

Polar metastability and an electric-field-induced phase transition in the disordered perovskite $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$

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We measure the effect of dc-electric-field-temperature sequences on the finite-frequency dielectric constant $\epsilon(\omega)$, and the thermally stimulated depolarization current of single crystals of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN). The results are interpreted in terms of a field-induced change in the low-temperature phase of PMN from glassy to rhombohedral ferroelectric. The latter transition has first-order characteristics, and occurs only if a dc field along $\langle 111 \rangle$ of 1.7 kV/cm or more is applied. The criterion for glassiness is the apparition of a long-lived metastable polarization, proportional to the applied field, without accompanying anomalies on the small-signal dielectric constant. It is believed that the well-known broad dispersive maximum in $\epsilon(\omega)$ near 270 K simply reflects thermal slowing down of strongly non-Debye dynamics, and is not related to a ferroelectric phase transition; the existence of a divergence in the static dielectric constant is unlikely. A phase diagram in the electric-field-temperature plane is proposed.

INTRODUCTION

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) is an oxide perovskite with Mg and Nb irregularly distributed over the B site in the ratio 1:2. In the past^{1,2} dielectric studies showed the existence of low-frequency relaxation, quite unusual for a nominally stoichiometric, undoped perovskite. The very-low-frequency motion is clearly seen in recent work by Colla *et al.*³ They actually measured that the frequency $\omega_p/2\pi$ of the maximum in $\epsilon''(\omega)$ goes from 10 mHz to 30 Hz when the temperature varies over a 7 K interval around 246 K (see Fig. 1). From a master plot analysis in the temperature interval 185–260 K, they derive that $\epsilon''(\omega)$ is seven decades wide at half maximum. Such behavior has features of undercooled liquid glass

formers (e.g., glycerol); but also of those crystalline materials that have been called orientational glasses (and that, in turn, are compared to spin glasses), and of diffuse phase transitions (that go to completion over a finite temperature interval, such as martensitic transformations).

In glass-forming liquids, the glass temperature T_g can be measured from a more or less smeared out discontinuity in the specific-heat or in the thermal-expansion coefficient. In the case of glycerol, the dynamics in the undercooled liquid have been probed by measuring the complex dielectric constant $\epsilon(\omega)$ over 14 decades in frequency.⁴ At any temperature above T_g , the relaxation is distinctly non-Debye; toward low temperatures the frequency $\omega_p(T)$ of the maximum in $\epsilon''(\omega)$ decreases faster than Arrhenius-type; dielectric relaxation data obtained at different temperatures can be collapsed into one master plot by appropriate frequency-temperature scaling procedures. These three characteristics of the dynamics are often considered to be universalities of the glass transition. For glycerol at the conventional calorimetric glass temperature (185 K), even a frequency as low as $\omega/2\pi = 10^{-3}$ Hz yields $\epsilon(\omega) = \epsilon_\infty$. Therefore, not much is known about the static dielectric constant ϵ_0 in the glass state.

When only dielectric data are available for a given material, one should realize that dielectric relaxation in solids quite generally proceeds in a markedly non-Debye (nonexponential) fashion.⁵ This is usually interpreted as due to a strongly sequential (or hierarchical) character⁶ of the relaxation process in a solid, as opposed to the parallel (or independent) relaxation in gases of polar molecules that Debye discussed originally;⁷ some authors prefer to say that dielectric relaxation in solids is intrinsically a many-body process. Another fairly common empirical result is time-temperature scaling; relaxation data at different temperatures in the time-domain scale as

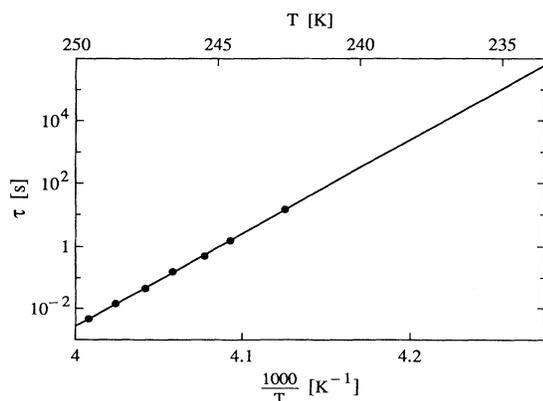


FIG. 1. Characteristic time $\tau = \omega_p^{-1}$ derived from the frequency ω_p for which $\epsilon''(\omega)$ is maximum at constant temperature. The sample is single-crystal PMN, and the electric field is directed along $\langle 100 \rangle$. Data are from Ref. 3. If the extrapolation is valid, τ becomes of the order of half a day at 235 K.

$\omega_p(T)t$, where ω_p is some temperature-dependent characteristic frequency; similarly, frequency-domain data scale as $\omega/\omega_p(T)$. In orientational glasses,⁸ the static susceptibility⁹ is expected to be Curie-Weiss-like at high temperature, and approximately constant at low temperature. The continuous (or at most, cusplike) changeover occurs by definition at the glass temperature T_g , which is higher than the Weiss temperature. Due to dynamic phenomena, the static susceptibility can only be obtained by extrapolation of finite-frequency results. In most cases, this extrapolation is considerably more difficult than in glass-forming liquids, since the half-width of $\epsilon''(\omega)$ is often more than six decades in frequency, as opposed to, typically, three decades in liquid glass formers, and 1.14 decades for a Debye process. No anomalies in the specific heat have been found at T_g , perhaps because orientational glasses resemble so-called strong structural glasses,¹⁰ where such anomalies are very smeared out.

In the case of PMN, optical and x-ray studies fail to show a structural transition, and it is now rather generally believed that peaks in the finite-frequency dielectric constant and slim hysteresis loops¹ do not by themselves imply the existence of a regular structural phase transition.¹¹ The first clear evidence that an electric field can induce such a phase transition at approximately 200 K came from an x-ray study by Arndt, Sauerbier, Schmidt, and Shebanov.¹² They also found an anomaly in the dielectric constant at that temperature upon heating the sample after poling.

It seems, therefore, that the transition in PMN can be changed from (as yet ill defined) glassy to structural under the effect of a dc electric field, and in this paper we hope to contribute some experimental criteria to distinguish between these two states. The methods used are finite-frequency, small-signal dielectric experiments for different sequences of dc-field application during cooling and heating, and for several fields up to 2.7 kV/cm (a preliminary account of these results has appeared in the proceedings of a conference¹³), and measurements of depolarization currents. A short discussion of depolarization currents in the presence of a large distribution of relaxation times is given in the Theoretical section.

EXPERIMENT

The samples are platelets of typical dimensions $4.5 \times 2.5 \times 0.15$ mm³ cut from one single-crystal boule of PMN grown by Titov (State Optical Institute, St. Petersburg). The large faces were (100), (110), or (111) planes, as verified in x-ray experiments by Schenk and Bonin (Institut de Cristallographie, Lausanne). Gold electrodes were applied to these faces by sputtering.

Each run started at 320 K (materials used in the sample holder determined this upper limit). From our earlier dielectric experiments¹³ that started at 400 K, we believe this temperature to be still high enough to erase nearly all effects of previous treatments. Some depolarization currents persist after reheating to 320 K, but their values are small and their contribution to the polarization is negligible; in the discussion we will neglect any depolarization currents measured above 250 K. From 320 K, the

sample is cooled down to 150 K (or 90 K in some cases) under a dc field [field cooling (FC)] or under zero field [zero-field cooling (ZFC)]. At the low temperature, the dc field is switched off, or maintained, or switched on, and after a typical waiting time of 10 min, the temperature is swept up again to 320 K. This part of the sequence is denoted as field heating (FH) or zero-field heating (ZFH). A complete experiment is indicated as field heating after zero-field cooling (FHZFC), etc.

The low-frequency (between 100 Hz and 100 kHz) dielectric constant was measured at 1 K intervals, with typical heating-cooling rates of 1 K/min, by a Hewlett-Packard 4284A automatic LCR meter using 0.3 V ac. Only the (111)-electroded crystal has been studied. Thermal depolarization was measured during heating in a ZFHZFC sequence with a Keithley 617 electrometer for all three directions of the electric field, and also on a ceramic sample. The error in our results for the polarization is of the order $0.2 \mu\text{C}/\text{cm}^2$ or 3%, whichever is greater. Before the ZFH ramp was started, the samples were kept for 10 min with short-circuited electrodes. In our discussion we neglect the isothermal depolarization that occurs during this period. Typical cooling rates were 5–10 K/min and heating rates 2–5 K/min.

All experiments presented here were performed in the same measurement cell, different from that used in our preliminary experiments. Due to temperature gradients, the actual sample temperature in the latter¹³ was approximately 5 K higher than the reported values in the 180–220 K range.

THEORETICAL

When a dc electric field E has been applied in the interval $-\infty < t < 0$, and is switched off at $t=0$, the polarization for $t > 0$ under isothermal conditions is given by

$$P(t) = \chi_0 E b(t), \quad (1)$$

where χ_0 is the static susceptibility and $b(t)$ the step-response function. To describe the temperature variation of $b(t)$, it is usual⁵ to make a scaling or master plot hypothesis:

$$b(t, T) = b[x(t, T)], \quad (2a)$$

$$x(t, T) = \omega(T)t, \quad (2b)$$

which supposes that the dimensionless function b depends only on a dimensionless variable x ; this variable is the product of a temperature-dependent characteristic frequency $\omega(T)$ and the time t , since the field was switched. An example is the stretched exponential (Kohlrausch) step-response function;

$$b(x) = \exp[-(x)^\beta] \quad 0 < \beta \leq 1. \quad (3)$$

Another type of step-response function shows power-law behavior both for short and long times:¹⁴

$$b(x) = \begin{cases} 1 - ax^{1-n} & x \ll 1 \\ \gamma x^{-m} & x \gg 1, \end{cases} \quad (4a)$$

$$(4b)$$

with $0 \leq n < 1$ and $0 < m \leq 1$. If these equations are valid,

the dielectric loss angle is frequency-independent below ω_p , and given by

$$\tan\delta = \cot(n\pi/2). \quad (5)$$

In our experiments, a long-lived polarization at low temperatures is created by applying an electric field E at high temperatures, sweeping down the temperature to a value T_0 , and switching off the field. We allow isothermal depolarization to occur for 10 min, then we start sweeping up the temperature again, measuring the thermal depolarization current $j(t)$. Only this second part of the experiment is discussed in this paper. We suppose that the process can be described by a generalization of the Debye formula,

$$j(t) = -\frac{dP(t)}{dt} = \frac{P(t) - P_e[T(t)]}{\tau(t, T)}, \quad (6a)$$

with

$$P_e[T(t)] = \chi_0[T(t)]E, \quad (6b)$$

and from Eq. (2),

$$(\omega\tau)^{-1} = -\frac{d[\ln b(x)]}{dx}, \quad (6c)$$

where the right-hand side of Eq. (6c) must be evaluated for $x = \omega[T(t)]t$. For a linear temperature ramp $T(t) = T_0 + qt$, the time variable t in Eqs. (6a) and (6b) can be replaced by the temperature T . With Eq. (3) one obtains

$$\frac{1}{j} \frac{dj}{dT} = -\frac{\beta(x^\beta - 1) + 1}{T - T_0} + \frac{\beta}{\omega} \frac{d\omega}{dT}. \quad (7)$$

If the second term on the right-hand side is large enough, the current will increase while the temperature goes up. For the Debye case ($\beta=1$) the maximum in $j(T)$ occurs when^{15,16} $\omega^2/q = d\omega/dT$. An approximate solution (x^β small) of Eq. (7) is

$$j(T) = P_0 \beta \omega^\beta(T) \left(\frac{q}{T - T_0} \right)^{1-\beta}, \quad (8)$$

which is independent of q only for the pure Debye case, $\beta=1$. For very small β (large deviation from Debye behavior) we nearly have that j is linear in q , and factors into separate q and T dependences. Under those conditions $P(T_0, q) - P(T, q)$ is independent of q and $P(T)$ behaves as an equilibrium quantity. A similar conclusion can be reached starting from Eqs. (4a) and (4b), in the limit n close to 1.

The above results have been derived using a scaling or master plot hypothesis, and assuming linear response. Neither of these conditions is necessarily valid in our experiments; our main aim was to point out that the Debye results¹⁶ are not representative of all classes of response functions, and that for very large distributions of relaxation times [n approaching 1 in Eq. (4a) or β approaching 0 in Eq. (3)], the thermal depolarization currents behave very nearly as true pyroelectric currents.

RESULTS AND DISCUSSION

Low-field regime: Metastability

As we have shown earlier,¹³ application of dc-electric fields below 1.7 kV/cm along $\langle 111 \rangle$, be it during cooling and/or heating, does not create anomalies on the small-signal dielectric constant. But by cooling down the sample under such fields to 160 K, a rather long-lived electric polarization is created as shown in Fig. 2. The first impression is that the polarization behaves as a quantity in thermal equilibrium, P_e (true pyroelectricity):

$$j(t) = -\frac{dP_e}{dT} \frac{dT}{dt} = -\frac{dP_e}{dT} q \quad (9)$$

for an experiment performed at constant heating rate q .

This implies that (a) in two experiments that differ only in q , the currents at any temperature are proportional to the heating rate; (b) at fixed q , the currents measured at temperature T in two experiments that differ only in the temperature T_0 at which the field was switched off after cooldown should be the same.

These two properties seem to be satisfactorily verified in Figs. 2(a) and 2(b), respectively. A further consequence of the equilibrium hypothesis is (c) if the heating

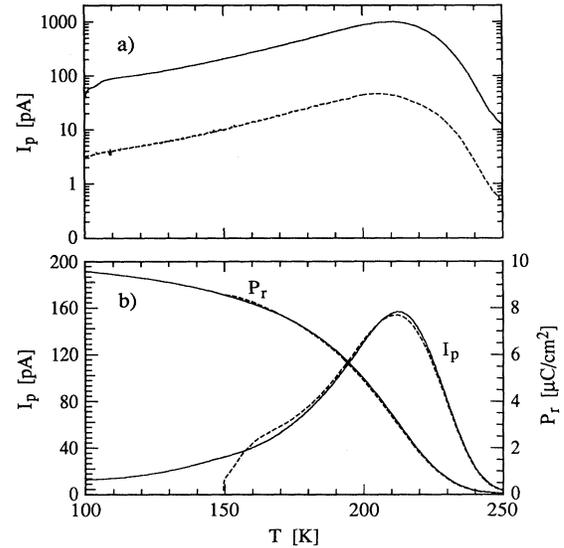


FIG. 2. (a) Depolarization current for two different heating rates q . Top curve $q=5$ K/min, bottom $q=0.2$ K/min. The crystal is electroded on (110) faces. Field during coolings 1.35 kV/cm. The currents are nearly in the ratio of the q 's, and the maxima nearly coincide, but, more precisely, the ratio of currents (below the maximum) is 20 ± 1 , and the maximum in the top curve occurs 6 K higher. (b) The same experiment as in (a), except that now q is the same for all curves, and the starting temperatures T_0 are different (dashed curves, $T_0=150$ K; full curves, $T_0=90$ K). The curves are virtually superimposed, suggesting again that the polarization is a quasiequilibrium quantity. Note that current scale is logarithmic in (a) and linear in (b). The value of the polarization is obtained by integration of the current.

rate q is reduced to zero, no isothermal depolarization should be observed.

This has been tested by halting the temperature sweep at 225 K for 2000 s, after which it was resumed. During that period, the polarization dropped to about $\frac{2}{3}$ of its initial value, the current being approximately a power law of t . Extrapolation of the power law indicates that eventually all polarization would be lost after a long enough period. Therefore, at 225 K, polarization is a metastable rather than an equilibrium quantity.

From a closer inspection of Fig. 2(a) it is seen that the temperatures of the maxima in $j(T)$ for the two experiments differ by 6 K, inconsistent with Eq. (9), and too large to be simply an experimental error; apparently the metastability is already seen at 210 K, and by extension we suppose that this polarization is metastable at all temperatures, and that Eq. (9) does not really apply. In the Theoretical section we have shown how this metastability and a current response close to Eq. (9) can result from a large distribution of relaxation times. The shift of the $j(T)$ maximum can be explained from Eq. (7) or its equivalent, based on Eqs. (4). Consistent with Eq. (8), a close analysis of Fig. 2(a) shows that below the maximum, $j(T)$ is proportional to $q^{1-\beta}$, with β approximately equal to 0.07. When Eqs. (4) are used instead, one obtains $n = 0.93$. This value can be correlated to the small-signal dielectric loss angle through Eq. (5). Our data (not shown) are slightly frequency dependent; analyzing 100 Hz data we obtain that n changes slowly from 0.96 at 140 K to 0.94 at 230 K.

To create a polarization at 150 K or below, thermal polarization is a much faster process than isothermal polarization with the same electric field. It is easy to obtain $P = 8 \mu\text{C}/\text{cm}^2$ at 150 K for $E = 1.35 \text{ kV}/\text{cm}$ in a 15 min thermal polarization, but isothermal polarization at this temperature, with the same field during the same time, will yield only a fraction of a $\mu\text{C}/\text{cm}^2$.

The $P(E)$ relation has been studied at 160 K, see Fig. 3. For values of E below approximately 1.7 kV/cm, it can be described as follows:

$$P^{\text{ms}}(T) = \chi_0^{\text{ms}}(T)E + \frac{1}{3}\chi_2^{\text{ms}}(T)E^3, \quad (10)$$

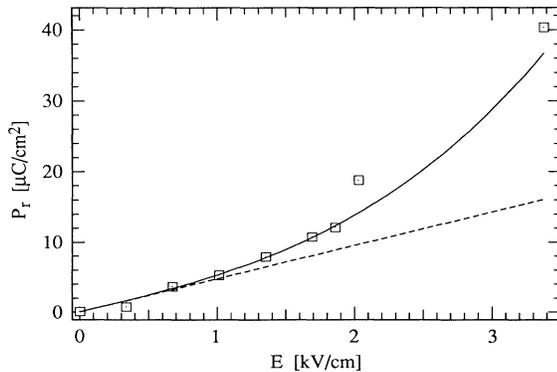


FIG. 3. The (metastable) polarization induced along $\langle 111 \rangle$ during field cooling to 160 K, for different applied fields. The fit is Eq. (10), full curve. The linear part of that equation is shown by the dashed line.

where the index ms refers to our conclusion that this polarization is metastable. The value of $\chi_0^{\text{ms}}(T)$ should provide a lower limit for the true static $\chi_0(T)$; the estimate may be useful in the temperature range 160–210 K (above that temperature we have clear indications of metastability even during the experiment, as mentioned above).

In Fig. 4 are shown $\chi_0(T)$ as obtained from finite-frequency dielectric measurements for $265 \text{ K} < T < 350 \text{ K}$, extrapolated to 250 K (in Ref. 3, it has been shown that this is allowed) and $\chi_0^{\text{ms}}(T)$ for $160 \text{ K} < T < 210 \text{ K}$, obtained from thermal polarization–depolarization measurements. The latter points have all been derived from a set of six experimental runs for different E , always cooling to 150 K, and calculating $P(T)$ at different temperatures from integration of one and the same $j(t)$ curve. If we accept the values of χ_0^{ms} as useful estimates for χ_0 , this figure suggests that between 210–250 K there is, at most, a cusplike singularity in χ_0 . It is well known¹⁷ that $\chi_0(T)$ above 250 K cannot be represented in simple Curie-Weiss form; fits of the type $\chi_0(T) = C/(T - \Theta)^\alpha$ have been proposed, with α approximately equal to 2.

High-field regime: Phase transition

Dielectric measurements in the high-field regime for several field–temperature sequences as shown in Figs. 5–7. Figure 5 gives the complex dielectric constant measured during FHFC, with a static field of 2.70 kV/cm. In addition to the strongly dispersive maxima^{1,2,17} of ϵ' and ϵ'' in the 250–270 K range, additional maxima^{12,13,18–20} appear at approximately 217 K. The amplitudes of these maxima are frequency dependent, but the temperature T_m where they occur is not, and is the same for ϵ' and ϵ'' . It is field dependent and disappears for dc fields below 1.7 kV/cm. This is also true for the other field sequences used (Fig. 6), but the temperatures T_m vary with E and are not the same for different sequences.

In Fig. 6 is plotted the change in the real dielectric constant provoked by different dc-field sequences: (a) FHFC, (b) ZFHFC, and (c) FC (measurements taken during initial cooling). It is found that the shape of the additional anomalies (but not their amplitude) is largely in-

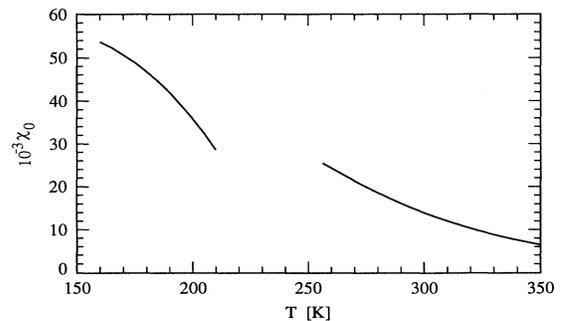


FIG. 4. Relative static susceptibility along $\langle 111 \rangle$, as a function of temperature, estimated by two different methods: between 250 and 350 K from extrapolation of finite-frequency dielectric constants and between 160 and 210 K from metastable polarization.

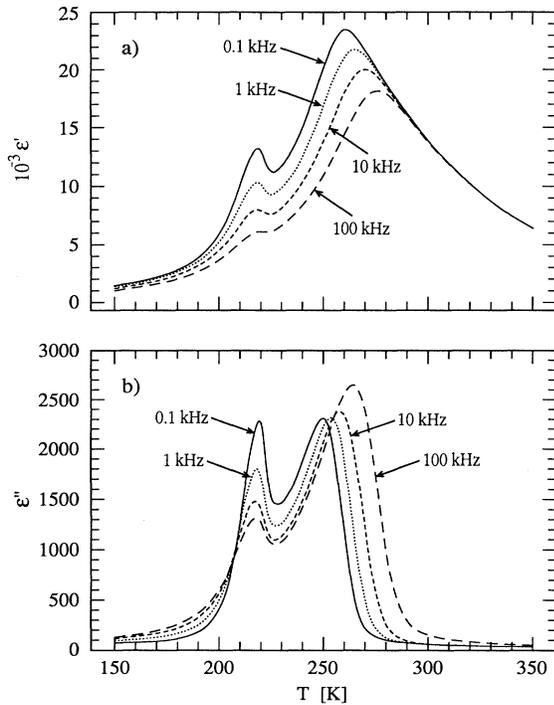


FIG. 5. Dielectric constant measured during heating of a (111) electroded sample at several frequencies. The crystal has been cooled under 2.70 kV/cm, and this field is maintained during heating (FHFC).

dependent of frequency. The field dependence of their maxima will be discussed later (in the Conclusion section). For the sequence FHZFC (not reproduced here), the additional maximum extends over a field-dependent temperature range, of which the high end coincides with T_m of the FHFC sequence. It is seen from Figs. 6(a) and 6(c), as compared to 6(b) that the dc field also affects the behavior of the usual maximum; we do not discuss this effect.

An experiment that gives something like the isothermal transition from the peak in Fig. 6(c) to the baseline in Fig. 6(b) is shown in Fig. 7. The sample was zero-field cooled to 209 K; a field of 2.70 kV/cm was applied for 18 h; the field was switched off, and the dielectric constant monitored during 7.5 h, while the temperature was stable within ± 50 mK. The curve is given by

$$\varepsilon(t) - \varepsilon(\infty) = [\varepsilon(t_c + \tau) - \varepsilon(\infty)] \left(\frac{t - t_c}{\tau} \right)^{-s} \quad (11)$$

for $t \geq t_c + \tau$, where t_c is the time at which the field is switched off. Its value is experimentally only known within a second or so, and it has been taken as an adjustable parameter, together with the characteristic time τ (1.4 ms) and the exponent s (0.21). The value of τ seems to be unrelated to the values appearing in Fig. 1.

The depolarization measurements in the high-field regime are shown in Figs. 8 and 9. The sharp peaks in the pyroelectric current (full curve in Fig. 8) are qualitatively different from the rounded maxima observed in the low-

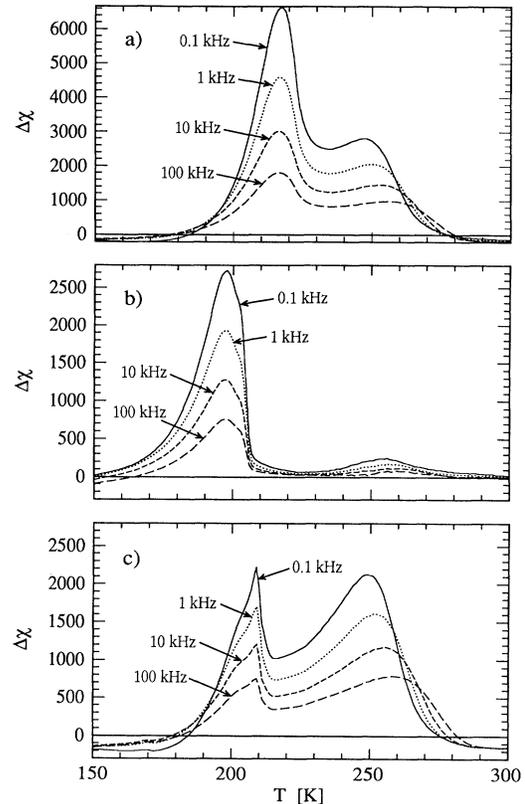


FIG. 6. Change in the real dielectric constant provoked by application of different dc-field sequences (the zero-dc-field values have been subtracted). The crystal is electroded on (111), and cooled under 2.70 kV/cm. Frequencies as in Fig. 5. (a) Represents the same data as in Fig. 5. (FHFC); (b) is taken during zero-field heating (ZFHFC); (c) during the initial cooling (FC).

field regime (Fig. 2). We have no specific explanation for the structure in the peak of the depolarization current in Fig. 8; maybe it is related to some domain-pattern formation. On the same sample under the same field, the struc-

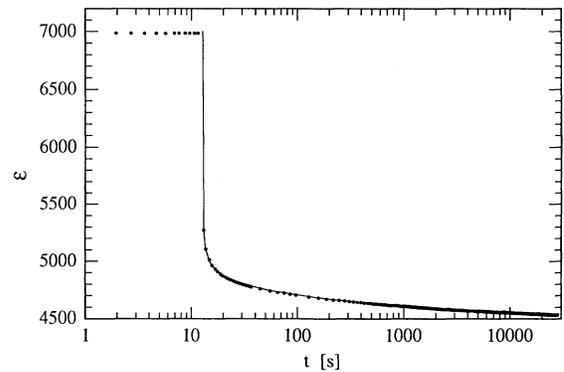


FIG. 7. Evolution in time of the dielectric constant (1 kHz) after isothermal polarization under 2.70 kV/cm along $\langle 111 \rangle$ at 209 K. The zero of the time axis is arbitrary; the field is switched off at approx $t_c = 12$ s. The curve follows Eq. (11).

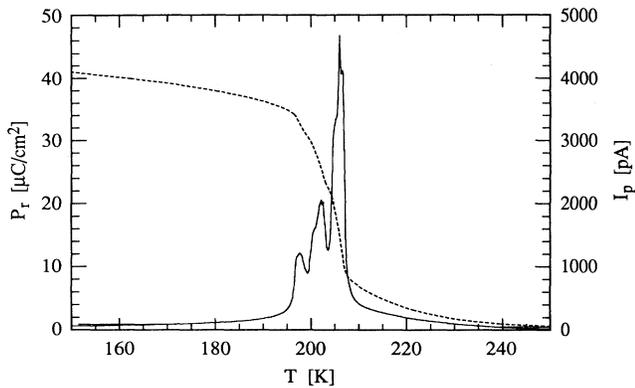


FIG. 8. The depolarization current (at $q=0.84$ K/min), and the polarization derived from it after cooling under 2.70 kV/cm along $\langle 111 \rangle$. The depolarization current at $q=0.17$ K/min (not shown) does not exactly superpose on the curve shown here, but the deviations are smaller than in Fig. 2(a).

ture is very reproducible. The polarization (dashed curve in Fig. 8) is seen to fall rather sharply over a 10° temperature interval. In terms of field sequence, Fig. 8 shows a ZFHFC experiment, and the peaks in Fig. 6(b) extend over the same interval. The residual polarization above 206 K is probably metastable, as in the low-field case. We think that below this temperature the polarization is truly remanent (P_{rem}), and that we see a first-order-type ferroelectric transition, with discontinuous disappearance of P_{rem} , and a divergence in the static dielectric constant. The shift in the transition temperature when going from ZFHFC to FHFC (Fig. 6) then is explained as the effect of an electric field (during the FH period) on a first-order phase transition. A similar explanation may be valid for the difference between the FC and ZFHFC curves.

Using still higher fields than we do, other authors¹² have observed rather square hysteresis loops between 180 and 203 K, with values of $P_{\text{rem}}(T)$ that compare very well with ours. It is not known whether this polarization remains switchable at practical frequencies for lower tem-

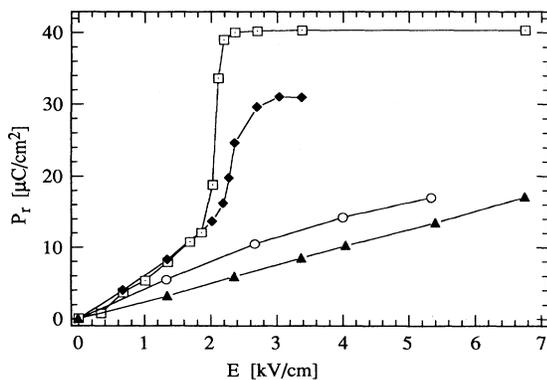


FIG. 9. Polarization induced by field cooling to 160 K. (□), field along $\langle 111 \rangle$; (◆), along $\langle 110 \rangle$; (○), along $\langle 100 \rangle$. (▲) shows the behavior of a ceramic sample.

peratures. We have tried unsuccessfully to obtain a P_{rem} by isothermal polarization at 150 K, applying 2.7 kV/cm for approximately 1 h. Indeed, extrapolation of line C in Fig. 10 (see the Conclusion section) predicts that at least 3.5 kV/cm are necessary at this temperature. On the other hand, keeping the 2.7 kV/cm field-cooled sample under zero field at 150 K for 7 h (after the 10 min period standard in our protocol) diminishes the measured polarization by only 0.1 $\mu\text{C}/\text{cm}^2$, which can easily be accounted for by temperature fluctuations.

Figure 9 shows the polarization induced during field-cooling to 160 K for different applied fields, for three directions of applied fields in single-crystal samples, and for a ceramic sample. For the $\langle 111 \rangle$ direction, there is an abrupt jump in the polarization at the same threshold field where the dielectric constant anomalies in Fig. 6 appear, and for higher fields, the polarization saturates. For the $\langle 110 \rangle$ direction, the threshold value is higher, and the saturation polarization is lower, but the initial value of χ_0^{ms} (compare the discussion of Fig. 3) is the same, as would be expected for an average cubic symmetry in the low-field regime. Assuming orthorhombic symmetry (local polarization along $\langle 111 \rangle$), and starting from the values $P_{\text{sat}}\langle 111 \rangle = 40$ $\mu\text{C}/\text{cm}^2$ and $E_{\text{sat}}\langle 111 \rangle = 2.3$ kV/cm, one expects $P_{\text{sat}}\langle 110 \rangle = 33$ $\mu\text{C}/\text{cm}^2$, $P_{\text{sat}}\langle 100 \rangle = 23$ $\mu\text{C}/\text{cm}^2$, and $E_{\text{sat}}\langle 110 \rangle = 2.8$ kV/cm, $E_{\text{sat}}\langle 100 \rangle = 4.0$ kV/cm. It is seen from Fig. 9 that the (110)-cut crystal behaves according to expectations; furthermore, we find that this polarization is stable up to the same temperature (approx 206 K). For the (100) electroded crystal the polarization remains metastable [as in Fig. 2(b)] rather than remanent (as in Fig. 8), and no plateau value is reached at 4.0 kV/cm; furthermore, the low field χ_0^{ms} seems to be lower than in the other directions, contrary to what is expected for average cubic symmetry. We also find that the finite-frequency dielectric constants for the (111)- and (110)-cut platelets are indistinguishable,

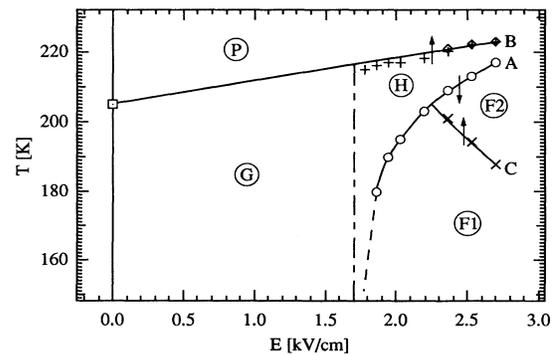


FIG. 10. The phase diagram in the electric field (along $\langle 111 \rangle$) and temperature plane. P is paraelectric, $F1$ and $F2$ are ferroelectric, H hysteretic, and G nonergodic (glassy). The boundaries have, in general, been determined by crossings at constant field in the direction of the arrows, except for the square on the T axis (the field-free depoling temperature). The latter has been obtained from an isothermal switch off of the field (from values above 1.7 kV/cm) at 150 K, followed by zero-field heating.

but the (100) one has measurably lower values. A similar qualitative difference between differently cut crystals has been reported in an x-ray study.¹² There is no explanation of this effect. The fact that the values for the ceramics in Fig. 9 are lower than those for the crystals in probably related to effects of density, grain size, etc. An x-ray study on ceramics poled at 10 kV/cm has shown a rhombohedral structure.²¹

CONCLUSION

The phase diagram in the E - T plane for a (111)-cut platelet of PMN based on dielectric experiments is shown in Fig. 10. The plusses on line B represent the maxima from FHFC experiments [as in Fig. 6(a)]. The diamonds (indistinguishable from the plusses) and the crosses on line C, have been derived¹³ from FHZFC measurements (not shown). The circles on line A indicate the sharp discontinuity on the FC peaks [Fig. 6(c)]. The square on the T axis represents the value of the high-temperature discontinuities on the ZFHFC curves [Fig. 6(b)]. Such discontinuities are reflected in the presence of peaks in the depolarization current (Fig. 8). Both characteristics are only observed when, during the field cooling, line A has been crossed. For fields above approximately 2.3 kV/cm, the induced polarization saturates.

Following these phase boundaries, we distinguish four different phases. Above line B is the paraelectric region, P , controlled by dynamic disorder. When this region is entered from below, slowly (but easily measurable) decaying polarization may persist. Below 206 K, and to the left of line A (roughly, fields below 1.7 kV/cm) is the glassy region G, in which long-lived metastable polarization may exist, that will depend in a nonlinear way on E , and also on the road taken in the (E - T) plane toward the specific point (E , T). Except for the existence of such nonergodic behavior over experimental time scales (up to hours), we do not want to imply specific properties of this glassy phase. To the right of line A, but below line C, in region F1, problems of ergodicity persist, but when crossing line A at constant field, a ferroelectriclike (as judged from the depolarization current) polarization (larger than any polarization that can be induced in region G) is obtained, that will decay upon crossing line B. Above line C, but below line A is the true ferroelectric phase F2. It has a field-independent value of polarization ($40 \mu\text{C}/\text{cm}^2$), at least when entering it by crossing line A. It is very likely that line C (plotted here from dielectric curves in the FHZFC regime) also plots the values of the coercive field found¹² in slow cycling hysteresis curves; this would imply that the polarization in F2 is field independent and can be reversed by a field. The lowest field at which phase F2 can be induced is found at tempera-

tures very close to the field-free depoling temperature (206 K). The remaining region H shows the hysteresis of a usual first-order ferroelectric phase transition, exhibiting both pure temperature (temperature cycling at constant field) and applied field (shift of Curie temperature by the field) effects.

The reasons to call the region G glassy are that a long-lived (supposed, but not observed, to decay) polarization can exist below 207 K and for cooling fields below 1.7 kV/cm, while no anomaly on the dielectric constant is seen under those conditions, and that in zero field the frequency-dependent dielectric constant³ (measured down to 180 K) suggests the existence of very slow dynamics (see also Fig. 1). Sometimes, deviations from Debye relaxation and Arrhenius behavior of the characteristic frequency are taken as indications of glassiness. As mentioned in the Introduction, these properties are detected in the undercooled liquid, rather than in the glass phase of glass formers. Furthermore, it is not unusual in general solids to find $\epsilon''(\omega)$ curves that are markedly (two or three times) larger than that for a Debye process, but in orientational glasses they can be five or six times larger. In several cases however, such widths have been inferred, using a master plot hypothesis, rather than observed directly. Criteria to distinguish glassiness using the experimental techniques of this paper, therefore, seem to be somewhat fuzzy. If long-time nonergodic behavior is the criterion, then PMN probably has a glassy phase. If more sophisticated elements of phase-transition theory were to be considered, one would perhaps require⁸ demonstration of a Parisi-type⁹ static susceptibility. Experimentally, however, this quantity is not accessible from available finite-frequency results (even those as low as $\omega/2\pi=3$ mHz), and for the moment the nearest we can get to fulfilling this requirement is shown in Fig. 4, where an important temperature region is lacking, and the low-temperature data probably only give a lower bound to the susceptibility.

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