Long-Time Relaxation of the Dielectric Response in Lead Magnoniobate

E. V. Colla, E. Yu. Koroleva, N. M. Okuneva, and S. B. Vakhrushev
A.F. Ioffe Physico-Technical Institute, 26 Politekhnicheskaya, 194021 St. Petersburg, Russia
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We measured the time dependencies of the dielectric permittivity of a single crystal lead magnoniobate in the zero-field–cooled regime. The logarithmic decay of the dielectric response was observed in the glassy phase. We measured the time τ from the moment of the field application for the phase transition from the glasslike to the field-induced ferroelectric state to take place, at temperatures below 220 K. The transition is accompanied by the emerging of the even harmonics of the permittivity. It is shown that $\ln \tau$ depends linearly on both the inverse temperature and the inverse applied field strength.

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Relaxor ferroelectrics, or ferroelectrics with diffuse phase transitions, have been under extensive experimental study and theoretical consideration for more than 30 years [1,2], but the nature of their peculiar physical properties has not been clear until now. The essential progress in the understanding of the relaxors is related to the new approach to the problem regarding these systems as analogs of the spin glasses [3–5]. The logarithmically broad spectrum of the spin (or dipole) relaxation times is the fundamental feature that directly reflects the ultrametric organization of the metastable states [6] and determines the most specific properties of the glassy system. According to the theoretical estimations for the maximum relaxation time, such systems could be considered as thermodynamically nonequilibrium ones at all experimental times. This nonequilibrium nature of the glassy state is clearly demonstrated by the processes of magnetic (or dielectric) relaxation on macroscopic time scales. These processes can be observed in time-dependent measurements of both the magnetization [7] and the ac susceptibility [8]. Many results have been published related to the long-time relaxation in spin glasses in both the zero-field–cooled (ZFC) [9] and the field-cooled (FC) [10] regimes and in aging and "waiting time" experiments [11]. The long-time relaxation in the structural glasses is less thoroughly studied. There are interesting papers on the relaxation in protonic glasses [12], doped potassium tantalate [13–15], and relaxor ferroelectrics [16–19]. At the same time we do not know of any papers related to the study of the time-dependent transition from the dipole glass to the ferroelectric state considered in the present Letter.

The complex perovskite lead magnoniobate $\mathrm{PbMg_{1/3}Nb_{2/3}O_3}$ (PMN) belongs to the already mentioned class of relaxor ferroelectrics and could be considered as a model object for the investigation of their properties. It was shown that without an external electric field PMN undergoes a transition to a nonergodic low-temperature phase without long range ferroelectric order [16]. This phase was interpreted by several authors as the dipole glass state [3,5]. Physical phenomena typical for spin glasses [20] and dipole glasses [21,22], such as a logarithmically broad spectrum of the relaxation times, the divergency of the nonlinear susceptibility (third harmonics) [23], and the appearance of history-dependent effects (splitting of the FC and ZFC curves) [16], were observed in the low-temperature phase of PMN. None of these facts separately could be considered as unambiguous evidence of the dipole glass nature of the state, but taken together these data provide a rather convincing basis for such a statement. Recently the glass nature of the low-temperature PMN state was argued and a model of the destruction of the phase transition and the formation of a nanodomain state was proposed [19]. However, in the model [19] neither nonlinear phenomena [3,23] nor neutron data on history-dependent effects [16] were taken into account. In the discussion of our experimental data we will stick to the dipole glass model, keeping in mind that some different approaches could exist.

The application of an external electric field makes the situation more complicated. Cooling of the crystal in a dc field stronger than the threshold value $E_t = 1.5$ kV/cm applied in the [111] direction results in the destruction of the glassy state and the appearance of the ergodic one with long range ferroelectric order [24,25]. The *E-T* phase diagram was obtained (Fig. 1) [25], but no systematic study was performed of the time-dependent behavior in either glassy (GL) or ferroelectric (FE) phases or of the kinetics of the GL-FE phase transition for the ZFC experiments.

In this Letter we present the results of time-dependent ac dielectric permittivity measurements (of both linear and nonlinear components). The objectives of our investigation were (i) to study the long time dielectric relaxation in the glassy phase and (ii) to obtain the conditions of the glassy phase destruction and the appearance of the polar state.

The measurements were performed on $5 \times 5 \times 1$ mm^3 samples cut from a PMN single crystal with large faces perpendicular to the [111] direction. Both the dc and ac

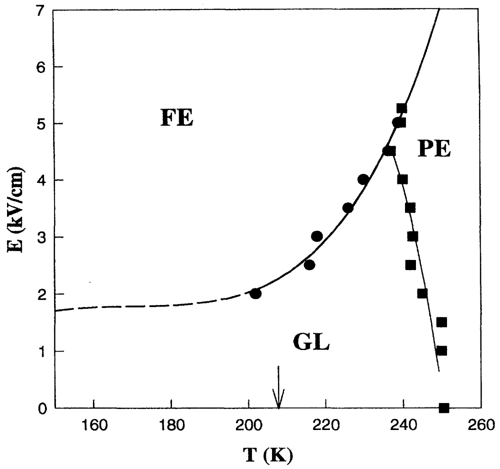

FIG. 1. Electric-field–temperature phase diagram for PMN obtained in the FC regime ($E \parallel [111]$).

fields were applied along the [111] axis. The measuring setup was described elsewhere [26]. All permittivity vs time measurements were carried out in the ZFC regime. Before each measurement the sample was annealed for one hour at 450 K. After that the sample was quickly quenched in zero field to the given temperature T_0 and the data recording was started. Special measurements were performed to ensure the absence of any remanent effects, and exact reproducibility of the results was observed. For additional monitoring of the zero-dc-field permittivity level we started the measurements without dc field and then (about 60 s later) the static field was applied. The measuring frequency was 10 Hz providing a time resolution of 2 s.

The phase diagram presented on Fig. 1 was obtained in the field-cooling (FC) regime, i.e., the formation of the FE phase is achieved by cooling the PMN in a dc field higher than E_t. Once formed, the FE phase is stable without field up to 208 K (arrow in Fig. 1). One could expect substantial change of the PMN behavior in the ZFC regime. Exploiting the analogy with spin glasses, one can consider the ZFC state as a nonequilibrium one, and so the properties of the crystal, including the phase diagram, are expected to be time dependent. The results of real time dielectric measurements for two temperatures ($T = 200$ K and $T = 165$ K) and the static field value $E = 3.0$ kV/cm are shown in Fig. 2. The switching on of the dc field results in the appearance of slow relaxation of the permittivity with a time dependence close to logarithmic. After a time τ both ε' and ε'' components undergo a stepwise change to values somewhat greater than the FC ones. We interpret these steps as a transition from a glassy phase to a ferroelectric one. The presumption of the polar nature of the new state is confirmed by the results of dynamic nonlinear permittivity measurements. The PMN nonlinear response (the second harmonic ε_2) as a function of time is shown in Fig. 2(c) and 2(f). Indeed, one can see that the abrupt changes in linear components are accompanied by emerging the even-susceptibility harmonics. Further relaxation of this term occurs at close to the logarithmic law but with a much smaller rate than before τ [Fig. 2(d) and 2(e)]. As we already mentioned, in the case of nonergodic systems the phase diagram and the properties of the phases could essentially depend on the trajectory in the E-T coordinates, so the FE phase obtained in the ZFC regime is not identical to that in the FC regime. In particular, the stability of the FC FE phase is different from the stability of the ZFC FE phase. For instance, at 190 K when the field is removed at 2000 s the crystal very quickly returns to the GL phase, while at 172 K the FE phase remains stable after removing the field. In the FC regime both temperatures lie in the region of the stable FE phase.

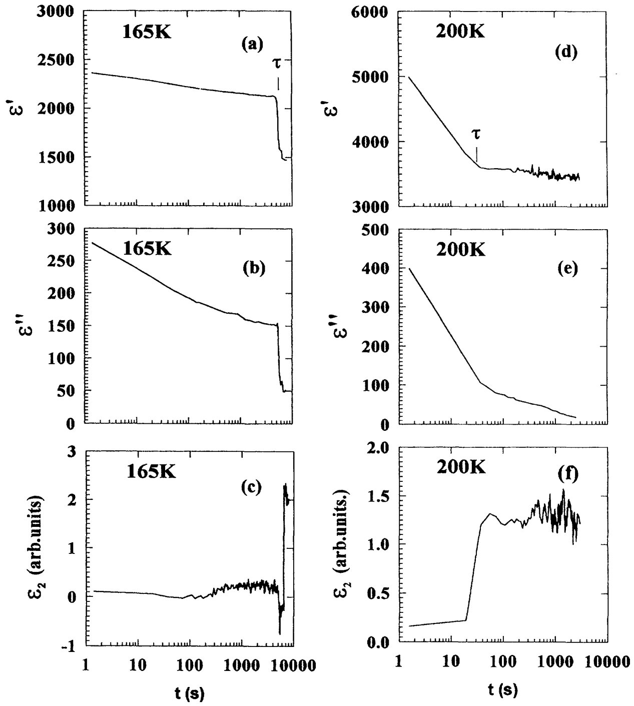

FIG. 2. Time dependencies of the components of dielectric response for PMN, $E = 3$ kV/cm; time t is counted from the moment of switching on the dc field; (a) (165 K) and (d) (200 K)—real parts of linear permittivity; (b) (165 K) and (e) (200 K)—imaginary parts of linear permittivity; (c) (165 K) and (f) (200 K)—amplitudes of the nonlinear response (second harmonics).

The measurements were performed in a broad temperature region ($160 < T < 200$ K) and at several values of the dc field, and we have found that τ is strongly dependent on both the temperature and the static field magnitude. In Fig. 3 the resulting τ vs T_1 dependencies are presented. In the reported temperature region a linear $\log_{10}\tau$ vs T_1 dependence is observed. For temper-

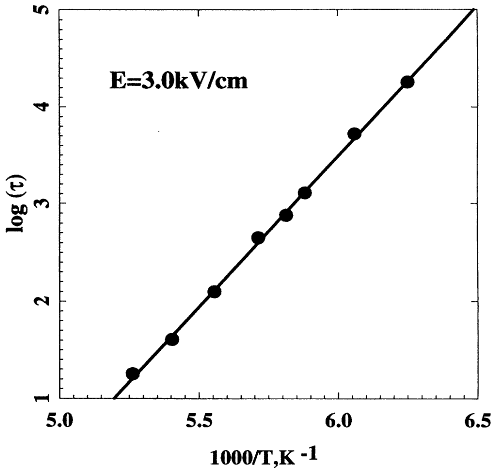

FIG. 3. Temperature dependence of the delay time τ.

atures higher than 200 K τ is too small and is outside our experimental possibilities, so the transition looks instant [Fig. 2(d)–2(f)]. The set of curves demonstrating the time-dependent transition into the FE phase for fixed temperature ($T = 175$ K) and different dc field values (E) is presented in Fig. 4. The inset shows τ as a function of E_1. One can see that in the studied region of E, $\ln \tau$ depends linearly on E_1. The additional waiting time experiments were performed to find the dependence of possible changes in the relaxation on the waiting time before the dc field application. The delay time was varied up to several thousands of seconds and no change of τ was observed.

Finally, we would like to point out that the presented experimental results are the first observation of the time-dependent transition from the GL to the FE phase. Our experiments have confirmed that the ZFC state is really the nonequilibrium one. The observed logarithmic relaxation could be considered as the direct consequence of the nonergodicity of the GL phase and the infinite degeneracy of the metastable states [20]. The application of the electric field results in the gradual growth of the average polarization of the crystal, as could be concluded from our neutron data published earlier [4] and from the time dependence of the linear birefringence [19]. After the polarization attains the critical value a steplike transformation to the FE phase takes place. The observed $\tau(T^{-1})$ and $\tau(E^{-1})$ dependencies (Figs. 3 and 4) can be explained by the obvious increase of the difficulty in achieving the critical polarization value with both cooling down from the freezing temperature and field weakening. The FE phase arising is still incompletely ordered as is clearly indicated by the persistence of the logarithmic relaxation processes at $t > \tau$ [Fig. 2(d) and 2(e)]. From the $\log_{10} \varepsilon''(t)$ dependence one can get an estimation for the time τ_0 when ε'' vanishes, i.e., the dispersion of the permittivity at low frequencies disappears. τ_0 is about 10^5 s and nearly temperature independent, which is surprisingly close to our estimation [23] for the mean relaxation time in the low-temperature PMN phase.

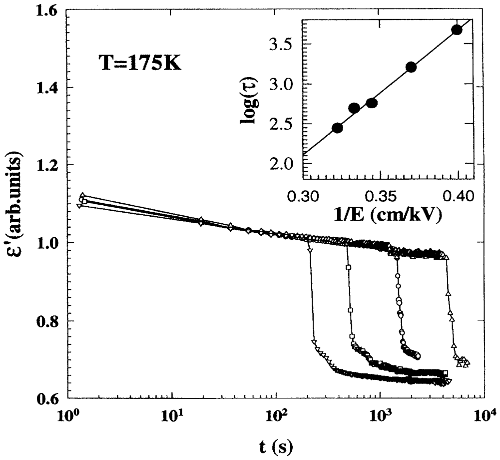

FIG. 4. Time dependencies of the normalized real parts of the dielectric permittivity at 175 K, obtained with different applied fields E; 1–3.1 kV/cm, 2–2.9 kV/cm, 3–2.7 kV/cm, 4–2.5 kV/cm; on the inset the $\log_{10} \tau$ as a function of E^{-1} is shown.

Our results could give light to some of the data published earlier. Vakhrushev *et al.* [4] have reported a neutron scattering study of the PMN glassy behavior in its low-temperature phase. It was shown that electric field application to the cooled crystal (ZFC regime) results in a gradual increase of the Bragg peak intensities and a decrease of the intensity of the diffuse scattering, thus indicating the ordering of ionic displacements. The time dependence of the Bragg intensity $I(t)$ was measured at several temperatures. It was shown that these dependencies were close to logarithmic at all temperatures. At $T = 188$ K an unexpected change of the $I[\log_{10}(t)]$ slope at $t \sim 10^2$ was observed that the authors failed to explain. Comparing those data [4] with our present results, we can explain the change of the slope by the transition of PMN from the GL to the FE state.

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