

# Glassy relaxation in lead (magnesium niobate)–titanate crystals

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The long-term polarization relaxation ( $t \leq 104$  s) in a  $0.87\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - 0.13\text{PbTiO}_3$  crystal in the dipole-glass phase has been studied. The results reveal the power-law relaxation predicted by the dynamic scaling, divergences of the static zero-field-cooled susceptibility at the transition to the mixed phase, and a difference between that susceptibility and the field-cooled susceptibility. This difference demonstrates a breakdown of ergodicity in the glassy phase. © 1995 American Institute of Physics.

Lead magnesium niobate,  $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$  (PMN), is a classic example of a ferroelectric with a diffuse phase transition (a relaxor).<sup>1,2</sup> Its solutions with lead titanate,  $\text{PbTiO}_3$  (PT), i.e.,  $(1-x)\text{PMN}-x$  PT, belong to the same category.<sup>3,4</sup> At  $x < 0.3$ , the physical properties of such solutions are similar to those of pure PMN. As  $x$  increases, the transition becomes noticeably less diffuse,<sup>5</sup> as can be seen from a significant decrease in the amplitude of the relaxation processes. This decrease makes it possible to follow the changes in the shape of the quasistatic (0.01-Hz) hysteresis loops during cooling.<sup>6</sup> These changes are clear evidence that the transition in PMN–PT crystals is diffuse because of the existence of intermediate phases—a dipole-glass phase and a mixed (partially ordered) phase—between the paraelectric and ferroelectric phases.<sup>6</sup> These conclusions are supported by x-ray studies of the structure of these crystals, which reveal a broadening of Bragg peaks in the region in which the dipole-glass phase presumably exists, along with rhombohedral distortions in the mixed and ferroelectric phases.<sup>7</sup>

Studies of the dispersion of the dielectric constant in crystals of  $0.87\text{PMN}-0.13\text{PT}$  also indicate the existence of an intermediate glassy phase with a characteristic power-law dispersion  $\epsilon(\omega)$  (Ref. 8). According to Ref. 8, a critical slowing in the paraelectric phase ( $T > T_{\text{DG}}$ ) of some relaxation mode with random atomic displacements and a reciprocal relaxation time  $\nu_0 \rightarrow 0$  leads to a dispersion of the following type, within the framework of the scaling hypothesis:

$$\epsilon(\omega) = \epsilon_1 \{ 1 - (\omega\tau)^\lambda [1 - i \tan(\pi\lambda/2)] \}, \quad \nu_0 \leq \omega \leq 1/\tau, \quad (1)$$

$$\epsilon(\omega) = \epsilon_0 [1 + (\nu_0\tau')^\lambda (i\omega/\nu_0 - c\omega^2/\nu_0^2)], \quad \omega \leq \nu_0. \quad (2)$$

The quasi-Debye (analytic) dispersion  $\epsilon(\omega)$  at  $\omega \leq \nu_0$  results from a relaxation of large-scale fluctuations of the polarization, with sizes exceeding the glass correlation radius  $\xi$ . The power-law dispersion at  $\omega \geq \nu_0$  stems from a relaxation of fluctuations with sizes smaller than  $\xi$ . In the glassy phase ( $T < T_{\text{DG}}$ ), it is most likely<sup>9</sup> that we have  $\xi = \infty$  and

that the power-law dispersion prevails at all  $\omega \leq 1/\tau$ . A dispersion  $\epsilon(\omega)$  of precisely this type has been observed in crystals of 0.87PMN–0.13PT near  $T_{DG} \approx 320$  K at  $10^{-2}$  Hz  $< \omega/2\pi < 10^4$  Hz.

The  $\epsilon(\omega)$  behavior in the limit  $\omega \rightarrow 0$  also determines, in an unambiguous way, the nature of the long-term relaxation of the polarization  $P(t)$  when a weak static electric field is applied or turned off.<sup>8</sup> The power-law dispersion in (1) thus corresponds to a relaxation of  $P(t)$  of the following type when the field  $E$  is turned on at  $t=0$  (Ref. 8):

$$P(t) = P_\infty [1 - (\tau/t)^\lambda], \quad \tau \leq t \leq 1/\nu_0, \quad (3)$$

$$P_\infty = \chi E, \quad \chi = [\epsilon(0) - 1]/4\pi. \quad (4)$$

In the glassy phase, with  $\xi = \infty$ , the power-law relaxation in (3) should prevail at all  $t \gg \tau$ . The static susceptibility in the zero-field-cooled regime (ZFC), which appears in (4),

$$\chi = \chi_{ZFC} = \lim_{\omega \rightarrow 0} \chi(\omega),$$

differs from the susceptibility in the field-cooled (FC) regime,

$$\chi_{FC} = \lim_{E \rightarrow 0} \partial P / \partial E.$$

This situation is a characteristic feature of the glassy phase, reflecting its nonergodicity.<sup>10</sup>

An experimental study of the polarization relaxation in the dipole-glass phase thus demonstrates the validity of the scaling laws used in the derivation of (3). It also demonstrates a nonergodicity of this phase. In the present study, we examined this relaxation by measuring the dynamic piezoelectric modulus  $d_{11}^{ZFC}(\omega)$ , induced by the application of a static field  $E = 30$  V/cm parallel to the [100] axis. In a cubic crystal such as 0.87PMN–0.13PT, at  $T > 296$  K, we have<sup>6,7</sup>

$$d_{11}^{ZFC}(\omega) = \partial e_1(\omega) / \partial E(\omega) = 2\theta_{11}P_1\chi(\omega),$$

where  $\theta_{11}$  is an electrostrictive constant, and  $P_1$  is the polarization induced by the field  $E$ . The time evolution of  $d_{11}^{ZFC}(\omega)$  which arises upon the application of a field thus follows the time evolution  $P_1 = P_1(t)$ .

The measurements of  $d_{11}^{ZFC}(\omega)$  were carried out on platelet samples with dimensions of  $5 \times 2 \times 1$  mm, cut parallel to natural faces of the crystals, which were grown by a method of a weak pulsating load at a frequency  $\omega/2\pi = 100$  Hz. The measurements of  $\chi(\omega)$  were carried out at the same frequency with the help of a P5083 ac bridge.

Figure 1 shows the results of a comparison of the experimental data with expression (3) in the interval in which the glassy phase exists,<sup>6,7</sup>  $296 < T < 320$  K. The comparison reveals a good agreement. Figure 2 shows the temperature dependence of  $\lambda$ ,  $\tau$ , and

$$d_{11}^\infty(\omega) = 2\theta_{11}\chi(\omega)P_\infty = 2\theta_{11}\chi(\omega)\chi_{ZFC}E,$$

found by a least-squares fit. Note the sharp decrease in  $\lambda$  toward the transition to the mixed phase at  $T_M \approx 296$  K. This sharp decrease is described well by a linear law  $\lambda = 1.310 \times 10^{-3}(T - 295.67)$  K. The sharp increase in  $d_{11}^\infty(\omega)$  as  $T \rightarrow T_M$ , on the other hand, reflects the anomaly  $\chi_{ZFC} \sim (T - T_M)^{-1}$  predicted by the phenomenological theory for such transitions.<sup>6</sup>

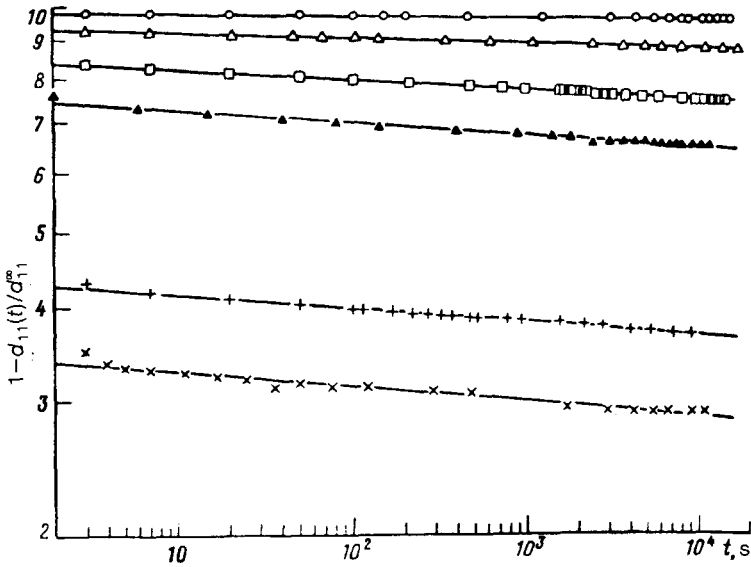


FIG. 1. Time evolution of  $d_{11}^{\text{ZFC}}(\omega)$ , in full logarithmic scale. Crosses—311 K; pulse signs—308 K; filled triangles—305 K; squares—303 K; open triangles—301 K; circles—298 K. The straight lines correspond to the power-law relaxation in (3).

The physical reason for the divergence of the uniform susceptibility at the transition from the glassy phase to the mixed phase is the onset, in the latter phase, of regions with a uniform spontaneous polarization (in addition to the regions with random polar displacements of atoms), which are seen in x-ray structural measurements.<sup>7</sup> Since there are no physical grounds for expecting significant anomalies in the behavior of  $\theta_{11}$  near  $T_M$ , we can determine the temperature dependence of  $\chi_{\text{ZFC}}$  quite accurately by examining the behavior of the quantity  $g_{11}^{\text{ZFC}} = d_{11}^{\text{ZFC}}(\omega)/\chi(\omega) = 2\theta_{11}\chi_{\text{ZFC}}E$ . As is shown in Fig. 3, the quantity  $g_{11}^{\text{ZFC}}$  can be approximated well by the power law  $g_{11}^{\text{ZFC}} = g(T/T_M - 1)^{-\gamma}$ , where  $g = 1.621 \times 10^{-16}$  C/N,  $T_M = 295.72$  K, and  $\gamma = 1.352$ . The exponent  $\gamma$  differs slightly from that predicted in the effective-field approach,<sup>6</sup>  $\gamma = 1$ . This discrepancy is apparently caused by fluctuations of the order parameter.<sup>11</sup> Shown along with  $g_{11}^{\text{ZFC}}$  in Fig. 3 is the quantity  $g_{11}^{\text{FC}} = d_{11}^{\text{FC}}(\omega)/\chi_E(\omega) = 2\theta_{11}\chi_{\text{FC}}E$ , where  $d_{11}^{\text{FC}}(\omega)$  is the dynamic piezoelectric modulus measured during cooling in a static field of the same magnitude,  $E = 30$  V/cm, and  $\chi_E(\omega)$  is the dynamic susceptibility in this field. At  $T > T_{\text{DG}} \approx 320$  K we have  $g_{11}^{\text{ZFC}} = g_{11}^{\text{FC}}$ , but at  $T < T_{\text{DG}}$  these properties are different, clearly demonstrating the breakdown of ergodicity in the glassy and mixed phases. Let us elaborate.

This difference cannot be explained under the assumption that the observed values of  $g_{11}^{\text{FC}}$  are nonequilibrium values as the result of a sharp increase in the Arrhenius relaxation time for hopping among disordered atomic positions separated by an energy barrier  $E_a$ :  $\tau_a = \tau_0 \exp(E_a/T)$ . In order to explain the relaxation over a time  $t > 10^4$  s at the typical values  $\tau_0 \sim 10^{-12}$  s we would be forced to assume exceedingly high values

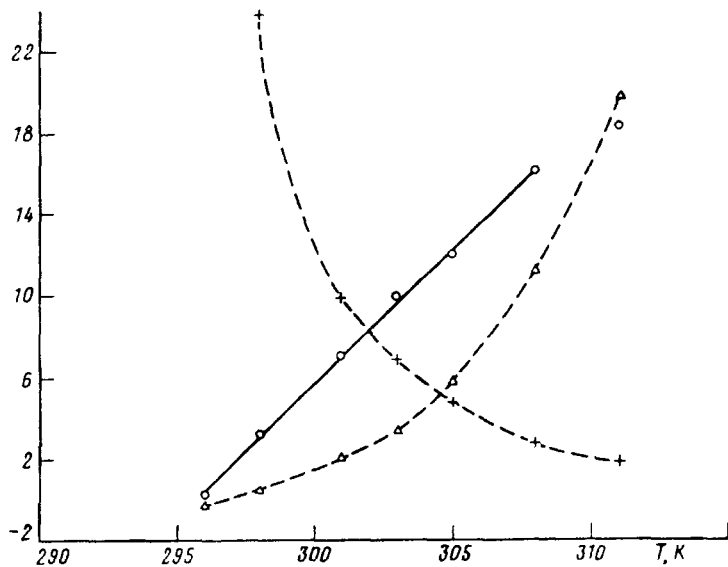


FIG. 2. Temperature dependence of  $1000\lambda$  ( $\circ$ ),  $\log[(1 \text{ s}/\tau)]$  ( $\Delta$ ), and  $10^{11}d_{11}^c(\omega)$ , in C/N ( $\times$ ).

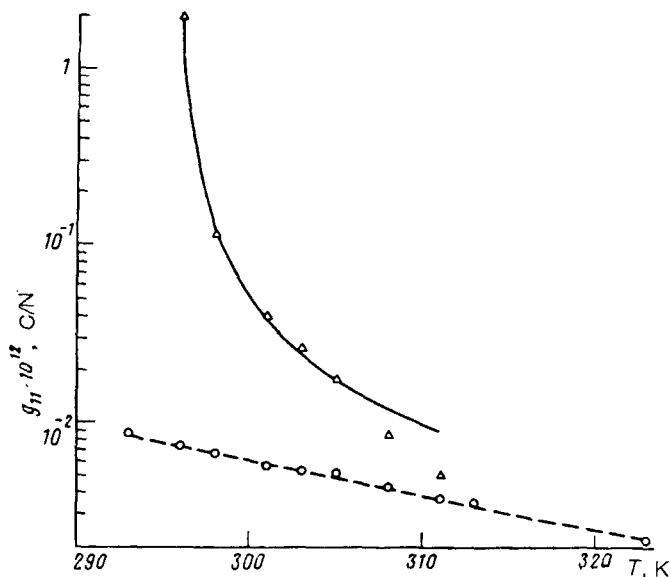


FIG. 3. Temperature dependence of  $g_{11}^{\text{FC}}$  ( $\circ$ ) and  $g_{11}^{\text{ZFC}}$  ( $\Delta$ ). The solid curve shows the power-law dependence discussed in the text proper.

$E_a > 1$  eV. In addition, a thermally activated relaxation of this sort should be exponential for both  $d_{11}^{\text{FC}}(\omega)$  and  $d_{11}^{\text{ZFC}}(\omega)$ . The power-law relaxation which is actually observed indicates the existence of a broad spectrum of relaxation times, stretching up to  $\tau = \infty$  (Ref. 8). Accordingly, the only way to explain the observed differences between  $g_{11}^{\text{FC}}$  and  $g_{11}^{\text{ZFC}}$  is to argue that they correspond to different metastable states which arise in the dipole-glass phase and which cause its nonergodicity.<sup>6,10</sup>

In summary, the results of a study of the long-term relaxation in 0.87PMN–0.13PT crystals draw a consistent physical picture which includes both the existence of a nonergodic glassy phase with an intravalley scaling (glassy) relaxation of the polarization and a transition from this phase to a mixed phase at  $T_M \approx 296$  K.

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