Evidence for domain-type dynamics in the ergodic phase of the $PbMg_{1/3}Nb_{2/3}O_3$ relaxor ferroelectric

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It was observed that the dielectric permittivity of $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) relaxor ceramics increases with increasing amplitude of the applied ac field. A strong nonlinearity occurs at temperatures where the frequency dispersion of the dielectric response is observed. A similarity was found between the effects of the amplitude and frequency on the permittivity. It was shown that, taken together, these data evidence that the relaxation phenomena in PMN are controlled by domain-type dynamics rather than thermally activated flips of the local spontaneous polarization.

The complex perovskite $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) (Ref. 1) is often considered as a ''typical'' representative of relaxor ferroelectrics (relaxors), which are characterized as highly disordered systems. Recently, experimental findings and ideas of the nature of the physical phenomena in relaxors have awakened fresh interest in these materials.

Current discussion focuses on two closely related problems. The first is how to describe the low-temperature state of relaxors, particularly PMN. Different experiments[2–4] show that on cooling, PMN undergoes a transition (at $T_c = 220$ K) into a nonergodic state without a long-range ferroelectric order. This state was interpreted by some authors as the dipolar glass state.[3–5] However, some findings, such as observation of Barkhausen jumps in the linear birefringence[2] and the sudden drops observed in the time variation of the dielectric permittivity,[6] rather support the idea[2] that at $T < T_c$ PMN has features of the microdomain state of ordinary ferroelectrics. The second problem is related to understanding the mechanism of the low-frequency dielectric relaxation. Relaxors are defined by the presence of a frequency-dependent maximum in the dielectric permittivity, ε', as a function of temperature,[1] which is observed at temperatures above T_c (in PMN the position of the maximum T_m is about 260 K when the measurement frequency ω is within the Hz–MHz range). A general phenomenological model[4,5,7] explains the variation in $\varepsilon'(\omega, T)$ in terms of a broad relaxation time spectrum, the width of which increases on cooling. More detailed models for relaxors take into account structural pecularities of these materials on the mesoscopic scale, namely, that there is a partitioning of the structure into the small regions of local spontaneous polarization (so-called polar regions) with a nanometre scale size,[8,9] and try to describe the dielectric properties of relaxors as a result of the response of an ensemble of the polar regions to the applied field. However, the mechanism of this response is not yet fully understood.

For some time,[10] it has been rather generally believed that the polar regions should behave like large, ''superparaelectric,''[11] dipole moments. It was assumed that upon the application of the external field, local polarization vectors reorient in the direction of the field by means of thermally activated flips across the energy barriers separating different orientation states. The distribution of the energy barrier heights brings about the spectrum of relaxation times. When the small-signal dielectric response was simulated from the superparaelectric model,[11] a good qualitative fit to the relaxor behavior[12,13] was obtained. However, now it is clear that another possible mechanism of the dielectric response should also be considered. If relaxors are similar to the microdomain state in ordinary ferroelectrics,[2] this will imply that the direction of the spontaneous polarization in each polar region is reversed not by means of a thermally activated flip, but by a dissipative motion of the boundary separating the parts with different orientation of the polarization vector, a process close to the domain-wall motion of ferroelectrics. Even though the analogy of domain-wall motion requires a detailed model, it is clear that introducing a distribution of the heights of local pinning barriers, one can account for the spectrum of the relaxation times in the system and explain the small-signal response of relaxors.

At this stage, when two ways to describe the response of an ensemble of the polar regions to the applied field have been proposed, it is imperative to find the experiment which could unambiguously discriminate between them. In this paper we shall show that measurements of the dielectric permittivity as a function of the ac field level provide us with the data which attest to the domain-wall motion process. By contrast, predictions of the superparaelectric model are inconsistent with these results. Also it is interesting that these data show that the domain-type process is relevant to the dielectric relaxation not only in the nonergodic phase at $T < T_c$ (as was suggested earlier[2]), but in the ergodic phase as well.

Measurements were performed on PMN ceramic samples which were prepared as described in Ref. 13. The dielectric permittivity, ε', was measured using a HP4284A LCR meter over the frequency range 20 Hz–100 kHz, on cooling from 340 to 190 K at 1 K/min. The amplitude E_m of the ac measurement field was varied from 0.01 kV/cm (the field level normally used in the measurements of the small-signal dielectric permittivity of relaxors) up to 2 kV/cm. Figure 1(a) shows the change in the dielectric permittivity measured at 1 kHz with increasing E_m, starting from the small-signal level (curve 1). The data measured at other frequencies share the

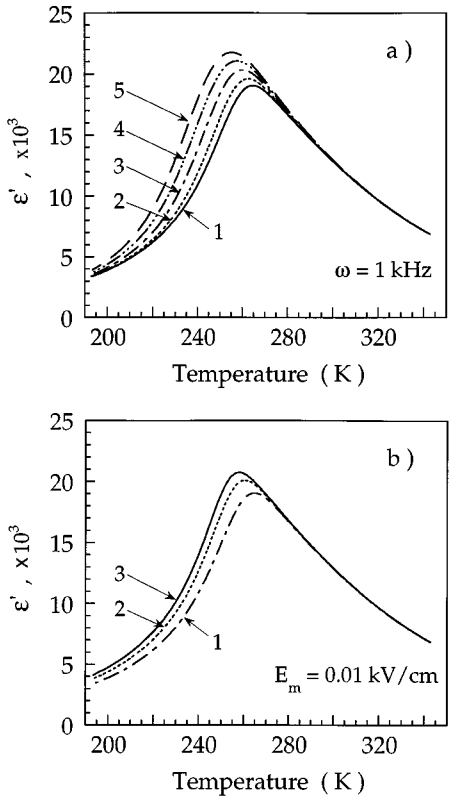

FIG. 1. Dielectric permittivity of PMN: (a) at various amplitudes, E_m (1–0.01, 2–0.5, 3–1, 4–1.5, 5–2 kV/cm), and (b) various frequencies, ω (1–1 kHz, 2–100 Hz, 3–20 Hz) of the ac field; curve 1 is the same in (a) and (b).

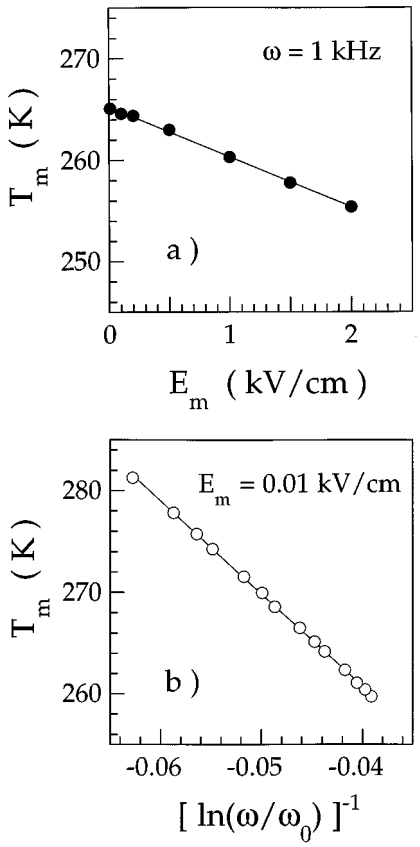

FIG. 2. Temperature T_m, corresponding to the position of the maximum in $\varepsilon'(T)$ of PMN: as a function of the amplitude (a) and the frequency (b) of the ac field.

same features in the field dependence of ε' with those at 1 kHz, with the only difference being that the magnitude of the effect of E_m is less pronounced at higher frequencies. In order to compare the effects of the amplitude and frequency on the dielectric permittivity, Fig. 1(b) was plotted. It demonstrates the change in the small-signal permittivity with decreasing measurement frequency. Note that in both parts of Fig. 1 curve 1 is the same. Referring to Fig. 1 one can list the most essential features of the nonlinear effect:

(i) the dielectric permittivity increases with increasing E_m;

(ii) at a given frequency, ω, a strong nonlinear effect is observed at temperatures below that where the small signal ε' deviates from the permittivity measured at frequencies lower than ω;

(iii) increasing E_m has the same effect on the maximum in the temperature dependence of ε' as decreasing frequency; namely, the maximum shifts to lower temperatures and its magnitude increases.

It should be noted that the first two results from the list are consistent with observations of earlier work on PMN single crystals,[14] where the data only for $E_m=0.06$ and 0.24 kV/cm measured at 1 kHz were presented. The comparison between the effects of the amplitude and frequency on $\varepsilon'(T)$ is extended in Fig. 2. Figure 2(a) shows the temperature of the permittivity maximum [from Fig. 1(a)] as a function of the amplitude of the applied field. We found that to a first approximation the data can be fairly well fitted to a linear law (which is shown as a solid line). The linear dependence of T_m on E_m was also observed at other frequencies used in this study. On the other hand, the temperature of the small-signal $\varepsilon'(T)$ maximum is a linear function of $(\ln(\omega/\omega_0))^{-1}$ [Fig. 2(b)], as is expressed in the well-known empirical Vögel-Fulcher relationship[5] [ω_0 is a constant, $\omega_0 \simeq 3\times 10^{13}$ s^{-1} was used in Fig. 2(b)]. Comparing the plots in Figs. 2(a) and 2(b) one observes that a linear change of the amplitude and a logarithmic change of the frequency of the applied field have a similar effect on T_m.

To open the discussion of the reported nonlinear effect it is useful to first recall a general picture of the temperature and frequency variation of the small-signal dielectric permittivity of relaxors [Fig. 1(b)]. A common approach is to consider the total dielectric response as a sum of responses of relaxators over a wide and smooth spectrum of their relaxation times, τ, and to present the permittivity as

$$\varepsilon'(\omega,T)=\varepsilon'_s(T)\int_{\tau=0}^{\infty} g(\ln\tau,T)\Delta(\omega,\tau)d(\ln\tau), \qquad (1)$$

where $g(\ln\tau,T)$ is a distribution function of relaxation times with a normalized condition $\int_{\tau=0}^{\infty} g(\ln\tau,T)d(\ln\tau)=1$. The parameter $\varepsilon'_s(T)$ is equivalent to the static permittivity, $\varepsilon'(0,T)$. A frequency-dependent factor $\Delta(\omega,\tau)$ represents the response of a single relaxator and is equal to $[1+(\omega\tau)^2]^{-1}$. For a sufficiently wide and smooth spectrum of relaxation times, the factor $[1+(\omega\tau)^2]^{-1}$ can be consid-

ered as a step function with a cutoff equal to ω^{-1}. Thus, relaxators can be ''fast'' ($\tau<\omega^{-1}$) or ''slow'' ($\tau>\omega^{-1}$), and only ''fast'' relaxators contribute to ε'. Clearly, the frequency dispersion of ε' will be observed only when the spectrum is so broad that the maximum τ is larger than ω^{-1}. That implies the existence of ''slow'' relaxators in the system, the fraction of them being frequency dependent. The lower the frequency, the smaller is the fraction of ''slow'' relaxators, and the larger the dielectric permittivity.

Keeping in mind this explanation one can compare again the data shown in Figs. 1(a) and 1(b). The fact, that a large change in the permittivity with increasing amplitude of the field occurs exactly at temperatures where at the small-signal level ε' becomes frequency dependent, clearly indicates that the observed nonlinear effect is related to the appearance of ''slow'' relaxators in the spectrum. Hence, one can suggest the following scenario: a larger amplitude E_m of the applied field forces ''slow'' relaxators to contribute to the dielectric response leading to the increase in the dielectric permittivity.

The suggested scenario seems to explain the positive sign of the nonlinear effect for any system of relaxators with the aforementioned properties of the spectrum. However, more detailed analysis of the problem shows that actually only one relaxation mechanism (of the two suggested by current discussion in the literature and already cited in the introductory part of this paper) provides a consistent interpretation.

Dielectric relaxation due to thermally activated flips of the local polarization over the anisotropy energy barriers is described in the superparaelectric model.[11–13] Following this model, the dielectric response is the sum of those of noninteracting polar regions. For the simplest case, when there are only two orientation states, the time variation of $\langle p\rangle$ (average dipole moment of a single polar region) can be described by

$$\frac{d\langle p\rangle}{dt}+\frac{\langle p\rangle}{\tau}\cosh a(t)=\frac{p}{\tau}\sinh a(t), \tag{2}$$

where τ is a relaxation time between the two orientation states, p is the absolute value of the dipole moment of the polar region, and $a(t)=E(t)/E_0$, (E_0 is a parameter equal to k_BT/p, T is the temperature, and k_B is the Boltzmann constant). Equation (2) was deduced from the standard consideration of the probabilities to find a dipole moment oriented parallel and antiparallel to the field direction. For a field applied in the form of an ac signal, $E(t)=E_m\sin\omega t$, the solution of Eq. (2) is sought as a periodic function, however, in the general case it does not exist in an analytical form, necessitating numerical integration. When $\langle p\rangle$ is known, one can find the value of Δ, the contribution from this polar region to the dielectric permittivity, which we defined as a ratio between the amplitude of first harmonic of the polarization response and E_m. In Fig. 3, Δ is plotted against $\ln(\omega\tau)$ for different values of E_m/E_0. Curve 1 corresponds to the small-signal response, when $E_m/E_0\ll 1$. At this limit, Eq. (2) yields a well-known answer for the Debye relaxation $\Delta(\omega,\tau)=[1+(\omega\tau)^2]^{-1}$. For curve 3, $E_m/E_0=2$. From Fig. 3 one can draw an important conclusion. The contribution to ε' from ''slow'' polar regions [$\tau>\omega^{-1}$, i.e., $\ln(\omega\tau)>0$] does increase with increasing E_m, as was expected. But the response of ''fast'' regions ($\tau<\omega^{-1}$) saturates at large field leading to a decrease in the magnitude of their contribution

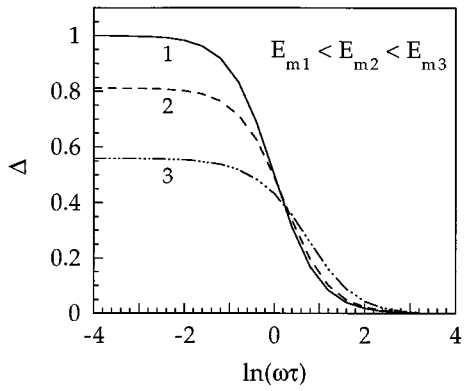

FIG. 3. Effect of the ac field level on the contribution Δ to the dielectric permittivity from a dipole moment flipping between two orientation states; for the curves 1 to 3 the normalized value of the field level, E_m/E_0, is equal to 0.01, 1, and 2, respectively.

to the permittivity. To find the sign of the nonlinear effect for the whole crystal, one should perform a summation of individual responses of the polar regions over the spectrum of their relaxation times. We obtained that the summation yields the following result: the dielectric permittivity *decreases* with increasing amplitude of the applied field. The physical reason for this result is the fact that, even at high field levels, ε' is mainly controlled by contributions from the regions with $\tau<\omega^{-1}$, for which the nonlinear effect is of negative sign. Thus, the prediction of the superparaelectric model—negative sign of the nonlinear effect—is opposite to the experimental observations.

Now suppose that the dielectric response of relaxors is related to a process similar to the dissipative motion of domain walls. In this case the frequency dispersion arises because each wall has a finite response time τ_r to the applied field, which is the time required for the wall to overcome a local pinning barrier. If there is a broad distribution of the heights of local pinning barriers it will result in an exponentially wide temperature-dependent spectrum of τ_r, similar to the spectrum discussed above in connection to Eq. (1). So, the small-signal dielectric response is expected to be similar to that predicted by the superparaelectric model. However, a quite different result is anticipated for the nonlinear effect. Let the field level E_m increase. This will result in a lowering of the pinning barriers and, consequently, in a decrease of the response time. The field dependence for τ_r can be expressed as

$$\tau_r=\omega_0^{-1}\exp\left(\frac{U_0-2P_sV_aE}{k_BT}\right), \tag{3}$$

where ω_0 is an attempt frequency, U_0 is a height of the initial pinning barrier, $2P_sV_aE$ is the decrease in the barrier height, P_s is the local spontaneous polarization, and V_a is an activation volume. From Eq. (3) one can conclude that some of the walls which originally, at the small-signal level, had $\tau_r>\omega^{-1}$, at larger field can contribute to the dielectric response. At the same time, one can expect that the motion of those walls, which at low fields had $\tau_r<\omega^{-1}$, will not be strongly affected by the increased E_m.[15] As a result, larger E_m will lead to an *increase* in the dielectric permittivity, since a larger number of domain walls can respond to the

external field. Furthermore, one can compare the effects of the amplitude and frequency of the applied field on ε'. When the maximum τ_r in the spectrum is larger than ω^{-1}, both lowering the frequency and increasing the amplitude will have the same result: the number of the domain walls responding to the external field will be larger, leading to an increase in the dielectric permittivity. By lowering the frequency a larger fraction of the spectrum contributes to the response, whereas by increasing the amplitude one effectively changes the spectrum of response times. From Eq. (3) it can be predicted that equivalent increases in ε' will result from a logarithmic change of ω and a linear change of E_m. In the case where at low fields all τ_r in the spectrum are smaller than ω^{-1}, one should not expect a change in ε' either with decreasing frequency, or with increasing E_m. Indeed, this interpretation, using analogy of domain-wall motion, is not quantitative yet, but seems to be qualitatively consistent with the experimental data on the nonlinear effect in PMN relaxor ceramics.

To summarize, we believe that the data presented for the nonlinear dielectric permittivity of PMN relaxor ceramics, measured as a function of the ac field level give some clue to the nature of the relaxation phenomena in relaxors and suggest that it is related to domain-type processes rather than thermally activated flips of the local spontaneous polarization. It is worth noting that the reported nonlinear effect was observed in the temperature interval extending above the point of the ergodicity breaking in PMN ($T_c = 220$ K). Thus, a domain-type process is relevant to the dielectric relaxation not only in the nonergodic phase,[2] but also in the ergodic phase.

Note added in proof. In the present paper, the superparaelectric model with a symmetrical double-well potential is analyzed. A strong negative dielectric nonlinearity of the fast dipoles, which was used as an important argument in the discussion, is a property of this model. As was indicated by Dr. M. Weissman, the incorporation of local random fields in the model results in a nearly complete suppression of this nonlinearity. Thus, to finally discard the superparaelectric model, an additional analysis of the problem is required.

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[15] If $\tau_r < \omega^{-1}$, the wall behaves as a pseudofree one, since there is enough time for it to leave the pinning center during every period of the time variation of the applied field. Hence, there is no reason for saturation of the response. Indeed, there exist other processes which can cause saturation and, consequently, a decrease in ε': e.g., an annihilation of two kinks of polarization of the opposite sense (that is neighboring domain walls). However, such processes occur at fields of different scale.