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Anisotropy of electric field freezing of the relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$

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The ferroelectric E-T phase diagram of relaxor ferroelectrics depends on the way the ferroelectric transition lines are approached. Here, we present the E-T phase diagram of relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ where the temperature was held constant and the electric dc bias field applied along the [111] and [001] directions was varied. Strong anisotropy was observed for both directions. For the [111] direction, the critical point was shown to exist at practically the same field as in the E=const, T=variable case, whereas no critical point could be determined for the [001] direction for $|E_{bias}|<20$ kV/cm. When the electric field was applied along the [111] direction, a strongly nonlinear first-order-type jump in the polarization due to the cooperative ordering transition was observed. In the [001] direction, on the other hand, only a smooth field dependence of the polarization was found, indicating the lack of cooperative ordering.

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I. INTRODUCTION

Canonical ferroelectric relaxors such as $Pb(Mg_{1/3}Nb_{2/3})O_3$—denoted as PMN—are perovskite solid solutions characterized by site and charge disorder.[1,2] On cooling, no long range order is established but rather broad and strongly frequency dependent peaks in the dielectric responses can be observed related to the glassy-type freezing.[1–11] The relaxors consist of small, randomly oriented polar nanoregions,[12–16] which, in view of their relatively large dipole moments, couple to the electric field more efficiently than individual dipoles in dipolar glasses. As a consequence and in contrast to dipolar glasses,[17] a ferroelectric phase can be induced in relaxors by applying a sufficiently strong electric field.[18–21] In this case, the Barkhausen jumps observed in the PMN [111] crystal signal an avalanchelike depinning of microdomains, thus indicating the existence of ferroelectric microdomains.[20]

It is well known[22] that the transition lines and the phase diagram of relaxor ferroelectrics depend on the way the ferroelectric (FE) phase is approached. In particular, it depends on whether E=const and T is varied or whether T=const and E is varied. Very recently, we studied the phase diagram of $Pb(Mg_{1/3}Nb_{2/3})O_3$ abbreviated as PMN. The dc bias field E was constant and the temperature T was varied[21] (Fig. 1). A ferroelectric phase, an ergodic phase, and a nonergodic relaxor phase have been found.[21] The transition from the ergodic to the nonergodic relaxor phase is accompanied by the divergence of the largest relaxation time at the freezing transition T_0 which breaks the ergodicity of the system. Another interesting point was the observation of the critical point above which the difference between the different phases disappears.

Here, we report on the phase diagram of PMN [111] and [001] for E=variable and T=const as well as on the difference in the dependence of the polarization on the bias field in these two cases. In particular, we wished to check whether a critical point[23] exists in the [001] direction, too.

II. EXPERIMENTAL PROCEDURES AND RESULTS

In order to study the polarization evolution across the relaxor ferroelectric line and its dynamics, measurements of the electric field–polarization hysteresis and static field-cooled polarization measurement were performed on a [111] and [001] single PMN crystal. The platelet-shaped samples were cut from a single crystal of the PMN perpendicular to either the [111] or [001] direction and polished. Gold electrodes were sputtered onto several samples with thicknesses from 0.34 to 1.35 mm by the evaporation technique. The time and the dc field dependences of the quasistatic dielectric polarization $P(E,T,t)$ were determined by cooling an annealed sample to a specific temperature, which was then stabilized and the dc bias field was applied. In the relaxation experiments, the polarization $P(E=\text{const},T=\text{const},t)$ was recorded as a function of time after a constant bias field was switched on. In the measurements of the field dependence, the field was slowly linearly cycled between positive and negative values of $|E_{max}|\sim 7$ kV/cm. In all polarization measurements, the corresponding polarization charge was measured by the Keithley 617 programmable electrometer.[24]

Since it is well known that history-dependent effects play an important role[5,25] in relaxor systems, the samples were annealed at 450 K for 1 h before each measurement. This was done in order to ensure identical conditions for all measurements and to eliminate the effects of previous treatments.[6,7]

Figure 1 shows the E-T phase diagram for PMN [111] and [001]. Figures 1(a) and 1(b) show the E-T phase diagram for PMN [111] obtained in a way described previously[26] (E=const, T=variable case) and in a different way where the low temperature transition line was obtained by changing the bias field at various constant temperatures (E=variable, T=const case), respectively. Depending on the way of the approach to the FE state, the first-order line separating the relaxor phase from the ferroelectric phase has a significantly different temperature dependence, as shown before by Refs. 22 and 27.

In the case of PMN [001], the critical response of the polarization order parameter was virtually absent in field-cooled experiments (Fig. 2). Only a very small and smeared anomaly can be observed on cooling with the small “jump” in polarization of ≈ 0.02 C m^{-2}. Consequently, no critical point could be determined in the [001] sample for fields be-

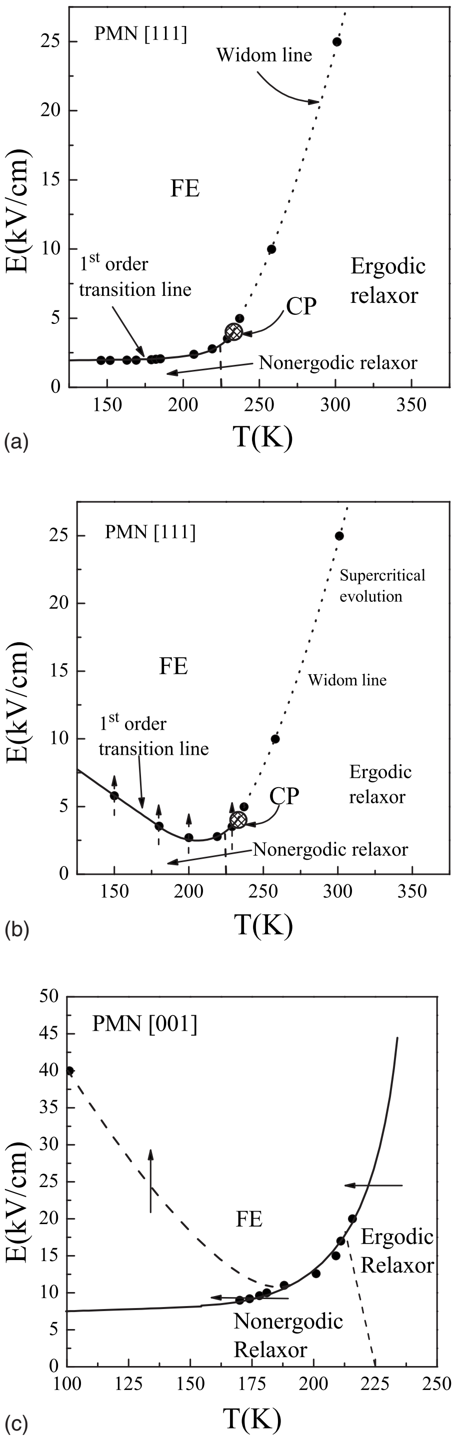

FIG. 1. Phase diagram of PMN for the bias field in the [111] direction: (a) E=const, T=variable and (b) E=variable, T=const. (c) Phase diagram of PMN for the bias field in the [001] direction. Here, arrows show the path of the approach to the FE state for different transition lines.

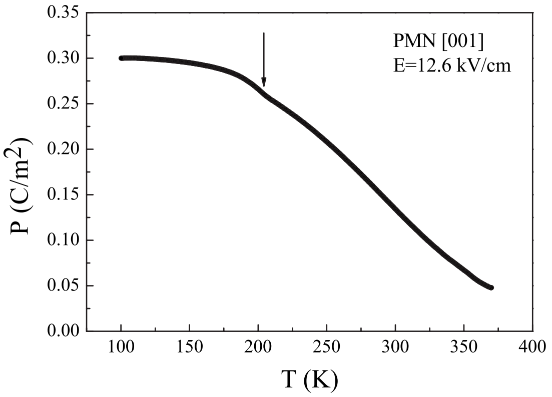

FIG. 2. Temperature dependence of the quasistatic polarization at E=12.6 kV/cm. The arrow denotes the position of the smeared anomaly related to the FE transition.

low 20 kV/cm in agreement with the data in Ref. 27. The E-T phase diagram in Fig. 1(c) for the [001] sample was constructed upon following the temperature and field dependence of this small anomaly. However, the question remains open whether this weak anomaly is not merely a consequence of the small misalignment in sample orientation.

The nonlinear polarization or dielectric field dependence in the presence of rather small electric fields was systematically studied before in relaxor materials.[25,28–31] Figures 3(a)–3(d) show the $P(E)$ hysteresis loops obtained at several constant temperatures for PMN [111]. At higher temperatures, a slim hysteresis loop is obtained as a consequence of the proximity of the steep ferroelectric conversion line, which prevents deeper penetration into the FE region even for larger bias fields. At lower temperatures, the polarization becomes increasingly saturated even at lower bias fields. This is related to the sharp discontinuous increase in the polarization order parameter on crossing the first-order ferroelectric conversion line. Note that the double (antiferroelectriclike) hysteresis loop feature can be observed in the vicinity of the ergodic-nonergodic glass transition line at which the longest relaxation time in the distribution of relaxation times diverges.[6]

This double hysteresis loop feature is not related to the antiferroelectric order or different domain types. The first steplike increase in the hysteresis loop on increasing the field

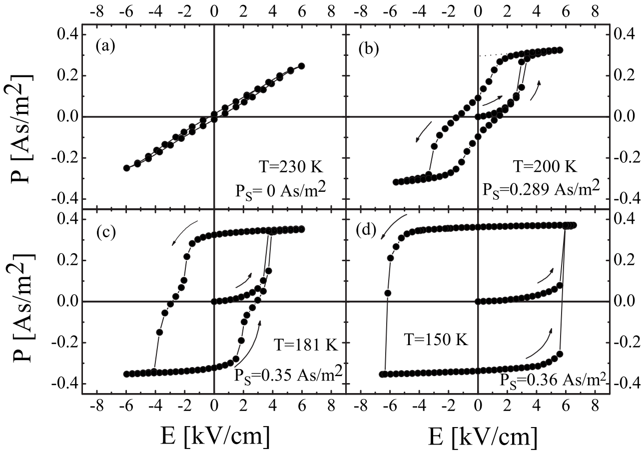

FIG. 3. Hysteresis loops for PMN at different temperatures (a) T=230 K, (b) T=200 K, (c) T=181 K, and (d) T=150 K. The bias field was applied along the [111] direction.

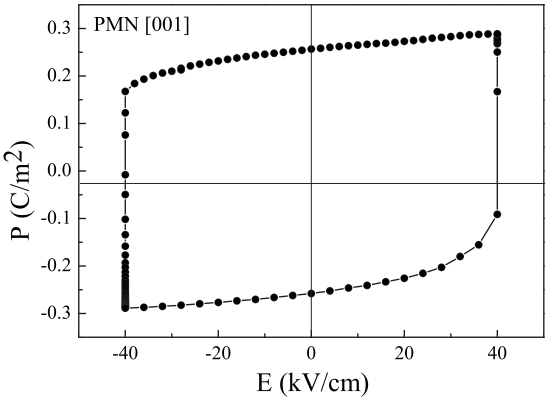

FIG. 4. Hysteresis loop for PMN [001] at T=100 K.

is related to the onset of the FE order at the FE phase transformation line at which P exhibits a rapid first-order-like increase. The polarization saturates at higher fields, and on reversal of the bias field, it starts relaxing to lower values. This causes the second steplike feature. Due to increasingly longer relaxation times as T is decreased, this relaxation becomes increasingly slower and the polarization becomes frozen even at larger negative bias values resulting in a rather broad boxlike hysteresis loop (see hysteresis at 150 K). It should be noted that a similar boxlike hysteresis loop can also be observed in the PMN [001] crystal, although in this case, a significantly higher electric field was necessary to obtain the same effect (Fig. 4).

As shown before,[5,25,32] the increase of the bias field has a significant impact on relaxation times (Fig. 5). They shorten dramatically and the system becomes monodispersive with increasing bias field (see relaxation curves at different bias fields in Fig. 5). As the field exceeds a specific threshold value on reversal, the polarization gets rapidly unfrozen. In analogy with the ferromagnetic materials exhibiting the broad hysteresis loops, the above experiments indicate that the long relaxation times of the polarization and, consequently, broad hysteresis loops could be related to the shape of the polar domains, which become strongly anisotropic with decreasing temperature.

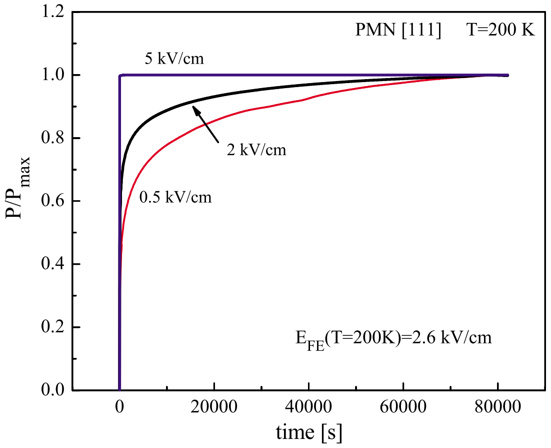

FIG. 5. (Color online) Time dependence of the quasistatic polarization at different bias fields and T=200 K. Note the distinct difference in the nature of time dependence for $E>E_{FE}$. Polarization response is normalized as the polarization values strongly depend on the dc bias electric field values.

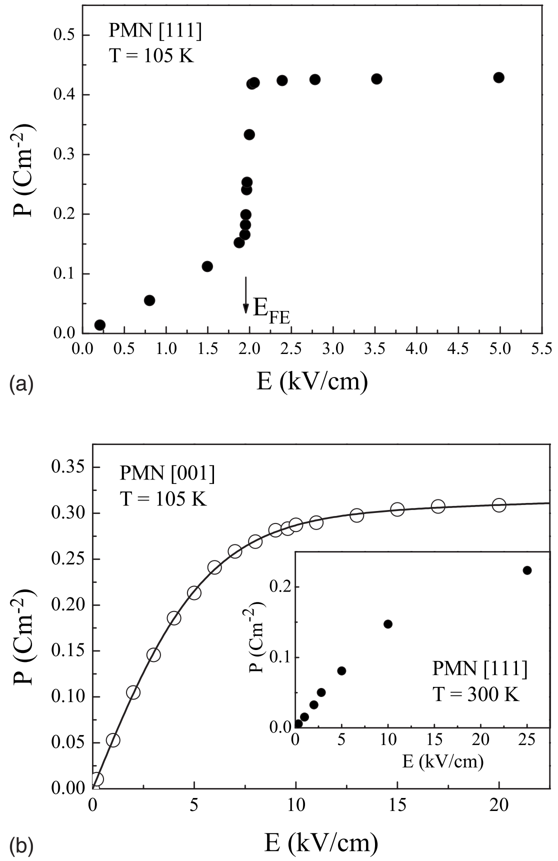

FIG. 6. Polarization at 105 K as a function of the bias electric field obtained in the field cooling runs. (a) Polarization of PMN for the bias field in the [111] direction. Note the strong nonlinear first-order-type jump due to the cooperative ordering phase transition. (b) Polarization of PMN for the bias field in the [001] direction. Note the smooth field dependence indicating the lack of the sharp cooperative ordering phenomena in the [001] direction. Solid line represents a fit to Eq. (1). The inset shows a similar noncooperative smooth behavior for the polarization of the PMN [111] sample at 300 K, i.e., at the temperature slightly above the ferroelectric conversion for the given range of the electric fields.

As indicated by the hysteresis loops at 180 and 200 K, PMN [111] transforms via the intermediate glassy state to another FE state with reversed polarization.

The double hysteresis loops are due to the interplay between the FE phase conversion and the conversion to the glassy state governed by the slow glassy dynamics. The FE+P state seems to be flipped to the $-P$ state via the intermediate glassy state where P=0. The bias field has a pronounced effect on the magnitude of the relaxation time as well as its distribution. The FE conversion line depends on the way how the E-T phase diagram is measured similarly as found in lanthanum-modified lead zirconate titanate (PLZT) ceramics.[22]

Our measurements of the quasistatic polarization as a function of the bias electric field also show the existence of a critical point in the PMN [111] E-T phase diagram, which terminates the first-order ferroelectric conversion line at a particular critical field value ($E_C \sim 4.5$ kV/cm). Above E_C, the supercritical evolution and the Widom line set in. The critical field for the critical point observed in the E =variable, T=const phase diagram (Fig. 1) has roughly the same value as the critical electric field for the critical point in the E=const, T=variable phase diagrams (Fig. 1). This is not surprising since, as shown before,[22,27] the main difference in the E-T phase diagram due to the two different paths of approach to the FE state is realized at much lower temperatures well below the critical temperature value.

A strong anisotropy in the polarization electric field dependence was observed in the field cooling experiments for the [111] and [001] axes. Figures 6(a) and 6(b) show the field-cooled polarization at 105 K as a function of the bias electric field for PMN [111] and PMN [001] samples, respectively. Anisotropy in the field dependence and the magnitude of the saturated polarization suggests different ordering mechanisms for two directions.

It is interesting to note that the $P(E)$ curve in Fig. 6(b) of PMN [001] could be well described [see solid lines in Fig. 6(b)] by the "activated polar cluster switching" expression

$$P(E) = \epsilon(T)\epsilon_0 E + P_0(T)\tanh\left[\frac{p(T)E}{kT}\right], \tag{1}$$

in which the polar cluster (ferroelectric nanodomain) reverses its polarization by flipping across some energy barrier via the activated process. Here, $\epsilon(T=105\text{ K})=770$, $p/kT(T=105\text{ K})=1.80\times 10^{-6}\text{ mV}^{-1}$ represents the local dipolar moment and $P_0(T=105\text{ K})=0.295\text{ C m}^{-2}$ denotes the saturated part of the spontaneous polarization. Similar field dependence of the polarization can be observed in the PMN [111] sample at temperatures above the ferroelectric conversion [see the inset in Fig. 6(b)]. This suggests that in the [001] direction, the already established polarized clusters reorient in the bias field, while in the case of the [111] direction, the long range cooperative ordering effect is induced by the bias electric field resulting in the observed first-order transition line, which is terminated in an isolated critical point.[23]

III. CONCLUSIONS

Critical points were found for the [111] but not for the [001] direction of the bias field when T was constant and E was varied. For the [111] direction, the critical point was at the same field as in the E=const, T=variable case. The electric field–polarization hysteresis measurements at lower temperatures show an extremely wide hysteresis with large dielectric losses and an unusual double-kink feature. We believe that these features can be attributed to the asymmetric shape of the percolating ferroelectric domains, which are rather difficult to reorient by the electric field and the slow glassy dynamics of nanopolar regions in a dc bias electric field, respectively.

This is supported by the strong anisotropy in the bias field dependence of the polarization for the [111] and [001] directions. When the electric field was applied along the [111] direction, a strongly nonlinear first-order-type jump in the polarization due to the cooperative ordering transition was observed. In the [001] direction, on the other hand, only a smooth field dependence of the polarization was found, indicating the lack of cooperative ordering.

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