Mechanism of polarization response in the ergodic phase of a relaxor ferroelectric

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It is shown that the effects of large dc bias and ac driving fields on the dielectric permittivity of single crystals of $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) relaxor ferroelectric exhibit very different behavior, including anisotropy and sign of the effect, which is traced up to the high-temperature interval in the ergodic phase. The observed phenomena strongly suggest that in the ergodic phase of PMN the dielectric response to the ac field is controlled by a side-way motion of the interphase boundaries of the polar regions, rather than by the thermally activated reorientations of the local spontaneous polarization. [S0163-1829(98)01801-3]

The nature of the dielectric response of relaxor ferroelectrics (relaxors), especially $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), has been one of the challenging problems in the physics of ferroelectrics for many years. At present, it is commonly understood that the features of the frequency dispersion of the small-signal dielectric permittivity of relaxors, which extends over many decades in frequency, unambiguously give evidence for the existence of an exponentially wide spectrum of relaxation times of elements contributing to the dielectric response. However, the question, ''what are these elements?'' still remains open. In general, it is almost impossible to get an unique answer for the whole temperature interval, because the interactions in the system, which play a more and more important role with decreasing temperature, can easily change the nature of these elements, e.g., from individual dipoles at high temperatures to domain walls at low ones.[1] At the same time, in the regime of relatively weak effective interactions, that is in the ergodic state at high temperatures, one can expect to have a definite answer on the above question. This seems to be a very important step for the understanding of the nature of relaxors, since this answer will actually imply the identification of the elements of which the ''relaxor ferroelectricity'' is ''made.''

At high temperatures, in the ergodic phase, in the limit where the interactions in the system can be neglected, three possible candidates for the elements contributing to the dielectric response are suggested by the current discussion in the literature.

(a) Thermally activated reorientation of the local spontaneous polarization vector $\vec{P}_s$ in the polar regions between several equienergetical orientation states. This possibility corresponds to dipole glass[2,3] or superparaelectric[4–6] model depending on whether at lower temperatures the interaction between $\vec{P}_s$'s of different polar regions is taken into account or not, respectively.

(b) The same as (a), but the reorientations of $\vec{P}_s$ are affected by a random-field environment. In general, this possibility corresponds to asymmetric two level systems.[7] For relaxors, this scenario was treated in Ref. 8 (possible sources of random fields in PMN were discussed in Ref. 9).

(c) The motion of the interphase boundary of the polar region without change of the orientation of $\vec{P}_s$ during the period of applied ac field.[10,11]

In a previous publication,[11] using the data on the ac field effect on the dielectric permittivity of PMN ceramics we showed that the case (a) can be excluded from this list and that the nonlinear dielectric response of PMN in the ergodic phase is consistent with the case (c) (domain wall type dynamics). However, using those data we could not eliminate case (b) which still could be considered a realistic scenario.

In this paper we continue the experimental study of nonlinear dielectric properties of PMN, now using single-crystal samples, and compare two types of the field effects: the change in the dielectric permittivity produced by large ac driving and dc bias fields. An unexpectedly big difference (including the sign, magnitude, and anisotropy) between these two effects is observed, even in the temperature range where both the frequency dispersion and nonlinearity of the dielectric response are relatively small. This feature is employed as the key argument in the discussion. The obtained experimental results enable us to eliminate the cases (a) and (b) in favor of the case (c). Thus, we show that the nonlinear dielectric properties of PMN strongly suggest that the mechanism of the dielectric response in the ergodic phase of this classical relaxor is the vibration of the boundaries of the polar regions.

The dielectric permittivity, ε' of PMN single crystals, was measured along $\langle 100 \rangle$ and $\langle 111 \rangle$ directions using a HP 4284A LCR meter, over the frequency range from 20 Hz to 100 kHz, always on cooling from $T=360$ to 150 K at 1 K/min. Two types of experiments were performed. In one experiment (ac field effect), only ac field was applied to the sample, and its amplitude E_m was varied from 0.02 to 2 kV/cm. In the other experiment (dc bias effect), a small ac measurement field ($E_m=0.02$ kV/cm) was superimposed on the dc field from the built in dc voltage source of the HP 4284A LCR meter. The dc field level E_b was changed from 0 to 2.5 kV/cm. In all the samples, we used Cr/Au electrodes which were deposited by evaporation.

With respect to the ac field, the dielectric permittivity of single crystals demonstrates the same behavior as in ceramics:[11] increasing amplitude of the driving field results in a change of the permittivity similar to that produced by lowering the frequency, i.e., ε' becomes larger in magnitude and the maximum in ''ε' vs T'' dependence shifts to lower temperatures. Figure 1 exhibits the nonlinear component of the dielectric permittivity, $\Delta\varepsilon'_{\sim}$ [defined as the difference be-

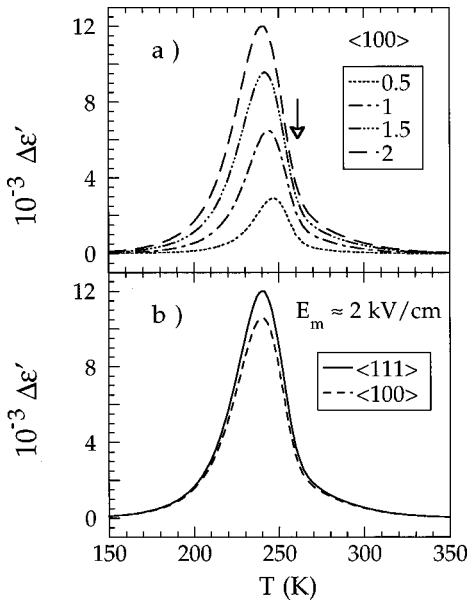

FIG. 1. Nonlinear part, $\Delta\varepsilon'_{\sim}=\varepsilon'(E_m)-\varepsilon'(0)$, of the dielectric permittivity of PMN measured at 100 Hz: (a) along $\langle 100\rangle$ direction at different ac field level E_m (in kV/cm); (b) along $\langle 111\rangle$ and $\langle 100\rangle$ directions at $E_m \approx 2$ kV/cm. The arrow indicates the temperature of the small-signal permittivity maximum at 100 Hz.

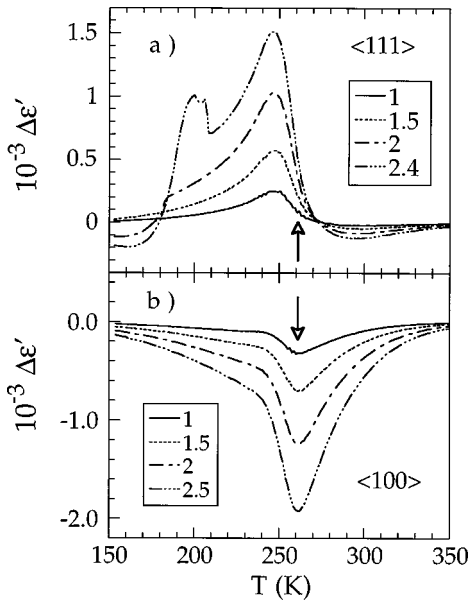

FIG. 2. Nonlinear part, $\Delta\varepsilon'_{=}=\varepsilon'(E_b)-\varepsilon'(0)$, of the dielectric permittivity of PMN crystals measured at 100 Hz at several dc bias levels E_b (in kV/cm): (a) along $\langle 111\rangle$ and (b) along $\langle 100\rangle$ directions. The arrow indicates the temperature of the small-signal permittivity maximum at 100 Hz.

tween the permittivity measured at a given amplitude, E_m, and the small-signal permittivity: $\Delta\varepsilon'_{\sim}=\varepsilon'(E_m)-\varepsilon'(0)$], measured at 100 Hz. In Fig. 1(a), $\Delta\varepsilon'_{\sim}$ is plotted for $\langle 100\rangle$ direction at several values of the ac field amplitude. It is always positive and passes through a maximum which lies somewhat below T_m [the temperature of the maximum of the small-signal permittivity measured at the same frequency; for 100 Hz, $T_m \approx 265$ K; it is arrowed in Fig. 1(a)]. Figure 1(b) illustrates the crystalline anisotropy of the ac field effect in PMN, showing that it is virtually independent of crystal orientation. One can see that for $E_m \simeq 2$ kV/cm, $\Delta\varepsilon'_{\sim}$ is almost the same for $\langle 100\rangle$ and $\langle 111\rangle$ directions.

Using the same samples as in the study of the ac nonlinearity, we measured the effect of dc bias field on the small signal dielectric permittivity. The data obtained qualitatively correspond to those reported earlier in the literature.[12–14] In Figs. 2(a) and 2(b), $\Delta\varepsilon'_{=}=\varepsilon'(E_b)-\varepsilon'(0)$ measured at 100 Hz is plotted as a function of temperature for $\langle 111\rangle$ and $\langle 100\rangle$ directions, respectively. In Fig. 2(a), one can notice the low temperature anomaly for $\langle 111\rangle$ direction at around 200 K for $E_b \geqslant 2$ kV/cm. It was attributed by several authors to the electric field induced phase transition from relaxor to a ferroelectric state.[12–14]

Leaving aside the problem of the field induced phase transition in PMN, we focus on the temperature range above 200 K, where the material remains in a normal relaxor state. Comparison of the plots in Figs. 1 and 2 shows a big difference, both qualitative and quantitative, between two nonlinearities:[15] in the anisotropy, sign and magnitude of the effect. For $\langle 100\rangle$ direction, $\Delta\varepsilon'_{=}$ is *negative* and passes through a *minimum*, position of which coincides with T_m [arrowed in Figs. 2(a) and 2(b)]. For the $\langle 111\rangle$ direction, $\Delta\varepsilon'_{=}$ is mostly *positive* and has a *maximum* which is slightly below T_m. But above the maximum $\Delta\varepsilon'_{=}$ changes sign and becomes negative at high temperatures, Fig. 2(a). We also note that at most temperatures, for the same field level the absolute value of $\Delta\varepsilon'_{=}$ is about an order of magnitude smaller than that of $\Delta\varepsilon'_{\sim}$ [cf. Figs. 2(b) and 1(a)].

Let us first of all discuss the experimental results within a general phenomenology. The simplest case is realized in the temperature range around and above T_m. There, the frequency dispersion of the dielectric permittivity is rather small, and, hence, one could expect that the presentation of polarization as a function of the instantaneous value of the electric field should be a reasonable approximation. Taking into account that crystal structure of PMN is cubic with a center of symmetry, and that around T_m the nonlinear effects are relatively small [compared to $\varepsilon'(0)$ which is about 2×10^4 at $T \simeq T_m$], one can write: $P=\varepsilon_0\varepsilon'(0)E+\varepsilon_0\beta E^3$ [where P is the polarization measured in the direction of the applied electric field E, ε_0 is the permittivity of the vacuum, constant β depends on the orientation of the field with respect to crystal axes, whereas the small-signal permittivity $\varepsilon'(0)$ does not]. Using this equation, the nonlinear components of the permittivity measured under ac field ($\Delta\varepsilon'_{\sim}$) and dc bias ($\Delta\varepsilon'_{=}$) can be found as

$$\Delta\varepsilon'_{\sim}=\frac{3}{4}\beta E_m^2, \quad \Delta\varepsilon'_{=}=3\beta E_b^2. \tag{1}$$

Comparison of Eq. (1) with the experimental data shows that the latter are inconsistent with the predictions of the simple phenomenological model considered above. Indeed, according to Eq. (1) two nonlinear effects are controlled by the same coefficient β, which excludes any difference in the anisotropy and sign of $\Delta\varepsilon'_{\sim}$ and $\Delta\varepsilon'_{=}$. Also, Eq. (1) predicts that the dc field effect must be stronger than the ac one, in contradiction to our experimental observations. Finally, there

is one more indication for nonapplicability of this phenomenological approach: in the experiments, $\Delta\varepsilon'_{=}$ was found to be a quadratic function of the field, whereas $\Delta\varepsilon'_{\sim}$ strongly deviated from predicted $\propto E_m^2$ dependence.[16]

Thus, the applied phenomenological scheme, which one could consider as a reasonable approximation, at least at $T \geqslant T_m$, cannot account for big qualitative difference between two nonlinear effects in PMN. Most likely, this ''failure'' indicates that there exist nonlinear relaxation phenomena, not taken into account by the scheme, and which determine the difference between effects of dc bias and ac field. Taking into account the known structural features of PMN on a mesoscopic scale (recent x-ray and neutron-diffraction studies[17] showed that there is a partitioning of the structure into small regions of local spontaneous polarization with a nanometer scale size), we believe that the origin of this relaxation is a very slow reorientation of the polar regions in the dc electric field. Incorporating the process of the reorientation into the model proposed for the explanation of the ac nonlinearity in our previous paper,[11] we can give the following interpretation of the observed phenomena.

According to that model,[11] the ergodic phase of PMN is treated as a system of polar regions embedded into a nonpolar matrix. They are elongated along the direction of the local spontaneous polarization (the shape which minimizes the effect of depolarizing field) which can be oriented in one of eight $\langle 111 \rangle$ pseudocubic directions allowed by the rhombohedral symmetry of the polar phase.[17] Without external field the polar regions are randomly oriented in the crystal, providing the macroscopic cubic symmetry of the material. The polar region pattern is determined by the spatial distribution of the pinning centers (as has been pointed out in Ref. 9, the internal random fields induced by the charge disorder can act as a source of the pinning centers in PMN).

We believe that within this microscopic picture of PMN, the proper approach for the interpretation of our results is the interface-roughening theory approach to the dielectric response of pinned interfaces.[18] Unfortunately, up to now this approach has been developed only for two ultimate cases: for the linear response and for the fields of the order of the coercive field, whereas the case of weak nonlinearity has not been analyzed. Not attempting to solve this theoretical problem, we will show how our data can be interpreted within this framework.

Consider an element S of the interface between polar and nonpolar phases, which is parallel to the spontaneous polarization $\vec{P}_s$. The element is assumed to be pinned by the random field environment. On the lines of Ref. 18, the variation of the electric dipole moment $\Delta\vec{p}$ caused by the bending of this element in the external electric field $\vec{E}$ can be estimated as

$$\Delta\vec{p} = \vec{P}_s \cdot \frac{L^2 S}{\Gamma} \cdot (\vec{P}_s \cdot \vec{E}), \tag{2}$$

where Γ is the surface tension of the interface and L is the scale on which the interface is effectively free (the case of $S \gg L^2$ is certainly considered). For the chosen element S, its contribution to the dielectric permittivity is proportional to $(\Delta\vec{p}\cdot\vec{E})/\varepsilon_0 E^2$ [in this expression, $(\Delta\vec{p}\cdot\vec{E})/E$ gives the projection of the induced dipole moment $\Delta\vec{p}$ on the direction of the field, and $(\varepsilon_0 E)^{-1}$ is introduced to calculate the corresponding contribution to the dielectric permittivity]. Therefore, according to Eq. (2), this contribution depends upon $\cos^2\theta$, where θ is the angle between the directions of $\vec{P}_s$ and the applied field $\vec{E}$, Fig. 3. With this remark, from Eq. (2), the contribution of the interphase boundaries of the elongated polar regions to the dielectric permittivity measured in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions in the crystal can be found in the form

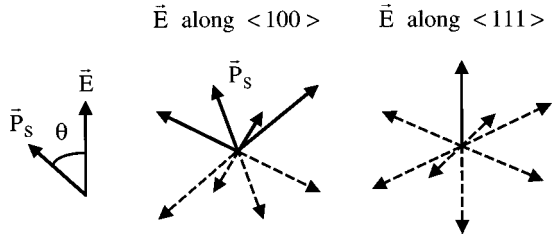

FIG. 3. Schematic drawing of eight possible orientations of the polar regions with respect to the direction of the electric field. Solid lines show the preferable orientations of the regions for the dc field $\vec{E}$ directed upwards.

$$\varepsilon_{100} = \frac{L^2 P_s^2}{\varepsilon_0 \Gamma} \cdot (NS) \cdot \frac{1}{3}, \tag{3}$$

$$\varepsilon_{111} = \frac{L^2 P_s^2}{\varepsilon_0 \Gamma} \cdot (NS) \cdot \left(n_{\parallel} + \frac{1 - n_{\parallel}}{9} \right), \tag{4}$$

where S and N are the average area of the interface of the polar regions and their concentration, respectively, and $n_{\parallel}$ is the fraction of the polar regions with $\vec{P}_s$ oriented along $[111]$ and $[\overline{1\,1\,1}]$ direction, Fig. 3. In the absence of the dc bias, $n_{\parallel} = 1/4$, due to the random orientation of the polar regions, and obviously we have $\varepsilon_{100} = \varepsilon_{111}$, corresponding to the average cubic symmetry of PMN.

Let us use Eqs. (3) and (4) for the interpretation of the observed ac nonlinearity. In terms of these equations, field induced depinning, which we consider as the origin of the effect, corresponds to the increase of the scale L with increasing ac field amplitude. To be consistent with weak pinning approach in general[18] this increase should not change the order of magnitude of L because usually the same scale is used for the estimates of both the coercive field and small signal response. Formally, Eqs. (3) and (4) also predict the isotropy of the ac nonlinearity. However, the strict extension of both of them to the case of the finite amplitude requires the validity of the relationship $\langle L^2 P_{si} P_{sj} \rangle = \langle L^2 \rangle \cdot \langle P_{si} P_{sj} \rangle$, where the angular brackets stand for the averaging over the polar region orientation. Thus, Eq. (3) is consistent with the positive sign of the ac nonlinearity and, under a certain condition, with the isotropy of the effect.

Now consider the effect of dc bias. It is threefold: (i) the external dc field changes the profile of the random fields and, therefore, changes the positions of the interphase boundaries, (ii) it provides a coalescence of neighboring polar regions resulting in the diminishing of the total area of their interface, and (iii) it redistributes the polar regions between eight possible $\langle 111 \rangle$ orientations favoring their alignment in the

direction of the applied field. In terms of Eqs. (3) and (4), the dc bias field will affect ε' mainly through (ii) and (iii), i.e., through the decrease in $N \cdot S$ and variation of $n_{\|}$, respectively. The decrease in the total area of polar regions boundaries in the dc field [see (ii)] should result in a decrease of the dielectric permittivity for any direction of the field with respect to the crystal axes. On the other hand, the redistribution of polar regions between the eight possible $\langle 111 \rangle$ orientations [see (iii)] should manifest itself differently for the different field directions. The ε_{100} is independent of the variation in $n_{\|}$, since in this case $\cos^2\theta$ is the same for all the eight possible $\langle 111 \rangle$ directions, Fig. 3. Thus, for the field applied along $\langle 100 \rangle$ direction of the crystal, the redistribution has no effect on the dielectric permittivity. However, ε_{111} does depend upon $n_{\|}$. The sign of the effect of the dc field on the dielectric permittivity through this dependence can be found from the following argument. In the absence of the field, $n_{\|}=1/4$, and therefore, the parentheses in Eq. (4) are equal to 1/3. In the limit of very strong field, $n_{\|}=1$ and consequently the parentheses are equal to 1, as well. This implies the increase in ε_{111} with increasing dc field through the reorientation of the polar regions (the possibility of nonmonotonical field dependence of ε_{111}, where the global growth does not necessarily imply a growth in the small field regime is considered as less probable).

All in all, if the field is applied along a $\langle 100 \rangle$ crystal axis, the dc bias must suppress the dielectric permittivity (thus, $\Delta\varepsilon'_{=}<0$), because only one factor [i.e., (ii)] controls the field dependence of ε'. However, for $\langle 111 \rangle$ direction two factors [(ii) and (iii)], showing opposite trends, are involved. Hence, in this case, both positive and negative signs of the nonlinear effect are possible, as well as the change of the sign of $\Delta\varepsilon'_{=}$ in different temperature intervals. As one can see, the experimentally observed behavior of the dc nonlinearity agrees with this scenario.

It is useful to indicate that the explanation of the difference between ac and dc field effects is valid for the situation where the reorientation of the polar regions is very slow, compared to the period of the time variation of the ac field. Thus, the ac field cannot reorient the polar regions, causing only vibration of their boundaries. However, this situation is quite realistic because the activation energies for ''vibration'' and ''reorientation'' processes can easily differ by a few orders of magnitude due to the difference of the volumes involved: compare the shift of the boundary on one unit cell with the volume of the polar region as a whole. That should result in a yet greater difference in the relaxation times related with both processes, which depend exponentially on the volume in which the polarization is reoriented.

In conclusion, we obtained the following qualitative picture of the nonlinear dielectric properties of PMN in the ergodic phase. The response to the ac field, at least in the studied range of amplitudes and frequencies, is only due to the motion of the interphase boundaries of elongated polar regions, the increase in the dielectric permittivity stemming from the their field induced depinning. On the other hand, the effect of dc bias field on the small-signal dielectric permittivity, is controlled by two mechanisms quite different from the one just mentioned: the dc bias redistributes the polar regions among eight $\langle 111 \rangle$ directions and diminishes the total area of their interfaces. In their turn, these two phenomena lead to the variation of the contribution of the polar regions boundaries to the permittivity. It is important to indicate that alternative scenario with thermally activated reorientation of the local spontaneous polarization in random-field environment, i.e., the case (b), is definitely inconsistent with the combined set of the data for the ac and dc nonlinear effects. The main reason is that in this framework, the same mechanism governs the ac and dc field effects. Thus, for the regime with weak frequency dispersion and small nonlinearity, a similar behavior of $\Delta\varepsilon'_{\sim}$ and $\Delta\varepsilon'_{=}$ can be expected, as was described by the phenomenological model discussed above. As we have seen, those predictions contradict the experimental data.

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