Nonferroelectric aging in the relaxor $PbMg_{1/3}Nb_{2/3}O_3$

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Three samples of $PbMg_{1/3}Nb_{2/3}O_3$ found to show no abrupt electric-field-driven phase transition to a polarized state are compared to a sample which has such a transition and whose dielectric properties resemble those of other samples previously reported to show that transition. The samples without the field-driven transition have lower kinetic freezing temperatures and lower dielectric constants, and one shows a new transitionlike susceptibility jump at about 180 K on cooling in zero field. Nonetheless, in each sample the distinctive spin-glasslike aging of the dielectric susceptibility follows the same aging pattern quantitatively. These results support pictures in which the glassy aging comes from different degrees of freedom than does most of the dielectric response, which is dominated by the orientations of ferroelectriclike polar nanoregions.

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INTRODUCTION

The enormous dielectric susceptibility of the perovskite relaxor $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and its close relatives is known to arise from polar nanoregions (PNRs) in which ferroelectriclike order is correlated on length scales of roughly 10 nm. (See, e.g., Ref. 1 for a recent reference and Refs. 2 and 3 for reviews.) Both neutron scattering[4] and NMR (Ref. 5) show that when the material is cooled below about 210 K, it forms a heterogeneous mixture of such partially ordered PNRs, in which the net polarization is predominantly along [111] directions, and of disordered regions with more isotropic distributions of polarizations. Although it is tempting to ascribe the absence of long-range ferroelectricity in zero field and the onset of glassy relaxor behavior to the effects of random fields on the PNRs,[6,7] such descriptions cannot easily account for the spin-glasslike aging properties found in the glassy regime of cubic relaxors.[8,9] Incorporation of random interactions among PNRs might lead to spin-glasslike aging effects, but would not easily account for the large field change required to disrupt aging memories,[10] and would have difficulty accounting for the temperature dependence of the Barkhausen noise magnitude[11] as well as the complicated multistage kinetics found for the field-driven conversion to a ferroelectric state.[12] Thus it has been proposed[10,12] that the glassy aging properties of PMN come not directly from the [111] average polar displacements of each PNR, responsible for almost all the susceptibility, but rather from a background of other degrees of freedom associated with much smaller dipole moments. In this paper, we present data showing that samples with a significant variety of dielectric and ferroelectric behavior nonetheless show almost identical aging behavior, supporting the hypothesis that different degrees of freedom are responsible for the aging. In the Discussion, we include comments on prior theoretical and experimental works pointing toward the most likely suspect for those other degrees of freedom.

The features which differ among the four PMN samples described here include the presence or absence of an abrupt field-driven conversion to a noncubic forced ferroelectric (FFE) state,[12–16] a range of temperatures T_P, at which the ac dielectric coefficient $\varepsilon'(T)$ peaks, a range of different values for the room-temperature ε', and the presence or absence of a poorly understood first-order jump in several properties near 180 K on cooling in zero field. Nevertheless, we find that the spin-glasslike aging effects at 180 K remain quantitatively close in all these samples. Although the causes (perhaps some form of disorder) of the differences in the dielectric constant and ferroelectric effects are not known, our main point in this paper is not to explain those differences or analyze them in detail but rather to argue that the constancy of the aging effects suggests that they arise from different degrees of freedom than those that are mainly responsible for the large dielectric response.

MATERIALS, METHODS, AND CHARACTERIZATION

Sample *A* was grown by Professor Luo's group at the Shanghai Institute of Ceramics using a modified Bridgman

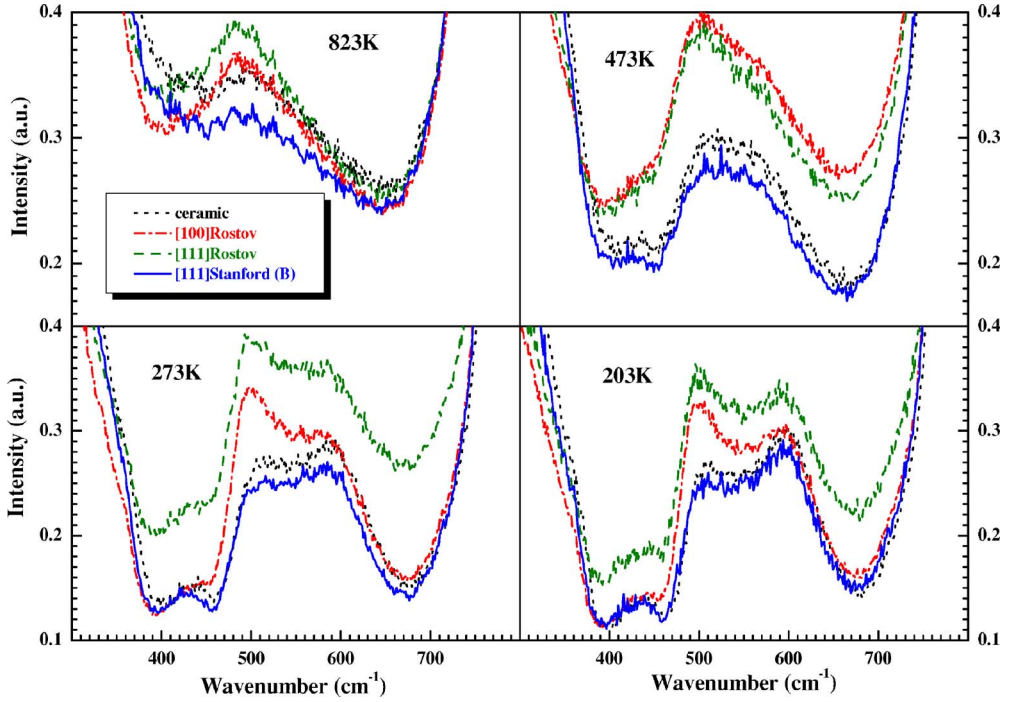

FIG. 1. (Color online) A section of the Raman spectra is shown at four different temperatures for our sample *B*, a ceramic sample, and two comparison samples from Rostov, similar but not identical to samples such as sample *C* of this work. Outside this frequency range, differences among samples were more subtle. Normalization of the spectra is approximate. A set of spectra at $T=93$ K closely resembled those at 203 K.

technique described elsewhere,[17] while sample *B* was grown by Professor Feigelson at Stanford University also by a modified Bridgman technique. Samples *C* and *D* are crystals from Rostov-on-Don grown by the Czochralski technique. Samples *A*, *B*, and *C* were all cut and configured with field along a [111] direction, while sample *D* had a [110] orientation.

Sample *A* was examined by both x-ray and neutron scattering techniques and found to be a high quality single crystal with a mosaic spread of less than 0.05° full width at half maximum (FWHM). Sample *B* was also examined by x-ray diffraction and found to be of high quality, although the mosaic spread was not quantified. Sample *A* was large, 1 mm thick, and 1 cm^2 in area. Sample *B* is 0.50 mm thick with an irregularly shaped area of 6.15 mm^2. Sample *C* is 0.8 mm thick with an area of 8.8 mm^2. These samples were configured as simple two-contact capacitors, with contacts consisting of evaporated films (of Au and Ag) covering the entire front and back sides. Sample *D* is 0.55 mm thick, with a contact pad of area 1.6 mm^2 covering part of one side. The geometrical factors in the capacitance, needed to extract the absolute dielectric constant values, were calibrated to better than 10% for samples *A*, *B*, and *C*, but not so well (perhaps to 25%) for sample *D*. Sample *A* spontaneously cracked after some thermal cycling, perhaps evidence of some internal strains.

Raman spectra were taken from $T=823$ K down to $T=93$ K on sample *B*. The most salient sample-dependent feature, shown in Fig. 1, was a peak at about 500 cm^{-1} wave number, which was present in two comparison crystal samples from Rostov-on-Don, but much weaker in a ceramic sample and in our crystal sample *B*. This peak becomes narrower upon cooling. It already exists to some degree above the Burns temperature (~630 K), below which dynamic PNRs form, so chemically ordered regions are likely to contribute to it. Thus sample *B* appears to have different chemical disorder than more typical PMN crystals.

The complex ac ε ε'-$i\varepsilon''$, was measured using standard ac lock-in methods. Temperatures were controlled with a standard transfer-line gas-flow cryostat, with the sample in vacuum.

Figure 2 shows the components of ε as a function of T for each sample. Sample *C* has properties similar to those of many other previously described samples which show a FFE (e.g., Refs. 12–16). Although the form of $\varepsilon(T)$ for all the samples is similar, the temperature T_P of the peak in ε' is lower in samples *A*, *B*, and *D* than in *C*. The overall dielectric constant in samples *A* and *B* (and probably also the less well-calibrated sample *D*) is significantly less than in sample *C*. Previous reports (e.g., Ref. 13) of T_P measured on other high-quality PMN crystal samples [such as those used in previous studies of the FFE (Refs. 12, 15, and 16) conversion] usually show values of T_P within about 2 K of that for sample *C*; thus the approximately 16 K reduction in T_P for samples *A* and *B* is highly significant. Some ceramic samples show similar variation in T_P and ε as a function of very small impurity content, indicating the important role of some form of disorder.[18,19] Annealing sample *B* for 8 h at 900 K in ambient atmosphere raised T_P by about 1.5 K, and raised the maximum of ε' by around 2%, with some uncertainty in ε' since the contacts were reapplied.

Figure 2 also shows the effect of field-cooling at 2.3 kV/cm, well above the threshold in [111]-oriented

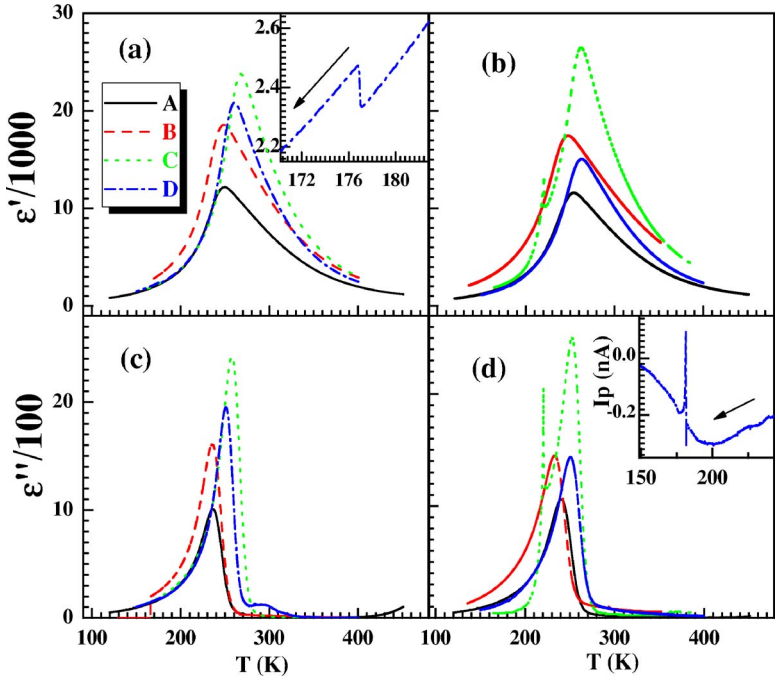

FIG. 2. (Color online) The real (parts a and b) and imaginary (parts c and d) parts of the dielectric coefficient are shown for the four samples under cooling in zero field (parts a and c) and cooling in a field of 2.3 kV/cm (parts b and d). The temperature sweep rates were roughly 4 K/min. Measurements were made at 100 Hz for curves shown in a and c, but at 1 kHz on sample *A* under field (i.e., in curves b and d). (Sample *A* was damaged before this type of 100 Hz data were taken.) The peak ε' of sample *A* in those curves would be shifted about 4 K lower at 100 Hz. The sharp features found under field in sample *C* are from the forced ferroelectric phase transition. The insert to (a) shows an expanded view of the anomalous step in ε' in sample *D* on cooling, with the axes labeled in the same units as the main plot. The inset to (d) shows the corresponding spike in pyrocurrent on field cooling.

samples for driving an abrupt FFE phase transition to a (possibly rhombohedral) polarized phase.[20] (A field of 2.9 kV/cm was used for sample *D*, since [110] samples have a higher threshold.) This FFE transition is clearly evident as sharp steps in both components of ε in sample *C*. The other samples show no sign of this transition.

Sample *D* always shows an unexpected small upward step in ε' on cooling at $E=0$, at temperatures which ranged from about 172 K to 191 K on a series of nominally identical cool downs. The same step showed up as a very prominent spike in the pyrocurrent under even small applied *E*, as shown in Fig. 2, with the sign of the current indicating *depolarization* upon cooling, opposite to the general trend to polarize on cooling. No corresponding step was found on warming. X-ray characterization by two of us (P.G. and B.D.), to be described elsewhere, of a sibling crystal shows a sharp step in the lattice constants at about 175 K, also found only on cooling and not warming.

High resolution neutron scattering measurements made on sample *A*, also to be described elsewhere, also show no field-driven symmetry change, in contrast to old neutron results on a sample with higher T_P and ε close to those of our sample *C*.[21] X-ray scattering on a sibling crystal to sample *D*, however, showed a clear FFE phase transition, exhibiting Bragg peak splitting. Since composition and most other short-range properties tend to be very similar between such siblings, it is possible that different long-range strains account for the different behavior of sample *D* and its sibling.

Thus samples *A* and *B* have a different empirical phase diagram than does sample *C*. Sample *D* is likely to be in a different phase than all the others at $E=0$ when it is cooled below what looks like first-order phase transition. Our point in this paper is not to sort out or further characterize the surprising variation in several properties, but rather to show that one property—glassy aging—is quite insensitive to whatever makes the samples have different dielectric and ferroelectric behaviors.

AGING METHODS AND RESULTS

The most distinctive qualitative features indicating spin-glasslike aging[22] are the combination of rejuvenation and memory, both present well into the frozen regime of all cubic relaxors reported so far.[8,9] Aging at temperature T_A reduces ε (especially ε'') near T_A, but the unaged $\varepsilon(T)$ is recovered (i.e., "rejuvenates") on further cooling. However, the loss of aging memory is only apparent since much of the dip in $\varepsilon''(T_A)$ is recovered on reheating. Heating above T_A erases this dip. The inset to Fig. 2 illustrates this aging-hole behavior for samples *A* and *C*. Samples *B* and *D* show the same behavior.

Figure 3 shows the time-dependent aging of ε'' (normalized to its starting value) in zero field after cooling to 180 K in each sample. On this particular cool down, the jump in dielectric properties in sample *D* had occurred at 191 K, before reaching 180 K. Similar aging (accompanied by a hole-like that shown in the inset to Fig. 2) was found on another run on sample *D* in which the jump occurred at 171 K on cooling below the aging *T*. Despite the substantial quantitative differences in the linear dielectric response, the presence in one sample of an anomalous zero-field transition, and the qualitative differences in far-from linear field-driven effects, all samples show aging following virtually the same quantitative pattern, with no adjustable parameters.

DISCUSSION

It is remarkable that samples with a significant range of dielectric behavior, including different empirical phase diagrams, show very similar aging effects, both qualitatively and quantitatively. Whatever property affects the Raman feature seems irrelevant. The jump in dielectric and lattice properties found in sample *D* appears to be irrelevant to aging. That jump does not even have a significant effect when it occurs after aging but before reading out the hole in ε'' on

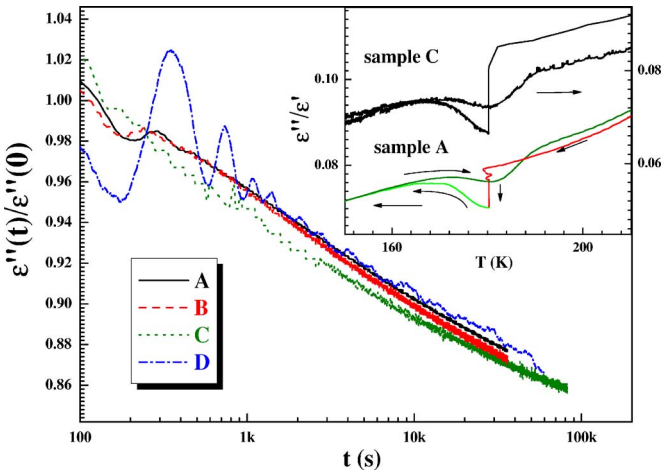

FIG. 3. (Color online) The aging of ε'' is shown as a function of time t spent at 180 K after rapid cooling from 400 K. The apparent anomalies for $t<1000$ s arise from the pattern of settling into the set temperature. The inset shows the development of an aging hole at 180 K in sample *A*. The aging time was 10 h, and the minimum temperature reached on subsequent cooling was 120 K. These measurements were made at 100 Hz.

subsequent warming. The insensitivity of the aging phenomena at 180 K to all these changes would be a remarkable coincidence if the aging resulted directly from the dynamics of the PNRs, since relaxor aging generally shows a variety of different behaviors in different regimes.[9,23,24] If, on the other hand, other degrees of freedom form the spinglasslike state, it would not be so surprising for its aging to be independent of factors strongly affecting the PNR.

One plausible candidate for such other degrees of freedom is suggested by scattering probes, which find local displacement components orthogonal to that net mid-scale polarization. Neutron scattering data have been interpreted to show that individual Pb displacements are predominantly [100]-type[4,25] or [110]-type,[1] but in any case not simply [111]. Spin-glasslike aging is indeed missing in the corresponding regime of uniaxial relaxors,[23] which lends strong support to the idea that such orthogonal polarization components play a role in the aging behavior.

Prior theoretical and experimental work sheds some light on the likely approximate nature of the local glassy correlations. The difference between the easy axes for PNR polarization and the preferred axes for unit-cell displacements indicates that long-range strain constraints inhibit the formation of domains of the locally favored polarization. Within related materials that lie closer to simple ferroelectric phases, tweed structures are seen for compositions near the relaxor-ferroelectric boundary,[26] providing more direct evidence of the role of strain constraints. It has been proposed, in the context of martensites, that the strain interactions in such tweed structures can lead to a type of spin glass in the presence of some quenched disorder.[27,28] It has also been suggested that such models may be relevant to relaxors.[26,29] Thus we suspect that the spin-glasslike aging properties of cubic relaxors such as PMN are driven by the same interactions that produce short-range tweedlike correlations among unit-cell displacements.

The PNR response, on which ε mainly depends, would be affected by the glassy order primarily because that order increases kinetic barriers for PNR reorientation. Similar effects have been found in simulations of related magnetic models.[30] The relation of glassy order to the kinetics of ferroic order would resemble that found for reentrant *xy* spin glasses, e.g., Ref. 31. However, the physics of the cubic relaxors would differ from that of such magnetic systems in two regards. One is the presence of random vector fields, forbidden by time-reversal symmetry in simple spin glasses. The other is the empirical partial spatial separation of the glassy and ferroelectric regions.[4,5]

Finally, we speculate a bit on what sorts of differences among these samples would be likely to have large effects on the PNR thermodynamics, but little effect on the aging kinetics. Random fields are known to play a large role in relaxors (e.g., Refs. 6 and 7), since although ε at T_P is very large compared to what could be reached for any collection of independent unit-cell dipoles, it is small compared to what would be obtained for a collection of free dipoles with the magnitude and density of the PNR. Among the sources of random fields, in addition to partially random stoichiometry, are more long-range strains created by chemically ordered regions,[32] known to exist in PMN (Ref. 2). Random fields (whether vector or tensor) correlated on scales larger than individual PNR will have coherent effects on PNR, suppressing ε, but would have little systematic effect on the sorts of nearly degenerate states with little net moment differences and little net strain differences implied by theoretical models of martensitic glasses.[27,28] The sign of the annealing effect on sample *B* is as expected if annealing reduces random fields, and the small effect suggests that very short-range diffusion would not suffice.

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