the variation of $r_c$ with temperature at 1 bar and at elevated pressures for PLZT 6/65/35. These results were deduced[4] from the pressure and temperature dependences of $\epsilon'$. We cannot determine the absolute value of $r_c$ in this way, but we can evaluate the relative change in this quantity. Hence in Fig. 5, $r_c$ is given in arbitrary units. The 1-bar results show the large increase in $r_c$ with decreasing temperature, a remarkable feature of the soft mode response of the system. The decrease of $r_c$ with pressure is nonlinear and largest near $T_m$ where it is estimated to be about $10^3$ larger than the decrease in the lattice constant of the host.[4] For example, at 440 K in Fig. 5 $r_c$ decreases by almost a factor of 3.4 between 0 and 20 kbar, and the corresponding correlation volume decreases by a factor of ~40, a large effect.

On the basis of the above results and discussion, the response of the present PLZTs can be understood as follows. With decreasing temperature at 1 bar in the PE phase, the rapidly increasing correlation radius for polar fluctuations couples the nanodomains into rapidly growing polar clusters and increases their coulomb interactions; however, thermal motion above $T_m$ is sufficiently strong so as to prevent the formation of an ordered state. These clusters become large at $T_m$ (hence the weak frequency dispersion in $T_m$), but not large enough to permeate the whole sample and precipitate a static, cooperative, long-range ordered FE state. Rather, some (a small fraction) of the clusters exhibit dynamic slowing down of their fluctuations at $T \leq T_m$ leading to the observed weak relaxor behavior. Because of the high polarizability (or large $r_c$) of the host lattice, further cooling reduces the thermal fluctuations of the large clusters and causes coarsening of the dynamically slowed down nanodomains leading to a cooperative FE transition at $T_c$. Evidence for coarsening is seen in TEM observations.[6]

Because PLZT 6/65/35 and 12/40/60 are close in composition to the normal-to-relaxor FE boundary, a relatively small decrease in $r_c$ is sufficient to induce full relaxor behavior. Indeed, as already noted, we observe such behavior in the high pressure data. With the decrease in $r_c$, the polar clusters or nanodomains do not become large enough at $T_m$ and exhibit dynamic slowing down at lower temperatures. Because $r_c$ decreases continuously with pressure, the polar clusters become smaller with increasing pressure -- a fact that accounts for the observed increase in frequency dispersion with increasing pressure. It is thus seen that the nFE-to-R crossover results simply from the decrease in $r_c$ with pressure.

In view of the above discussion, the explanation for the effects of changing La content at 1 bar 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 $r_c$ becomes sufficiently short, the polar clusters 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. There is thus an analogy between increasing pressure and increasing La content, but it is the pressure results that clarify the physics.

ACKNOWLEDGEMENT This work was supported by the United States Department of Energy under Contract DE-AC04-AL85000. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy.

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M98002807

Report Number (14) SAND--97-1683C

CONF-971201--

Publ. Date (11) 19980310

Sponsor Code (18) DOE/DP, XF

UC Category (19) UC-700, DOE/ER

DOE