Glassy polarization behavior of relaxor ferroelectrics

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The polarization behavior of La-modified lead zirconate titanate relaxors has been investigated for various electrical and thermal histories. The field-cooled and zero-field-cooled behaviors were both studied. The magnitude of both polarizations were found to be equal above a critical temperature. A macroscopic polarization developed, when the zero-field-cooled state was warmed with a bias applied. The temperature of the maximum charging current decreased with increasing bias field. This decrease was modeled using the deAlmeida-Thouless relationship [J. deAlmeida and D. Thouless, J. Phys. A **11**, 983 (1978)], which predicted an average moment size freezing of approximately 3×10^{-27} C m. A glassy polarization mechanism was subsequently proposed with correlations between superparaelectric moments leading to the development of effective nonergodicity in a frozen state. Arguments are presented that this freezing process is dispersive due to a distribution of correlation strengths. The time dependence of the polarization was also investigated.

I. INTRODUCTION

La-modified lead zirconate titanate with a [Zr]/[Ti] ratio of 65/35 (PLZT) and La contents between 4 and 14 at. % are relaxor ferroelectrics. Relaxors are characterized by a frequency dispersion of the complex permittivity, where the temperature of the permittivity maximum (T_{max}) shifts to higher temperatures with increasing measurement frequency. Relaxors have an inability to sustain a remanent polarization until temperatures significantly below the temperature of the permittivity maximum, but a local polarization is believed to exist at much higher temperatures.[1] The implication is that the local symmetry is lower than the global symmetry. Randall has observed contrast on the nanometer level using transmission electron microscopy (TEM).[2,3] It is believed that the composition is locally homogeneous on a scale of approximately 50 Å. This local chemistry is believed to prevent the establishment of normal long-range polar ordering at a Curie temperature, instead the system establishes polar moments on the scale of the local chemistry. The size of these regions is such that the orientation of the polarization is believed to be thermally reversible,[4] analogous to superparamagnetism.[5] Cross has recently shown that the polarization fluctuations undergo a freezing,[6] analogous to spin and dipole glasses.[7,8] It was suggested that interactions between superparaelectric regions were responsible for this freezing. The freezing temperature (T_f) was also shown to correlate with the collapse in the remanent polarization.

The zero-field-cooled (ZFC) state of the relaxor appears cubic to x rays down to liquid-nitrogen temperatures, implying that the scale of the polar behavior is too small to give additional diffraction peaks and is relatively temperature independent. The field-cooled (FC) state appears rhombohedral even at room temperature. Xi[9] has previously measured the polarization behavior of PLZT. He found no macroscopic polarization in the ZFC state, but upon application of a bias, polarization developed. He interpreted his results in terms of a microdomain to macrodomain transition. Somewhat similar differences between the ZFC and FC states have been found in spin and dipole glasses.[8] The reorientating moments in spin glasses are believed to freeze devoid of long-range order, due to frustrated interactions. On application of a bias, the moments tend to order, and properties characteristic of a normal ferromagnetic state are observed. The differences between the ZFC and FC states in spin and dipolar glasses are usually attributed to a breakdown of ergodicity in the frozen state.[8]

II. EXPERIMENTAL PROCEDURE

The samples used in this study were PLZT ceramics with [Zr]/[Ti] ratios of 65/35 and La contents of 8 at. %. They were donated by Honeywell Inc. of Bloomington, Minnesota. The samples were electroded with gold. The pyroelectric current was measured as a function of temperature on heating using a HP4140B pA meter. The polarization was then calculated by integration. Various measurement procedures were used reflecting different electrical histories. The sample was first cooled under zero bias and then heated under bias while measuring the pyroelectric current, designated as zero-field-cooled–field-heated. The sample was subsequently cooled and heated, both under bias, while measuring the pyroelectric current, designated as field-cooled–field-heated. The remanent polarization was also measured by

cooling under a bias, removing the bias, and measuring the pyroelectric current on heating. The field levels used were 1, 3, 5, 6, 7.5, 8.5, and 10 kV/cm.

III. RESULTS AND DISCUSSION

The remanent polarization (P_r) as a function of temperature for PLZT-8 is shown in Fig. 1. P_r collapsed near 60 °C [defined as $T_f(0)$] and seemingly tailed to zero at higher temperatures. This figure also shows other polarization curves. These curves were measured by heating the poled (field-cooled) sample to temperatures below $T_f(0)$, subsequently recooling the sample ($E=0$), and reheating measuring P_r. After this procedure, P_r did not return to the previous low-temperature value, but rather remained at the value of the highest temperature reached. This behavior is unlike a normal ferroelectric which would return to the low-temperature value of P_r on recooling. The implication is that the scale of the polar ordering in relaxors is strongly dependent on the electrical and thermal histories. The field-cooled state exhibits properties similar to a normal ferroelectric such as domains and anisotropy, whereas the zero-field-cooled state is devoid of long-range order and is isotropic. These results are suggestive of a glassy polarization mechanism, similar to the dipole and spin glasses.[8] The differences between the ZFC and FC states in these glassy materials are well known.

The polarization of PLZT-8 is shown in Figs. 2(a) and 2(b) for various electrical histories. The ZFC and FC polarizations are both shown in Fig. 2(a) for a bias level of 3 kV/cm. The ZFC polarization exhibited a maximum of approximately 0.17 C/m^2 near 50 °C. The FC polarization was approximately 0.3 C/m^2 at −100 °C, and decreased with increasing temperature, approaching a value of 0.22 C/m^2 near 50 °C. Near the temperature of the maximum ZFC polarization (T_{ZFC}), the FC and ZFC polarizations were not equal. This difference is probably a reflection of a very broad relaxation time distribution; consequently, the polar regions in the long-time tail remain in their ZFC configuration until above T_{ZFC}. But, on field cooling from high temperatures, these regions freeze into an ordered configuration; consequently, the polarization is higher for the FC measurement than for the ZFC. Figure 2(b) shows similar data at a bias levels of 5 kV/cm. The difference between the ZFC and FC polarizations decreased with bias. With increasing bias the polar regions in the long-time tail of the distribution can probably be perturbed from their ZFC configuration; consequently, the ZFC and FC polarizations are approximately equal near T_{ZFC}.

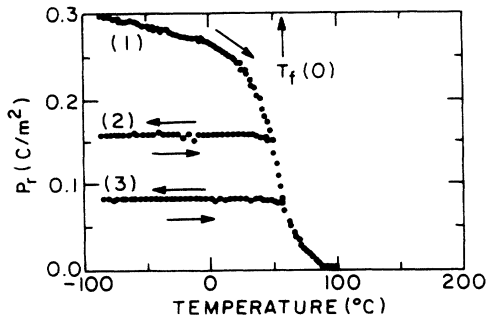

FIG. 1. Remanent polarization (P_r) as a function of temperature, where $T_f(0)$ is a freezing temperature. The top curve, (1), was measured by heating to temperatures above $T_f(0)$. The bottom curves, (2) and (3), were measured by heating to temperatures below $T_f(0)$, subsequently recooling and measuring P_r.

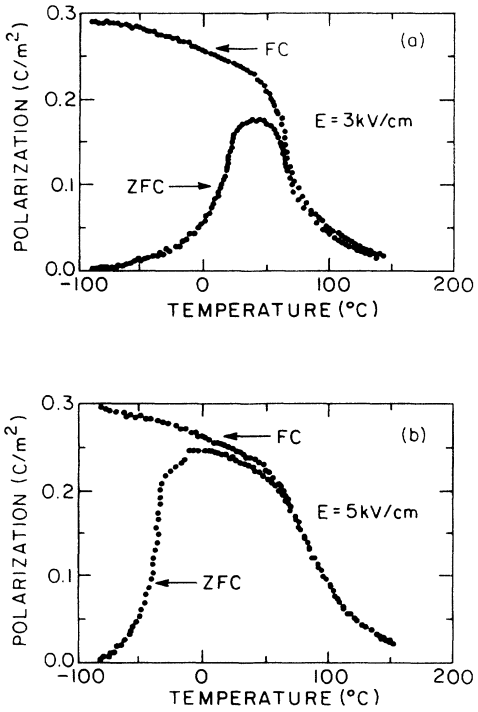

FIG. 2. Polarization as a function of temperature for various electrical histories and bias levels, where FC means field-cooled–field-heated and ZFC means zero-field-cooled–field-heated. (a) Bias level of 3 kV/cm, and (b) bias level of 5 kV/cm.

Figure 3 shows plots of the time dependence of the polarization at various temperatures. The polarization was measured by applying 3 kV/cm, cooling down, removing the bias, and measuring the pyroelectric current as a function of time. The maximum polarization at each temperature, $P(t=0)$, was assumed to be that of the 3-kV/cm FC state [see Fig. 2(a)]. The polarization as a function of time was then calculated by subtracting the integral of the pyroelectric current. The decay of the polarization became slower with decreasing temperature. The decay was seemingly exponential at all temperatures. At any particular temperature, the configurations with an activation energy (E_a) less than kT are metastable. Raising the temperature will allow the system to move across higher barriers: consequently, the ZFC polarization approaches the FC values. On removal of the bias, the quasilogarithmic decay of the polarization may then occur as the thermal energy scrambles the FC state and the system searches configurational space finding the lowest local minima. The analogous magnetic viscosity

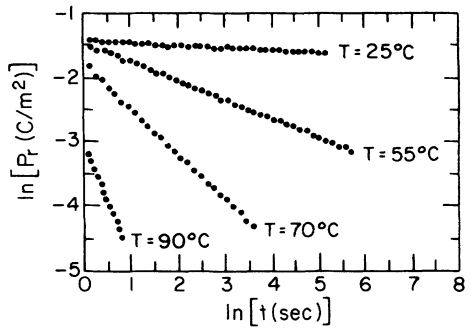

FIG. 3. Remanent polarization as a function of time at various temperatures.

has been modeled using many approaches,[7,11] mostly involving a t^{-n} exponent.

A small anomaly in the ZFC permittivity has been observed by Xi.[9] This anomaly was shown to correlate in temperature with the maximum charging current, and the temperature decreased with increasing bias. Figures 4(a) and 4(b) show plots of the ZFC pyroelectric current under 3 and 5 kV/cm, respectively. The temperature of the maximum charging current decreased with bias. The freezing temperature of the ZFC state, $T_f(0)$, has been shown to correlate with the extrapolation of the remanent polarization to zero.[6] $T_f(0)$ is shown in Fig. 1 to be approximately 60 °C. Clearly a characteristic temperature associated with the frozen state is decreasing with bias and is suggestive of a breakdown of ergodicity below T_{ZFC}.

If nonergodicity is occurring, then the decrease in this temperature with bias should follow the deAlmeida-Thouless relationship[10] given in Eq. (1):

$$E = A\left[\frac{T_f(0)-T_f(E)}{T_f(0)}\right]^{3/2}, \tag{1}$$

where A is an adjustable parameter, and $T_f(0)$ and $T_f(E)$ are both in units of K. The measurement field is plotted against $\{[T_f(0)-T_f(E)]/T_f(0)\}^{1.5}$ in Fig. 5. The experimental behavior is compatible with Eq. (1), but is by no means a unique representation. The best fit was obtained with an experimental value of 1.2, rather than the 1.5 as given in Eq. (1). The deAlmeida-Thouless relationship was used because of its theoretical significance in describing the transformation from the FC to the ZFC states. A best parameter fit for A using Eq. (1) yielded a value of 30 kV/cm and is shown as a solid line in the figure. The parameter A has been indentified as $kT_f(0)/p$ (Refs. 10 and 12), where p is the average magnitude of the polar moment freezing. A value of 3×10^{-27} C m can then be deduced for p. This is close to the expected value of the superparaelectric moment in $Pb(Mg_{1/3}Nb_{2/3})O_3$ relaxors,[13] which is approximately 5×10^{-27} C m. With increasing La content, the scale of the polar behavior is believed to decrease.[9] Consequently, the field level necessary to decrease $T_f(E)$ by a unit amount would be expected to increase, i.e., $A = kT_f(0)/P_s V_{\text{moment}}$, where P_s is the magnitude of the local spontaneous polarization and V_{moment} is the volume of this moment, which is experimentally observed.[9] These results give strong evidence that the individual moments undergoing freezing are superparaelectric and that the glassy character is a reflection of correlations between these moments.

It is believed that a spin glass possesses many quasidegenerate ground states.[14] The small energy differences

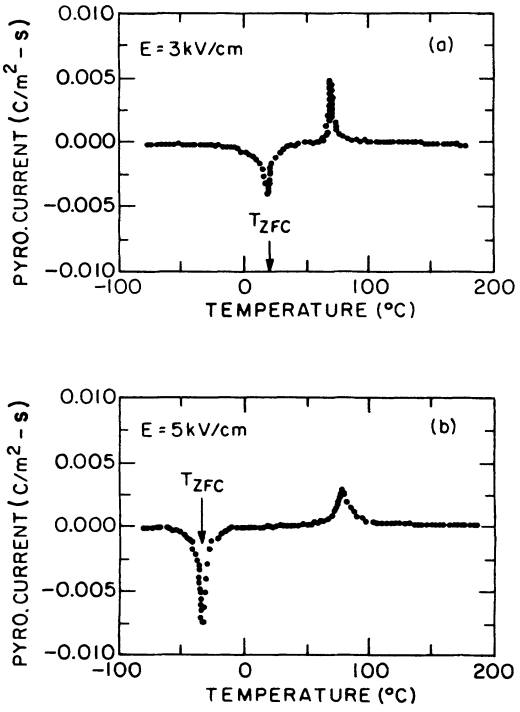

FIG. 4. Pyroelectric current as a function of temperature at various bias levels. (a) Bias level of 3 kV/cm, and (b) bias level of 5 kV/cm.

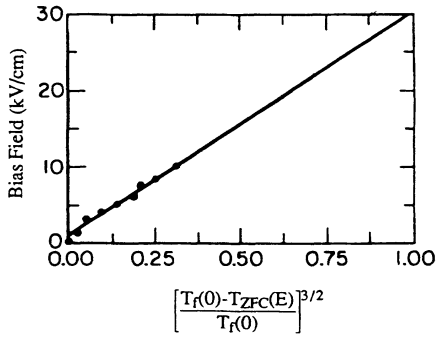

FIG. 5. Plot of the applied bias (bias field) as a function of the temperature of maximum charging current, where $T_f(0)$ is the freezing temperature of the ZFC state and the solid line is the curve fitting to the deAlmeida-Thouless relationship given in Eq. (1).

between these configurations may lead to the system being stabilized in one of them below $T_f(0)$, consequently breaking the ergodicity. This model has been substantiated by computer simulations.[15,16] A similar model may be extended to correlated superparaelectric moments. Local configurations of moment orientations are believed to exist on the scale of approximately 200 Å,[13] effectively charge compensating the local polarization. There may be many minima in configurational space associated with various combinations of moment orientations, all of nearly the same energy. But near $T_f(0)$, other configurations may becoming increasingly inaccessible as the relaxation time distribution approaches the macroscopic time scale; consequently, effective nonergodicity may set in. Nonergodicity has previously been suggested to arise in $K_{1-x}Li_xTaO_3$ dipole glasses[8] due to a freezing of superparaelectric moments. An analogy was made to the models of hierarchical spin-glass dynamics[17,18] in which some clusters must wait to relax until a number of neighboring clusters, are in favorable positions, which is somewhat similar to the concepts suggested in this paragraph for PLZT.

On application of a bias in the ZFC state, the degeneracy may be partially broken reflecting a preferred alignment. The system may then find the most favorable local configurations and over time adjust to the global equilibrium. The logarithmic time dependence (polarization viscosity) may then arise from readjustments in configurational space between local minima. Under higher biases the splitting of the degeneracy increases; consequently, a global equilibrium can be established from the ZFC state at lower temperatures. The implication is that, at a fixed temperature, the polarization fluctuations may be nonergodic at zero bias but ergodic at finite biases. Any point below the maximum ZFC polarization (Fig. 2) would then correspond to metastable local minima since sufficient time has not been allowed for equilibrium, near T_{ZFC} the system may start to approach a global equilibrium. The difference between the ZFC and FC polarizations near T_{ZFC} indicate that the freezing is dispersive, such a difference was not observed in dipole glasses.[8] Between the temperature of the onset of local polarization (T_{Burns}) and $T_f(0)$, the susceptibility is nonlinear[13] and strong deviations from Curie-Weiss behavior develop.[19,20] The implication is that between T_{Burns} and $T_f(0)$ the energy surface is not featureless, but rather local minima which are correlated in configurational space exist. It can be anticipated that a significant dispersion of correlation strengths exists as a reflection of the cluster size dispersion observed by TEM.[3,21] The implication is that the smaller polar regions may remain ergodic to lower temperatures and that the larger clusters may remain nonergodic to higher temperatures (as also suggested by the tailing of P_r, shown in Fig. 1).

The FC state has a domain structure on the scale of 1–10 μm, whereas the scale of the polar behavior in the ZFC state is too small to produce additional diffraction lines narrow enough in width to be observed. The implication is that the scale of the polar behavior is field dependent, and, in fact, the correlation length has recently been found to increase with bias.[22] This does not reflect a simple dipole alignment but rather the establishment of a normal ferroelectric state, i.e., a microdomain to macrodomain transition. The bias must act to override the chemical inhomogeneity which normally prevents the establishment of long-range polar ordering. A possible mechanism is the growth of the polar regions across the antiphase boundaries which are known to separate them.[3] Similar generic behavior is observed in spin glasses. The ZFC state is isotropic with no evidence of long-range magnetic ordering, whereas the FC state has remanence, hysteresis, and irreversibility analogous to a normal ferromagnet. A switching from local configurations in the ZFC state to a macrostate (global equilibrium) under bias is seemingly observed in most glassy materials.

IV. CONCLUSION

The polarization behavior of the FC and ZFC states of relaxor ferroelectrics have been compared and shown to be similar to spin and dipole glasses. The field dependence of a characteristic temperature has also been shown to follow the deAlmeida-Thouless relationship. A glassy polarization mechanism was subsequently proposed in which correlations between superparaelectric moments lead to the development of nonergodicity near a glass transition temperature.

ACKNOWLEDGMENT

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