PHYSICAL REVIEW B **78**, 054103 (2008)

Polarization-independent aging in the relaxor $0.92PbMg_{1/3}Nb_{2/3}O_3$-$0.08PbTiO_3$

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(Received 7 March 2008; revised manuscript received 30 May 2008; published 6 August 2008)

Spin-glass-like aging, showing rejuvenation upon cooling and a hole in susceptibility vs temperature at the aging temperature on warming, was found in the relaxor ferroelectric $(PbMg_{1/3}Nb_{2/3}O_3)_{0.92}(PbTiO_3)_{0.08}$ (PMN-PT 8%). The magnitude and form of the aging memory hole produced at zero field showed little sensitivity to the magnitude of the previously induced polarization, up to near saturation. This result is incompatible with any picture in which the glassy aging arises from interactions among polar nanodomains, which account for most of the polarization. The results therefore support a picture in which the glassy aging arises from degrees of freedom other than the orientation of polar nanodomains.

DOI: 10.1103/PhysRevB.78.054103 PACS number(s): 77.80.−e, 75.10.Nr, 77.84.−s

I. INTRODUCTION

The enormous dielectric susceptibility of the perovskite relaxor family $(PbMg_{1/3}Nb_{2/3}O_3)_{1-x}(PbTiO_3)_x$ (PMN-PT) at low PT concentrations arises almost entirely from ferroelectriclike polar nanoregions (PNRs) (see, e.g., Refs. 1–4). The susceptibility shows kinetic freezing with non-Arrhenius temperature and frequency dependences (e.g., Refs. 5 and 6) roughly similar to those of spin glasses[7] and other fragile cooperative glasses.[8] This strongly non-Arrhenius temperature dependence of the kinetics of canonical relaxors indicates that some sort of growing thermodynamic correlations play a major role in the glassy freezing. However, it does little in sorting out whether these correlations are simply the growth of independent PNRs in random fields (e.g., Refs. 9 and 10), collective correlations among PNRs (e.g., Ref. 11), some combinations of these (e.g., Ref. 1), or some other degrees of freedom.[12,13] As is common for glass transitions, the absence of simple order parameters makes it hard to use static correlation measurements to determine what drives the freezing.

The detailed aging behavior of the susceptibility is sensitive to the type of glassy order formed.[14] The aging of the susceptibility in the disordered frozen state of cubic relaxors, such as PMN [or near-cubic ones, such as PMN-xPT with low x (Ref. 15)], shows distinctive qualitative features reminiscent of spin glasses.[16–19] This behavior strongly indicates that the kinetics is controlled by the collective effects of a complicated glass, not just the kinetics of individual domains or simple domain walls. Although there have been some speculations that the interacting PNRs might form a spin-glass-like state (e.g., Ref. 11), a variety of evidence has indicated that the most distinctive aging properties of the glassy kinetics come from degrees of freedom other than PNR polarization orientations.[16–19] In particular, the rejuvenation and memory effects found for aging PMN-PT well into the frozen state are absent for several Ising-type relaxors[12,20] (except near the freezing temperature[21,22]), suggesting that polarization components orthogonal to the [111]-type easy axes for the PNR are responsible for these low-temperature aging effects. Such orthogonal components are known to exist from Raman-, neutron-, and x-ray-scattering analyses.[1,23–26] There are theoretical reasons to believe that strain constraints on such components can lead to an effective Hamiltonian of the same form as a spin glass[27,28] and that in Potts-type models there can be phases in which one form of simple long-range order coexists with frozen glassy order.[29]

In this paper we show that aging with distinctive rejuvenation and memory effects persist in frozen states of PMN-PT (8%) even when the polarization is near the nominal saturation level, unlike in actual spin glasses, which lose their slow kinetics when partially aligned (e.g., Refs. 7 and 30). This result unambiguously rules out the possibility that the spin-glass-like aging effects arise from the degrees of freedom responsible for most of the polarization, i.e., polar nanodomain orientations, and thus requires that other degrees of freedom be involved.

II. METHODS AND RESULTS

Single crystals of the nominal composition $0.90Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.10PbTiO_3$ were grown at Simon Fraser University from a high-temperature solution by a top-seeded solution growth method which was described previously.[31] The starting chemicals, PbO (99.99%), TiO_2(99.99%), MgO (99.9%), Nb_2O_5(99.9%), and B_2O_3(99.9%), were weighed according to the stoichiometric composition of PMN−10%PT (solute) with a flux to solute molar ratio of 60:40. The weighed chemicals were thoroughly mixed and loaded into a platinum crucible of 50 mm^3 in volume, which was then placed into a vertical tubular furnace to melt. A small PMN single crystal was used as a seed and the saturation temperature of the solution was determined accurately by repeated seeding trials. The crystal growth took place upon cooling from 1180 to 1100 °C at a rate of 0.2 °C/h. At the end of slow cooling process, the grown crystal was pulled out of the melt surface and then cooled down to room temperature at a rate of 15 °C/h. Because of the phase segregation during the growth of solid solution crystals, the composition of the grown crystals can be different from the nominal composition.

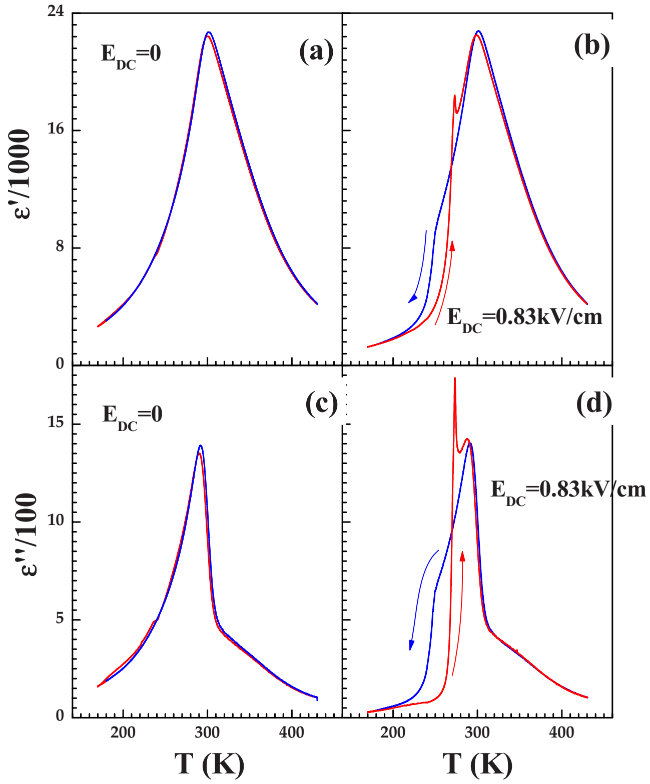

FIG. 1. (Color online) The real and imaginary susceptibilities at 100 Hz shown on cooling and warming in zero field and 830 V/cm. The sharp features in the in-field data come from the first-order transition to a long-range polarized state. Cooling and heating rates were about 4 K/min.

A (111)-oriented platelet was cut off a grown crystal and mirror polished down to a thickness of 120 μm. It was configured as a single disk capacitor with an area of about 1 mm^2, using gold electrodes on a several-angstrom underlay of chromium. The two components of the susceptibility, ε' and ε'', were measured as a function of temperature T by standard lock-in techniques at a frequency of 100 Hz. Temperatures were controlled with a standard transfer-line gas-flow cryostat, with the sample in vacuum. Figure 1 shows the results, which are typical for this material, with $x \approx 0.08$, judging by comparing the temperature of the maximum permittivity, T_P, with reference values based on ceramic samples.[15]

The primary experimental technique employed here was to prepare the sample in various polarization states prior to cooling to $T_A = 180$ K, at which the sample was aged for 10 h. Aging at T_A was then followed by a "readout" consisting of further cooling and warming. Polarization currents $I_P(t)$ were measured throughout using an AD549 op-amp configured as a current amplifier. These $I_P(t)$ had to be corrected for backgrounds from the amplifier, since under most conditions (e.g., aging at fixed E and T), $I_P(t)$ was very small. The total sample polarization after aging could, however, be accurately determined by measuring integrated $I_P(t)$ on subsequent warming, which produced relatively rapid depolarization.

In several cases, to obtain nearly complete polarization, the sample was directly cooled in a dc field $E = 830$ V/cm after annealing for 2 h at 440 K. Figure 2 shows the T-dependent current $I_P(T)$ on cooling in the field and warming at $E=0$. The substantial hysteresis associated with the transition to the aligned state is evident, indicating that the transition is first order, as often found before.[13,32–36] (Correcting for the shift in the transition temperature as a function of E would increase the hysteresis.) The fine structure of $I_P(T)$ is substantially more complicated than in some other samples,[13] probably indicating some inhomogeneity.

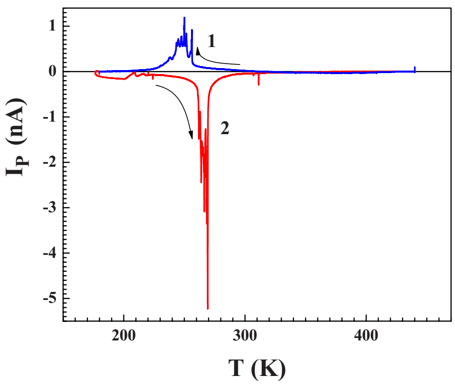

FIG. 2. (Color online) $I_P(T)$ is shown on cooling in 830 V/cm and subsequent warming at $E=0$, with approximate rates of 4 K/min.

To reach partial polarizations, after annealing the sample was cooled to 205 K, and then $E = 830$ V/cm was applied for a variable time. Figure 3 shows the polarization obtained (as determined by subsequent warming) by this procedure. Since the results were quite reproducible, it was possible to systematically prepare different polarization states by varying the in-field waiting time. The field was then set to zero at 205 K, and the sample cooled to 180 K for a standard zero-field aging experiment. Both ε' and ε'' as well as I_P were monitored on the subsequent cooling and warming.

The characteristic spin-glass rejuvenation and memory effects consist of a deviation of $\varepsilon'(T)$ and $\varepsilon''(T)$ from reference curves, which were taken on cooling and heating without aging at 180 K. One of the more stable indicators, used for

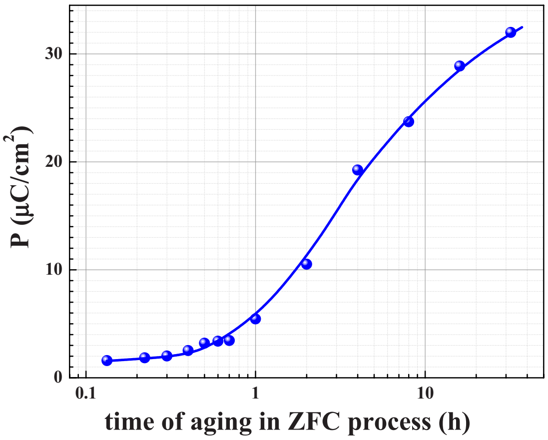

FIG. 3. (Color online) The net polarization, measured by integrating I_P on subsequent zero-field heating, obtained by aging in $E = 830$ V/cm at $T = 205$ K as a function of aging time.

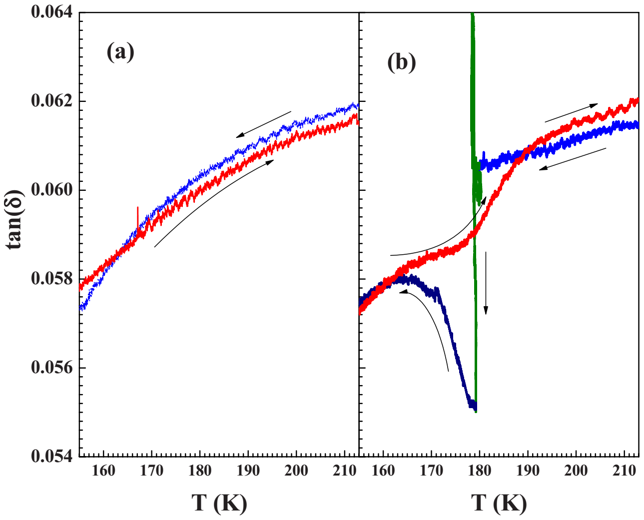

FIG. 4. (Color online) $\varepsilon''/\varepsilon'$ [i.e., $\tan(\delta)$] on heating and cooling with no aging (a) and with aging at 180 K (b). Transients in (b) occurred as the temperature stabilization started. Cooling and heating rates were about 1 K/min.

economy of presentation, is the loss tangent $\varepsilon''/\varepsilon'$. In classic spin-glass aging, this decreases during aging but then recovers (rejuvenation) to the reference curve on cooling. On subsequent warming, the reduction near T_A is partially recovered, before a return to the reference curve just above T_A, leaving a "hole" near T_A. Figure 4 illustrates this hole for simple zero-field cooling, in keeping with prior results on similar materials. A measure of the size of the hole was obtained by making a smooth (ninth-order polynomial) fit to the data from 155 to 200 K and calculating the dip of the curve below the lowest line tangent to the curve from above.

Figure 5 compares the sizes of the memory holes for runs taken on a variety of different polarization states, ranging from completely unpolarized to nearly saturated (field cooled). Each is normalized to the total aging effect measured at that polarization. There appears to be little systematic effect of polarizing the sample on this characteristic form of aging. (We do not know what accounts for the one anomalously low point, but there are several possible transient effects that can reduce memory.) Figure 6 illustrates the T dependence of $\varepsilon''/\varepsilon'$ on warming after aging for three different polarizations, with a best-fit base line and the slope of the data in the range 160–198 K subtracted. These detrended data overlay well for the least and most polarized cases. The base line and slope, which do not contribute to the hole, are very sensitive to the polarization.

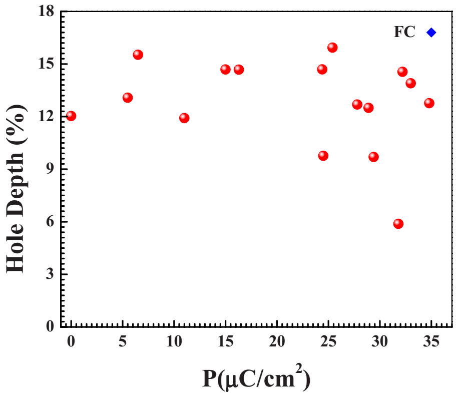

FIG. 5. (Color online) The percentage of the total aging at 180 K which persists as a memory hole on reheating is shown as a function of net polarization reached at 205 K. One point taken on field cooling is included.

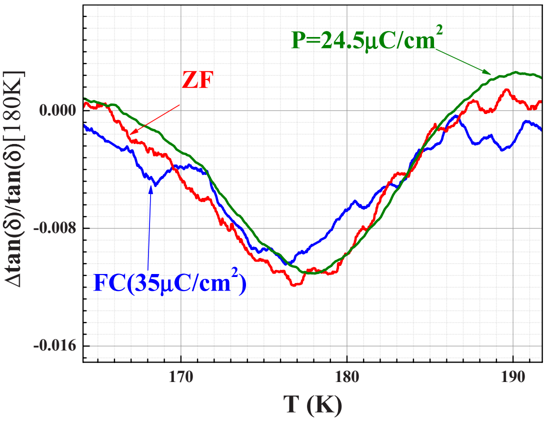

FIG. 6. (Color online) Smoothed detrended memory holes are shown for simple zero-field cooling (ZFC) and FC cases and one intermediate case. The figure shows the difference between $\tan(\delta)$ and the best linear fit to $\tan(\delta)$ over the range from 160 to 198 K, expressed as a fraction of $\tan(\delta)$ at 180 K.

III. DISCUSSION

The spin-glass-like aging properties of cubic and near-cubic relaxors suggest two rather different classes of possible origins. One would be that the PNRs interact strongly enough to form a complicated glass. The other would be that a collection of unit-cell polarizations form a glass which contributes little to the net polarization but strongly affects the kinetics of the PNR and hence the observed polarization kinetics. In the former case, once most of the PNRs are aligned, spin-glass kinetics should no longer be present, since, regardless of whether the Hamiltonian is Ising type or Heisenberg type, there are strong crossovers out of the spin-glass kinetic regime when partial polarization is reached, both according to theory (as reviewed in Ref. 7) and experiment (e.g., Ref. 30). In the case of PMN-8%PT the results seem unambiguous in that the distinctive aging effects persist even when the PNRs are aligned almost to saturation. That result seems flatly incompatible with a picture of a glassiness arising from a collection of interacting PNRs. It is, however, fully compatible with a picture in which the kinetics are controlled by degrees of freedom which contribute little to the susceptibility and which do not saturate at modest fields.

It is interesting to consider the relation of the low-temperature aging to different components of the dielectric response. It has been proposed that below the temperature of the peak susceptibility, the dielectric response becomes dominated by relatively small polar degrees of freedom, perhaps associated with a minority of nearly independent unit cells.[37] A simple thermodynamic calculation of the direct contribution to ε of any collection of independent unit-cell dipoles shows that these could account for not more than 5% of the actual susceptibility at 180 K, even if every unit cell were involved. Therefore it is certain that the observed susceptibility arises almost entirely from regions with ferroelectric correlations, i.e., the PNR. Nevertheless, the idea that qualitatively different forms of response are involved above and below T_P is supported by the drastic reduction in Barkhausen noise below T_P.[38] A model in which large-angle rotations of PNR are possible above T_P but only small-angle rotations and domain wall motion occur much below T_P would be compatible with the magnitudes of the susceptibility and the Barkhausen noise. The barriers to these polarization changes, however, would come from their random coupling to the orthogonal polarization components, which appear, judging by the distinct aging effects, to form a spin-glass-like state. At any rate, the low-temperature glassy aging effects do not come from PNR orientations.

One intriguing question concerns whether the most important glassy effects arise from the experimentally[1,23–26] and theoretically[39,40] known disordered regions between PNR or from the known orthogonal polarization components within each PNR.[1,23–26] The latter possibility is more interesting, since it involves a glassy order parameter coexisting locally with an ordinary ferroelectric order parameter.[29] A particularly plausible form would have either unit cells or very small clusters[41,42] oriented along [100]-type directions but forced by strain constraints to form [111]-type nanodomains, with roughly equal numbers of [100], [010], and [001] components. The glassy states would then be the many nearly equivalent distributions of those local deviations from the average [111] direction. The techniques of this paper, however, are not suited to distinguish between glass outside of PNRs and intra-PNR orthogonal glass.

ACKNOWLEDGMENTS

This work was initially funded by NSF Grant No. DMR 02-40644 and used facilities of the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under Grant No. DEFG02-91-ER4543. Work performed at Simon Fraser University was supported by the U.S. Office of Naval Research (Grant No. N00014-06-0166). We thank A. Bokov for a thoughtful exchange of ideas.

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