Aging and slow dynamics in $Sr_xBa_{1-x}Nb_2O_6$

Lambert K. Chao, Eugene V. Colla, and M. B. Weissman
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080, USA

Dwight D. Viehland
Department of Materials Science and Engineering, Virginia Tech, 201 Holden Hall (0237), Blacksburg, Virginia 24061, USA
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The uniaxial "relaxor" ferroelectric $Sr_xBa_{1-x}Nb_2O_6$ (SBN) is found to crossover from holelike to cumulative aging as it is cooled into the frozen relaxor regime. The cumulative aging contrasts sharply with the behavior of cubic relaxors, supporting ideas that the spin-glasslike aging in cubic relaxors is connected with polarization components orthogonal to the net ferropolarization. In the relaxor regime, small dc fields are found to suppress much of the dissipative response, similar to long-time aging. Pyroelectric currents are measured, along with limits on pyroelectric noise, allowing limits to be set on dynamically coherent domain sizes. Large nonlinear susceptibilities are found near the freezing transition.

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INTRODUCTION

Relaxor ferroelectrics[1,2] constitute a broad class of materials which show medium-range ferroelectric order at high temperature, but upon cooling kinetically freeze into a nonferroelectric state, usually dubbed the relaxor regime. In most cases this kinetic freezing is a steeper function of temperature than can be obtained from an Arrhenius expression with a reasonable attempt rate, so some sort of barrier growth at lower temperature, i.e., thermodynamic cooperativity, is involved. The types of glassy freezing involved in relaxor transitions have not been well characterized and may be quite diverse. Most familiar relaxors are perovskites with cubic symmetry (at high temperature), but a few, such as $Sr_xBa_{1-x}Nb_2O_6$ (SBN), are uniaxial. It has been proposed[3] that SBN may exemplify the random field Ising model (RFIM),[4] in contrast to cubic relaxors. In this paper we present a variety of measurements on SBN, including aging studies showing that the SBN relaxor regime is qualitatively distinct from the relaxor regime in several cubic materials. Other low frequency dynamic measurements are presented which we hope will stimulate calculations of similar properties for ideal RFIM's and other relevant models for comparison.

Aging is a generic feature of disordered systems,[5] for which there are a variety of metastable states unrelated by symmetries. As a disordered material approaches thermal equilibrium, it settles into states of progressively lower free energy. Typically, although not inevitably, these states have lower electrical or magnetic susceptibility. Thus the existence of aging *per se* is not a particularly useful diagnostic indicator. However, the behavior of aging under a variety of temperature and field histories can vary radically between different types of disordered systems.[5] The simplest types of aging involve growth of ordered domains. The domain size is a simple order parameter, and the aging at different temperatures is cumulative. At the other extreme, spin glasses show aging "holes," in which aging at one temperature (T_A) affects susceptibility only in a narrow window around T_A, and the aging hole is remembered so long as $T < T_A$.[5] Such behavior is associated with complicated order parameters, for which the lowest free energy states at different T's may be dissimilar.[6–8]

Cubic relaxors such as $PbMn_{1/3}Nb_{2/3}O_3$ (PMN) have been found to show a variety of different aging effects near the relaxor freezing temperature T_P.[9,10] [Here we employ a model-independent, but measurement-frequency-dependent, definition of T_P as the temperature at which $\varepsilon'(50\ \mathrm{Hz})$ peaks.] However, well below T_P (e.g., at 0.6 T_P), their aging is remarkably universal, and closely similar to spin glasses, including hole memory.[9,10] We have reported[11] one measurement on SBN doped with La which, in contrast, shows almost entirely cumulative aging at 0.63 T_P. Others have reported[12,13] that just below T_P, the aging produces a substantial hole component in other doped SBN samples. Here we shall show that there is a gradual crossover between these behaviors. The time course of the aging is found to show major deviations from simple scaling laws, as noted previously,[13] allowing extraction of a characteristic time and of an activation energy.

The effect of electric fields E on aging have been studied somewhat in relaxors (e.g., Refs. 14–17), in analogy to the effects of magnetic fields on aging in spin glasses[18,19] and other magnetic systems.[5] Here we report somewhat different effects of electric fields, primarily the ability of relatively small fields to systematically accelerate the reduction of the out-of-phase susceptibility.

We also report pyroelectric measurements on SBN, along with some attempts at measuring noise in the pyroelectric current. The low values of the pyroelectric noise will help set a limit on the sizes of the cooperative domains involved in the relaxation of induced polarization.

Finally, we examine the temperature and frequency dependence of a drop in susceptibility found at low T, finding again simple Arrhenius activated kinetics. We explore the connection between the activated process found in the aging and that found in the susceptibility itself.

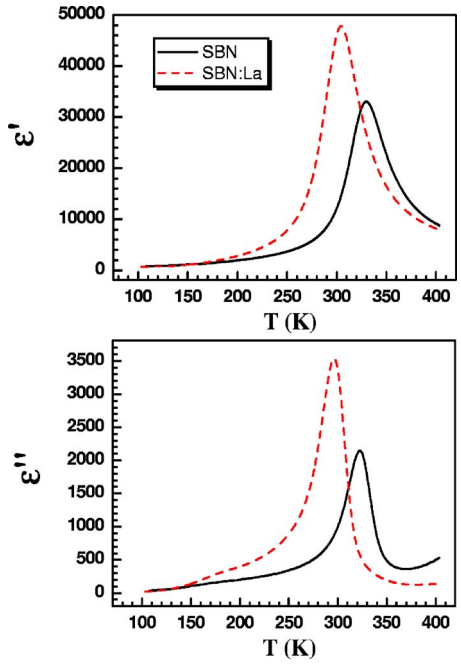

FIG. 1. (Color online) The complex dielectric coefficients (ε' and ε'') for the two samples are shown as a function of T at f =100 Hz. Data were taken on cooling at about 4 K/min (SBN) and about 2 K/min(SBN:La) and at rms fields of 13 V/cm (SBN) and 0.7 V/cm (SBN:La).

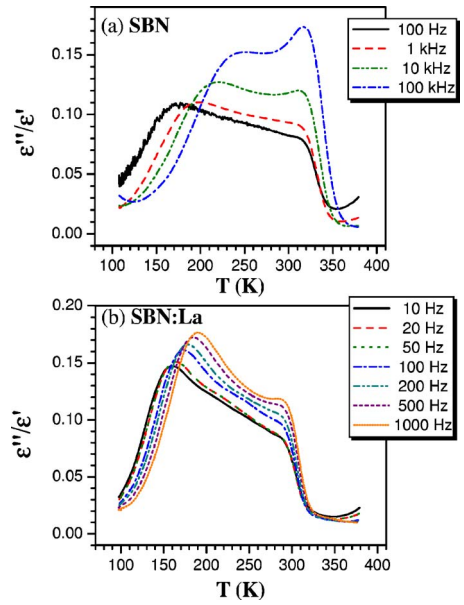

FIG. 2. (Color online) Temperature dependence of $\varepsilon''/\varepsilon'$ is shown for a range of frequencies, including both at T_P and at the lower-T kinetic freeze-out.

EXPERIMENT AND RESULTS

We studied two single crystals, one of SBN with 60% Sr and 40% Ba, the other of similar composition but with 1% La doping. The crystals were grown at Rockwell International Science Center, (Thousand Oaks, CA) using techniques previously described.[20] All qualitative behavior of the two samples was similar.

The samples were configured as capacitors with the electric field along the [001] axis, with thicknesses of 0.38 mm (SBN) and 1.4 mm (SBN:La), and areas of 0.68 and 11 mm^2, respectively. The complex dimensionless dielectric constants for the two samples are shown as a function of T in Fig. 1. Due to aging, such curves are somewhat dependent on the thermal history even when taken without applied dc fields, especially since these materials show some cumulative aging. The freezing transition is evident at around T_P =326 K (SBN) and T_P=305 K(SBN:La). The increase of dispersion at the highest T's shown, most evident at the lowest frequencies, is due to some electrical conduction process.

At around T=180 K in each sample there is a strongly frequency-dependent freeze-out of the response, particularly the out-of-phase response ε''. Figure 2 illustrates the frequency-dependent drop in $\varepsilon''/\varepsilon'$ (also known as the loss tangent). The T dependence of the frequencies for which $\varepsilon''/\varepsilon'$ is maximized at this lower-T feature are plotted in Fig. 3, showing a standard Arrhenius dependence with activation energies of 4000 and 5040 K and attempt rates of 7×10^{11} and 3.5×10^{14} Hz for SBN and SBN:La, respectively. The activation energies are accurate to better than 200 K, so the attempt rates are accurate to about a factor of three. Activated processes in solids typically have attempt rates the range of around 10^{12} Hz. (They are quite different from the prefactors of the critical dynamics near the higher-T peak in ε', which have been found to be in the range of 10^7 Hz.[3]) This freeze-out is evidently a purely kinetic phenomenon, i.e., a simple Arrhenius slowing down involving fixed barriers, rather than a thermodynamically cooperative effect in which barrier heights change. As such it is manifestly distinct from a lower-T cooperative phase transition found in some similar materials.[21] (We argue below that domain wall motion is the obvious process involved.)

A series of experiments on aging at zero field, followed by cooling then warming past T_A, show a gradual crossover in properties as T_A is lowered below T_P. Figure 4 shows a typical behavior of $\varepsilon''/\varepsilon'$ for a range of T_A/T_P, including examples from each sample. Of the various possible combinations of ε'' and ε', we pick $\varepsilon''/\varepsilon'$ for these plots because the holelike aging components are a bit more evident in it than in, say ε'' itself. For T_A near T_P on warming there is

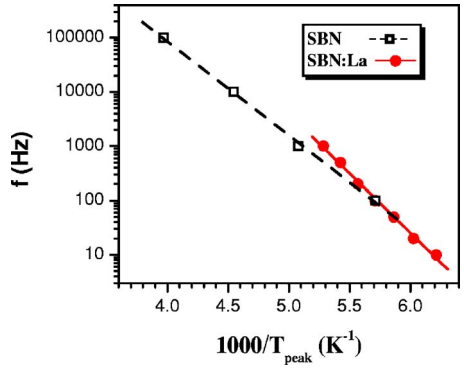

FIG. 3. (Color online) T dependences of the frequency for which $\varepsilon''/\varepsilon'$ is maximized are shown in an Arrhenius plot.

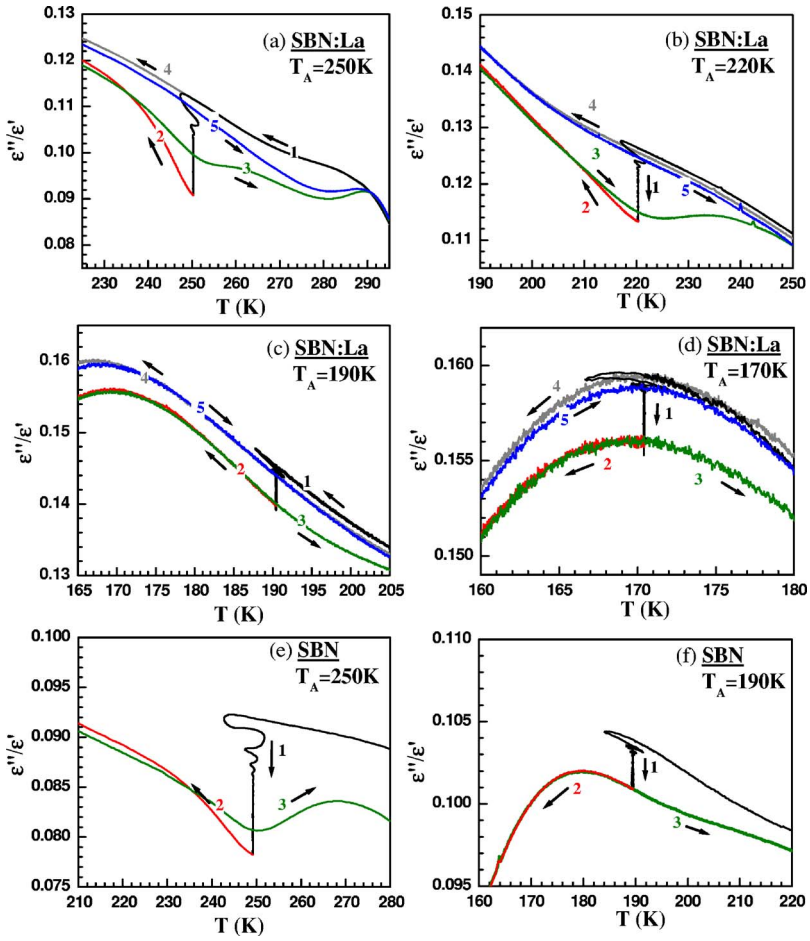

FIG. 4. (Color online) Aging behavior of $\varepsilon''/\varepsilon'$ is shown for a range of T_A. All T sweeps were made at roughly 3 K/min. ε was measured with an rms field of 0.7 V/cm at 50 Hz for SBN:La and with 13 V/cm rms at 100 Hz for SBN. In panels (a) through (c) curve 1 is taken on cooling from 350 K to T_A, at which T was fixed for 16 h. Curve 2 was taken cooling to a lower T_B, with immediate reheating to 350 K along curve 3. Curves 4 and 5 are reference heating and cooling curves. For panel (d) the starting T was 300 K and the aging time 17.6 h. T_B's were 180, 180, 140, and 120 K, respectively. For panels (e) and (f), the initial annealing T was 450 K, aging at T_A lasted for 5 h, and T_B was 150 K.

memory of a distinct hole at T_A, along with some cumulative aging. The holelike aging occurs in ε'', while the aging of ε' is nearly cumulative. At lower T_A the hole in ε'' becomes very small, while the cumulative aging persists.

A comparison of the aging of the susceptibility of SBN at different measurement frequencies (Fig. 5) shows even near T_P where holelike memory is found, there is no $\omega\tau$ scaling, i.e., both ω and aging time τ matter, not just the product. Similar results were found for SBN:La. Thus there was no regime which showed the combination of memory, rejuvenation, and scaling characteristic of spin glasses.

When SBN is cooled in an electric field, ε'' is substantially reduced, as shown in Fig. 6. The effect nearly saturates by around $E=180$ V/cm. (In SBN:La a very similar effect is found, but with the saturation E of roughly 250 V/cm.) After cooling in zero field to the midst of this temperature range 250 K, the initial effect of applying E is to undo some of the aging that occurred after cooling. (See Fig. 7.) The sample then ages toward approximately the same state reached in field cooling, more rapidly as $|E|$ is increased. Subsequently

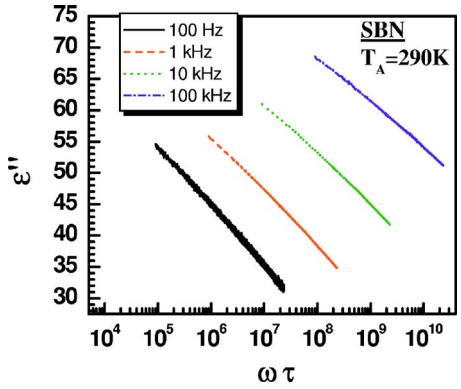

FIG. 5. (Color online) Comparison of the aging of ε'' in SBN at different measurement frequencies is shown. The starting time for t_W was taken to be when T first reached 290 K. We find no regime with $\omega\tau$ scaling, i.e., both ω and τ matter, not just the product.

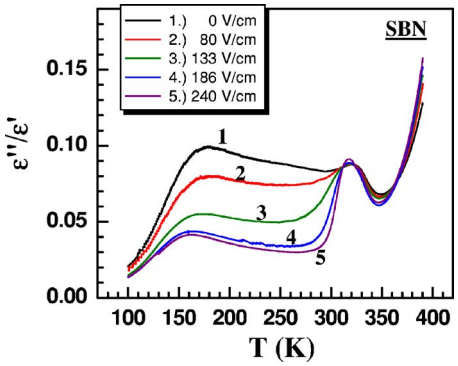

FIG. 6. (Color online) Dependence of $\varepsilon''/\varepsilon'$ on the electric field in which the SBN sample is cooled is shown. The measurement frequency was 100 Hz and the rms ac field was 27 V/cm.

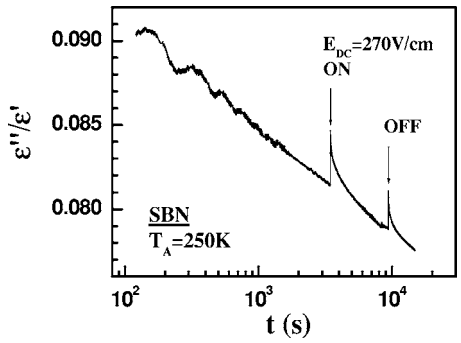

FIG. 7. Transient effect of a temporarily applied electric field on the aging of $\varepsilon''/\varepsilon'$ is illustrated. The initial oscillations come from oscillations of T.

resetting to $E=0$ leads to a transient loss of aging, followed by recovery to approximately the curve that would have been reached had the field stayed on.

For SBN, plots of $\varepsilon''/\varepsilon'$ versus time at different T and E show clear characteristic aging times τ_C at which $d(\varepsilon''/\varepsilon')/d\ln(\tau)$ is maximal, as seen in Fig. 8. (In contrast, for SBN:La, we found approximately logarithmic relaxation, without any clear characteristic time.) These aging times also can be fit with Arrhenius expressions, as illustrated in Fig. 9. The attempt rate, around 10^{14} Hz, is again not too far from typical values. The activation energy (e.g., 11 300 K at $E=773$ V/cm) is significantly larger than the activation energy found directly in the freeze-out of the dielectric response. Extrapolation of the somewhat E-dependent activation energy to $E=0$ would give a value of about 14 000 K, even more different from the 4000 K found in the frequency dependence of the $E=0$ response itself. The same E dependence of the activation energy indicates that a dipole moment change of around 3000 K $k_B/(800$ V/cm,) or about 6×10^{-23} C cm is involved in the rate-limiting aging step, equivalent to coherent realignments of some 2×10^4 unit cells in SBN.

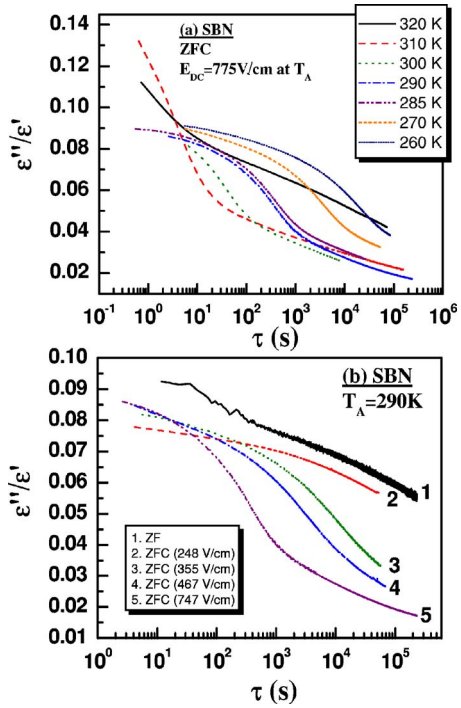

FIG. 8. (Color online) Plots of $\varepsilon''/\varepsilon'$ versus aging time (starting from when E is turned on) at different T and E show clear characteristic aging times τ_C at which $d(\varepsilon''/\varepsilon')/d\ln(\tau)$ is maximal.

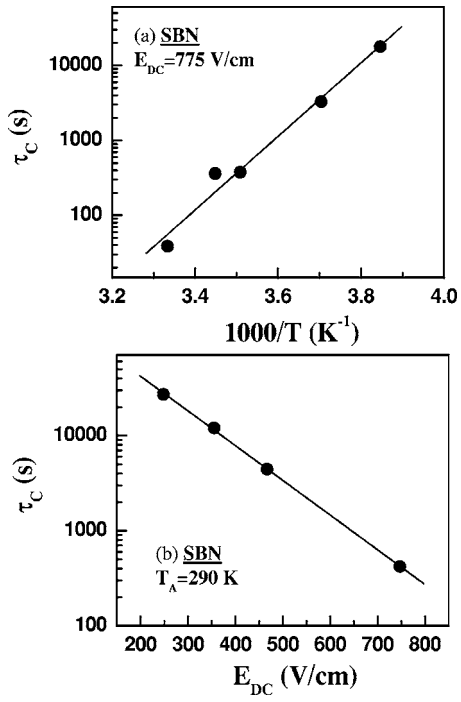

FIG. 9. Characteristic aging times, as seen in Fig. 8, are shown in an Arrhenius plot and versus electric field at fixed T.

Pyroelectric measurements were taken under several conditions. The most useful involved applying a constant voltage bias during cooling, removing the bias, and measuring current on warming. T was monitored during the warming, with typical rates being very roughly 30 K/min. Typical results for SBN are shown in Fig. 10. (Similar results were found for SBN:La, except that the anomalous self-poling in zero field was negligible.) The most striking feature is that a substantial polarization tail persists above T_P. While a roughly similar tail has been found in similar measurements

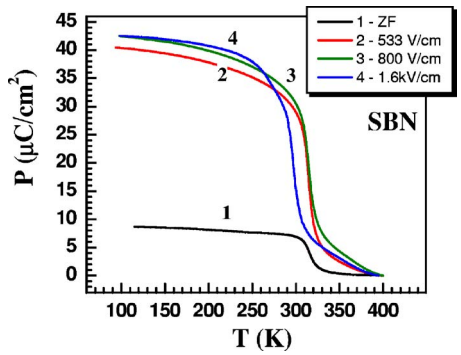

FIG. 10. (Color online) Net polarization versus T, as measured from integrated pyroelectric current, is shown for the SBN sample. Current was measured on warming at rates of roughly 30 K/min in zero field after cooling in several different fields.

on Ce-doped SBN,[22] the interpretation focused on possible critical behavior below T_P. The high-T polarization tail found here shows a distinct feature, indicating that some distinct process is present.

We also measured the current noise during rapid heating of the SBN sample to see if pyroelectric Barkhausen noise was detectable, since that could be used to estimate the sizes of the units that depolarize coherently. In the simplest picture, the depolarization would occur as a collection of discrete abrupt steps. Then in a current noise measurement, the pyroelectric noise would show up as a collection of independent current spikes, giving a frequency-independent spectrum with magnitude proportional to the current and to the size of the independent dipole relaxations. This spectrum would appear against a background of intrinsic fluctuation-dissipation noise from the sample (with a spectrum approximately proportional to f), low frequency noise resulting from unevenness in heating rates and other artifacts, and amplifier noise. Amplifier noise was not a major problem for these experiments. Low frequency artifacts led to poorly reproducible spectra below 1 kHz. For the remaining noise, subtraction of the equilibrium polarization noise background is crucial. Since the pyroelectric current peaks in the region where ε'' is a rapidly increasing function of T, this subtraction is prone to systematic errors because T must change rapidly in a pyroelectric measurement. Nevertheless, we found that any Barkhausen noise was significantly less than equilibrium noise in the 1–2 kHz range, allowing us to set an upper bound on the magnitude of the typical abrupt coherent depolarization step, about 4×10^{-22} C cm. That corresponds to an upper limit on the volume depoling in a single abrupt step of around 10^{-17} cm^3, i.e., about 10^5 unit cells. Since the E dependence of the aging indicated coherent units slightly smaller than that, that result is not surprising. Future work will deal with apparent pyroelectric noise found in SBN:La and explore whether the limits on the noise in SBN are due to small coherence regions or to depolarization events not being abrupt.

We also note in passing that SBN has been reported to show huge nonlinear susceptibility in the neighborhood of T_P as determined by harmonic generation.[23] Our results replicated those findings closely enough to not require more detailed presentation.

DISCUSSION

Perhaps the most significant implications at this point concern the patterns of zero-field aging. No $\omega\tau$ scaling was found at any T.[13] At temperatures of around 0.7 T_P, essentially no hole-type aging occurs. These results contrast sharply with cubic relaxors, which at comparable T/T_P show near-universal spin-glasslike behavior, including aging holes, lack of cumulative aging, and $\omega\tau$ scaling.[9,10] That contrast strongly indicates that the fundamental physics of the frozen state of SBN is unlike that of typical cubic relaxors. It is consistent with the proposal[11] that the glassy behavior of the cubic relaxors comes primarily from the local polarization components (known from scattering studies, e.g., Ref. 24) orthogonal to the principal polarization direction of the meso-scale ferro-order rather than from interactions among ferroregions.

The distinct activation energies in pure SBN for the dielectric response and the aging may have a relatively simple interpretation. Well below T_P, both the response and the aging should be dominated by domain growth processes, since in an Ising picture domain wall positions are the only important parameter in the frozen state, and extraneous processes such as ionic conductivity are believed to freeze out.[25] So the question becomes why different measures of the domain dynamics give different activation energies. The T dependence of ε'' gives an initial clue. Roughly speaking, $\varepsilon''(f,T)$ comes from processes with activation energies of $k_BT\ln(f_A/f)$, where k_B is Boltzmann's constant. Although there is a peak in $\varepsilon''/\varepsilon'$ at a well-defined T, there is a large plateau in $\varepsilon''/\varepsilon'$ at higher T, but not at lower T. That indicates that the activation energy measured for the peak describes the *minimum* of a distribution of activation energies found for short-range domain wall motion. In the presence of intrinsic disorder, it is not surprising that these activation energies are distributed. One expects there to be a minimum barrier, corresponding to the barrier to switching of the polarization of one unit cell in an environment where the two polarization states have roughly equal energies.

Aging presumably involves extensive growth, or at least rearrangement, of domains. The activation energy for such a multistep process is not the average of the barrier height of the steps but rather the *maximum* barrier height. That includes steps in which domain walls have to depin from locations favored by the disorder, and thus would be expected to be significantly larger than the typical barrier. This picture is essentially the same as that used before[25] to account for the change in long-time dielectric relaxation in the presence of illumination. The difference between the activation energy for short-range motion and that for long-range motion is also reminiscent of similar effects seen for impurity diffusion in metals.[26] The absence of a clear relaxation time in the SBN:La aging may indicate that in the presence of stronger disorder the tail of the distribution function for the domain-wall pinning strength extends out to very large values. The large dipole changes in the rate limiting step inferred from the small field scale required to speed up the aging in SBN nicely fits this picture.

Our measurement of a characteristic size of dipole realignments from the E dependence of the aging rate give an estimate of a dynamical coherence volume of 2×10^4 unit cells. Such dynamical units can be smaller than the static correlation volumes, i.e., the domain sizes themselves, if domain wall motions typically do not eliminate domains. They could be larger than the domains if there are correlated realignments involving many domains. Typical domain size distributions in slowly cooled Ce-doped SBN, estimated from imaging techniques,[3] extend to around 3×10^6 unit cells, if the unmeasured depths are comparable to the imaged dimensions. With obvious caveats involving comparisons of different materials, it seems likely that the coherent aging dynamics involve domain wall motions which usually involve a small domain or a fraction of a larger domain, rather than cooperative changes in many domains.

Direct tests of the relation between our other measured slow dynamical properties and those of the RFIM and other

models await further theoretical calculations. However, we shall comment on some of the more intriguing features.

Near T_P, reversing E has mainly a transient effect on aging. That implies that in that regime the main aging process in a field cannot be growth of the favored domain direction, since that process would reverse and lead to a slow increase in ε after E reversal. In fact, the holelike aging at $E=0$ just below T_P already indicated that in this regime aging is dominated by some more complicated process involving detailed domain-wall structure, rather than by simple domain growth.[12] At lower T it is difficult to perform the same test, since field reversal does not lead to polarization reversal except for very large fields.

At 250 K, there appear to be two distinct processes contributing to the aging. Any field change leads to a transient loss of aging, suggesting that quick domain wall motions erase some aging of detailed domain wall configurations. It is natural to identify this component with the one that shows holelike behavior as a function of thermal history, as previously suggested.[12] However, a larger component of the aging, while accelerated by nonzero E, appears cumulative even as E is switched off. It is natural to attribute this component to the net growth of domains, including the loss of small domains.

The pyroelectric measurements show polarization persisting above T_P, apparently due to some sort of process distinct from the main domain polarization, since a partially resolvable separate peak appears in the pyroelectric current. We do not have any particularly convincing explanation for this effect, but we believe that it implies that one needs to use great caution in interpreting the details of the T-dependent polarization in terms of critical phenomena.

Note added in proofs. J. Kurchan and L. Cugliandolo have pointed out to us that the partially hole-like aging found near the ferroelectric freezing point may simply reflect a heterogeneous collection of RFIM regions, with a range of different freezing points. Each region would show particularly strong aging just below its own freezing point, near the same temperature at which it makes the largest contribution to the susceptibility.

ACKNOWLEDGMENTS

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