Crossover from Glassy to Inhomogeneous-Ferroelectric Nonlinear Dielectric Response in Relaxor Ferroelectrics

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The temperature dependence of the dielectric nonlinearities in a PMN single crystal and in 9/65/35 PLZT ceramics has been determined by measuring the first and third harmonic response as well as the dielectric behavior as a function of the dc electric field. In zero field a paraelectric-to-glass, and, in a high enough dc field, a glass-to-ferroelectriclike crossover in the temperature dependence of the nonlinear response have been observed. Both crossovers agree with the predictions of the spherical random-bond–random-field model. Relaxors thus undergo in zero field a transition to a spherical glass, while above the critical field a transition into a ferroelectric state occurs.

The nature of the diffuse phase transition in relaxor ferroelectrics, which are typically characterized by a broad frequency dispersion in the complex dielectric constant and slowing dynamics [1–3], has long been the subject of controversy [3–8]. Because of some contradictory experimental results, the basic question of whether the relaxor state in zero electric field is (i) a ferroelectric state broken up into nanodomains under the constraint of quenched random electric fields [5,8], or is (ii) a glass state similar to one in dipolar glasses with randomly interacting polar nanoregions in the presence of random fields [3,4,6,9,10] still remains open.

In a system with centrosymmetrical cubic symmetry the relation between polarization P and electric field E can be written as a power series $P = (\varepsilon_1 - 1)E - \varepsilon_3 E^3 + \dots$. This can be inverted into $E = a_1 P + a_3 P^3 + \dots$, where $a_1 = 1/(\varepsilon_1 - 1)$ and $a_3 = \varepsilon_3/(\varepsilon_1 - 1)^4 \approx \varepsilon_3/\varepsilon_1^4$. The temperature dependence of the dielectric nonlinearity a_3 may, in principle, provide an answer to the open question about the nature of the relaxor freezing process. The scaling theory of the second order phase transition predicts that the nonlinear dielectric coefficient a_3 should vanish at the ferroelectric transition [11], while it should diverge at the freezing transition in dipolar glasses [12], as indeed observed [13].

Very recently, it has been shown that the temperature dependence of the Edwards-Anderson order parameter q_{EA} and the dielectric nonlinearity a_3 in lead magnesium niobate (PMN) can be well described by the spherical random-bond–random-field (SRBRF) model [14,15]. Nonetheless, a controversy remains since the observed increase in a_3 with decreasing temperature is in disagreement with the results obtained by measuring the permittivity ε' as a function of a dc bias field E [16]. Namely, it has been argued [16] that the quantity $\hat{a}_3 = [\varepsilon'(E = 0) - \varepsilon'(E)]/3E^2 \varepsilon_S^4$, where ε_S is the static dielectric constant, is decreasing with decreasing temperature in the temperature range above the relaxor freezing transition temperature, ostensibly contrary to the predictions of the SRBRF model. Indeed, a mono-

tonic decreasing behavior of $\hat{a}_3$ would be more in agreement with the ferroelectric background picture of relaxors than with the glassy one.

It has been pointed out [9,10] that many of these seemingly contradictory interpretations could be due to the fact that the corresponding experimental results have been obtained in different regions of the E-T phase diagram [6,10]. Namely, by cooling the relaxor in an electric field higher than the critical field E_C a long-range ferroelectric phase is formed [17–20].

In order to resolve this controversy we have conducted high resolution measurements of the temperature dependence of the dielectric nonlinearities a_3 and $\hat{a}_3$ measured at various frequencies and dc electric bias fields in a broad temperature range.

In this Letter, we report experimental data on the dielectric nonlinearities obtained in lanthanum-modified lead zirconate titanate ceramics $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ with $x = 0.09$ and $y = 0.65$ (denoted as 9/65/35 PLZT) and in a PMN single crystal. We show that in agreement with some previous results [16], the static a_3, measured in zero bias electric field, as well as $\hat{a}_3$ are indeed gradually decreasing with decreasing temperature at higher temperatures. However, some 80 K above the freezing temperature T_f in PMN and ≈ 100 K above T_f in PLZT a crossover from the decreasing to an increasing temperature behavior occurs both in a_3 and in $\hat{a}_3$, as predicted by the static SRBRF model. Furthermore, a bias electric field $E > E_C$ induces another crossover from the glasslike increasing temperature dependence to the monotonously decreasing behavior above the transition temperature T_C, typical for an inhomogeneous ferroelectric state. It is shown that this crossover behavior can be well described by the recently introduced SRBRF model [14] of relaxor ferroelectrics.

The 0.52-mm-thick platelet of 9/65/35 PLZT hot pressed ceramics was covered with evaporated gold electrodes having surface dimensions of 4.7×3.5 mm^2. In the case of the PMN single crystal, where electrodes and dimensions were prepared similarly as in the PLZT

sample, the dielectric response was always measured perpendicular to the (001) plane. The first, ε_1, and third, ε_3, harmonic dielectric responses were measured simultaneously at several frequencies between 1 Hz and 10 kHz by using a HP35665A Dynamic Signal Analyzer. Simultaneous measurement of both harmonics greatly reduces noise in the subsequent computation of the ratio $a_3 = \varepsilon_3/\varepsilon_1^4$.

Prior to each measurement, the samples were annealed at 410 K for 1 h in order to ensure equal conditions for all measurements and to eliminate the effects of previous treatments. In the case of temperature scanning runs, the rates were typically ± 25 K/h.

In another run, the ratio $\hat{a}_3$ was measured by using the same experimental technique as described in Ref. [16]. Here, the complex dielectric constant ε^* was measured as a function of the dc bias electric field at a given temperature by using a HP4282 Precision LCR meter. The amplitude of the probing ac electric signal, applied to both 9/65/35 PLZT and PMN samples, was always smaller than 100 V/cm for all measuring frequencies.

The main difference in the measurements of a_3 and $\hat{a}_3$ is essentially lying in the path of approach toward the low-temperature phase. While a_3 is measured at a given dc bias electric field in a temperature scanning run, $\hat{a}_3$ is measured as a function of the dc bias electric field between 0 and 3 kV/cm at a given temperature, thus applying a rather more complicated field-temperature line of approach toward the low-temperature relaxor phase.

Figure 1a shows the dielectric nonlinearities a_3 and $\hat{a}_3$ obtained in the PMN single crystal as a function of temperature. The open circles in Fig. 1a represent a_3 obtained in zero bias electric field via measurements of the third harmonic response at 3ω at various measuring frequencies, while the open triangles show the a_3 data in a dc electric field $E_{dc} = 1.5$ kV/cm smaller than the critical field $E_C = 1.7$ kV/cm [6]. It should be noted that a_3 strongly increases as the temperature approaches the freezing temperature $T_f \approx 220$ K, where ergodicity is effectively broken due to the divergence of the longest relaxation time [9]. In the vicinity of T_f, however, the a_3 data in PMN (see the inset of Fig. 1a) as well as in PLZT (see Fig. 2) show a frequency dispersion, i.e., the static character of the response breaks down due to the strong increase of the relaxation times [21].

In Fig. 1a and in the inset of Fig. 2, data for both PMN and PLZT systems are presented solely in the static regime. In accordance with Ref. [16] it was found that at higher temperatures both quantities a_3 and $\hat{a}_3$ decrease with decreasing temperature. However, on further approaching the freezing temperature T_f both a_3 and $\hat{a}_3$ start to increase, thus showing a crossover from the decreasing "paraelectriclike" to the rapidly increasing "glasslike" temperature behavior.

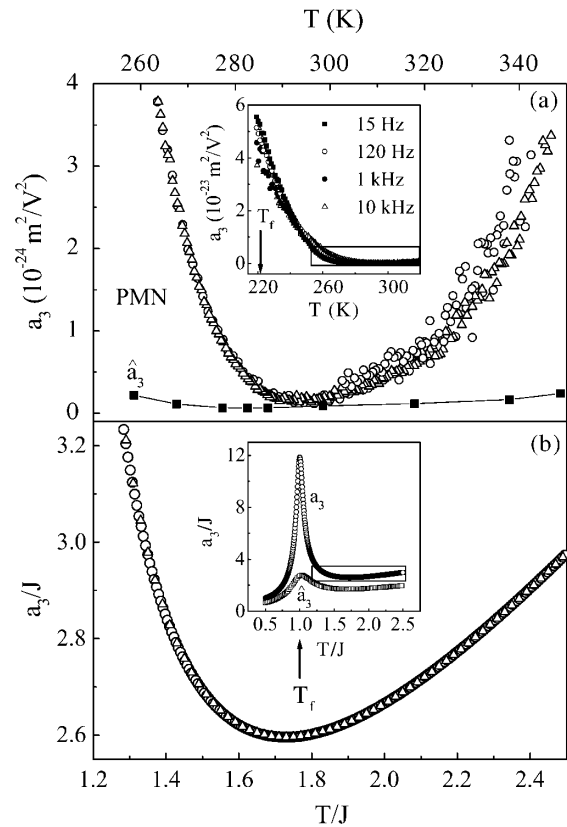Thus our dielectric nonlinearity data do not support the idea that relaxor systems undergo in zero electric field

FIG. 1. (a) The dielectric nonlinearities a_3 and $\hat{a}_3$ in a PMN single crystal as functions of the temperature in the range around the minimum as indicated by the box in the inset. Open circles and triangles show a_3 in $E_{dc} = 0$ and $E_{dc} = 1.5$ kV/cm $< E_C$, respectively. Solid squares show $\hat{a}_3$ data scanned in the range $0 < E_{dc} < 3$ kV/cm. Inset: a_3 obtained at various frequencies in zero dc bias field. (b) Temperature dependence of a_3 calculated from the SRBRF model using $\Delta/J^2 = 0.001$. Note that the results obtained for $E = 0$ (open circles) and $E = 0.85E_C$ (open triangles) overlap in this temperature interval, in agreement with the data in Fig. 1a. The inset shows the temperature dependence of a_3 and $\hat{a}_3$ calculated from the SRBRF model for $E = 2E_C$ and $\Delta/J^2 = 0.001$ on going through the freezing transition.

a transition to a ferroelectric state broken up into nanodomains under the constraint of quenched random electric fields. Rather, the observed temperature dependences of the dielectric nonlinearities show that a transition to a glassy state takes place.

The observed crossover behavior can be described by the SRBRF model based on the reorientable polar cluster picture [14,15]. The Hamiltonian is written in the form

$$H = -\frac{1}{2}\sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j - \sum_i \vec{h}_i \cdot \vec{S}_i - g\sum_i \vec{E} \cdot \vec{S}_i,$$

$$(1)$$

where $\vec{S}_i$ is a dimensionless order parameter field, related to the dipole moment of the ith polar cluster. Randomly frustrated bonds J_{ij} are characterized by the mean value of the coupling J_0/N and the variance J^2/N, and the random
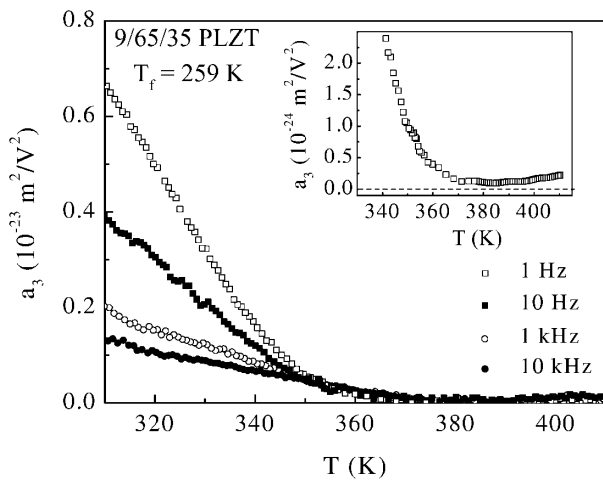
FIG. 2.   The temperature dependence of the dielectric nonlinearity a_3 obtained at various frequencies in zero dc bias field in 9/65/35 PLZT ceramics. The inset shows results obtained at the frequency of 1 Hz—averaged by the fast Fourier smoothing method—which demonstrate the occurrence of the same crossover from the decreasing to increasing temperature behavior, as found in the PMN single crystal.

fields $\vec{h}_i$ are characterized by the variance Δ. Finally, $\vec{E}$ is an applied electric field and g is an effective dipole moment corrected by the appropriate local field factor.

The calculation of the average free energy yields [15] that if $J_0 < \sqrt{J^2 + \Delta}$ a spherical glass without long-range order is formed, whereas a ferroelectric state becomes stable if $J_0 > \sqrt{J^2 + \Delta}$. The resulting equations for the spherical glass order parameter q and polarization P are

$$q = \beta^2 J^2 (q + \Delta/J^2)(1 - q)^2 + P^2, \qquad (2)$$

$$P = \beta(1 - q)(J_0 P + gE). \qquad (3)$$

Numerical solutions of Eqs. (2) and (3) yield $q(E, T)$ and $P(E, T)$, from which the derivatives $\varepsilon_1(E, T) = 1 + \partial P/\partial E$ and $\varepsilon_3(E, T) = -(1/6)\partial^3 P/\partial E^3$ can be obtained.

Figure 1b shows $a_3 = \varepsilon_3/\varepsilon_1^4$ (open circles) calculated as a function of temperature by using $J_0/J = 0.9$, $\Delta/J^2 = 0.001$, and $E = 0$, corresponding to the glass phase. The model also predicts the observed crossover from a decreasing to an increasing temperature behavior in a_3, which can be clearly seen in Fig. 1a. Moreover, in the temperature interval of the crossover regime the theoretical results calculated at $E = 0$ and $E = 0.85E_C$ overlap, in accordance with the experimental results of a_3 taken at $E_{dc} = 0$ kV/cm and 1.5 kV/cm (cf. Fig. 1a).

The inset of Fig. 1b shows a_3 calculated in a broader temperature interval. Note that the static a_3 exhibits a fairly sharp peak at the "freezing" temperature $T_f \simeq (\sqrt{J^2 + \Delta})/k$. This peak of the static a_3 is practically impossible to probe experimentally, because of the breakdown of the static response due to the slowing down of the relaxor dynamics, which appears typically just above the freezing transition [21].

The inset of Figure 1b also shows the theoretical temperature dependence of $\hat{a}_3 = [\varepsilon'(E = 0) - \varepsilon'(E)]/3E^2\varepsilon_S^4$, calculated using $E = 2E_C$ and $\Delta/J^2 = 0.001$. It should be noted that, with decreasing temperature, $\hat{a}_3$ also exhibits a crossover from the decreasing to the increasing behavior. However, in the whole temperature interval, $\hat{a}_3$ is smaller than a_3, and the increase of $\hat{a}_3$ when approaching the freezing transition is much less pronounced than in the case of a_3 due to the more rounded and suppressed peak at the freezing temperature. Such behavior is also in accordance with the experimental results presented in Fig. 1a; actually, it is the consequence of the applied dc bias electric field. By definition $\hat{a}_3$ cannot be associated with a pure zero-field relaxor state at $E = 0$, but should rather be viewed as a mean response over the relaxor-to-ferroelectric crossover region [22].

Furthermore, for $J_0 > \sqrt{J^2 + \Delta}$ and $E > E_C$ the model predicts the monotonously decreasing temperature dependence of a_3 on approaching the relaxor to inhomogeneous-ferroelectric transition temperature T_C [15,23]. As shown in Fig. 3, this has indeed been observed for 9/65/35 PLZT ceramics at $E = 8.5$ kV/cm $> E_C$. Here the a_3 data were calculated from the additional peaks in the temperature dependence of ε_1 and ε_3 at T_C, superimposed on the broad dielectric relaxor maximum, which was subsequently subtracted, as described in detail in Ref. [22]. The same a_3 behavior has also been found in a ferroelectric triglycine sulfate (TGS) monocrystal, as shown in the inset of Fig. 3.

To check why the ferroelectric state can be established in relaxors much more easily than in dipolar glasses, we tried
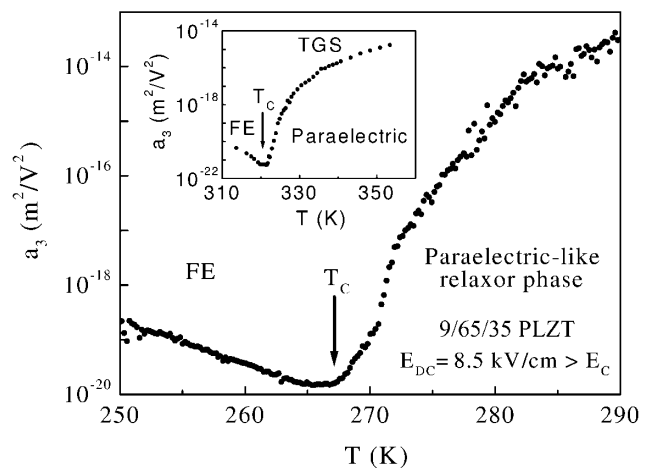

FIG. 3.   The temperature dependence of the dielectric nonlinearity a_3 measured at $E = 8.5$ kV/cm in 9/65/35 PLZT ceramics at 400 Hz in the vicinity of the relaxor to inhomogeneous-ferroelectric transition. Note the monotonous decrease of a_3 above the transition temperature T_C as predicted by the SRBRF model [14,15]. The same temperature behavior was also found in the ferroelectric TGS monocrystal, as shown in the inset.
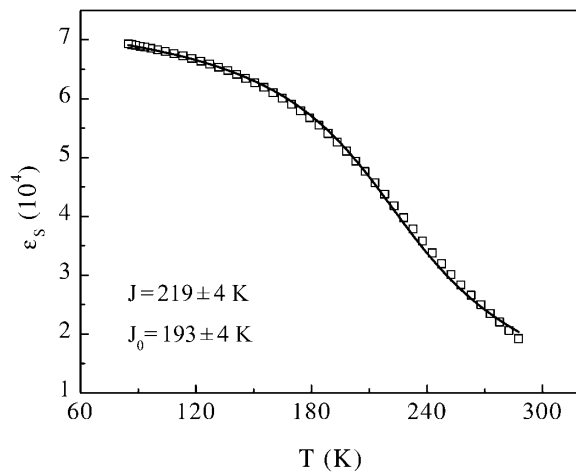
FIG. 4. Comparison between the experimentally obtained temperature dependence of the static dielectric constant ε_S in PMN (open squares) and the fit to the SRBRF model (solid line) for $J = 219 \pm 4$ K, $J_0 = 193 \pm 4$ K, and $\Delta/J^2 = 0.001$.

to fit the temperature dependence of the static dielectric constant ε_S of PMN by the SRBRF model. Figure 4 shows $\varepsilon_S(T)$ measured, as described in Ref. [9], together with a new fit to the SRBRF model. The fit [15] is rather good and shows that in zero bias field $J_0 = 193 \pm 4$ K is indeed smaller than, but rather close to, $J = 219 \pm 4$ K. It should be noted that recent data on the E-T phase diagram in PLZT ceramics [22] and on x-ray scattering in PMN [24] as well show that in zero dc bias field J_0 is very close to, but smaller than, J. Since $J_0 = J_0(E)$, the condition $J_0 > \sqrt{J^2 + \Delta^2}$ seems to be satisfied in relaxors in much lower bias fields than in dipolar glasses, where typically $J_0 \ll J$ [25].

In conclusion, high resolution measurements of the dielectric nonlinearities a_3 and $\hat{a}_3$ have been performed by using two different experimental techniques in order to resolve the controversy over their temperature behavior and thus to resolve the basic question about the nature of the zero-field relaxor state. A crossover from decreasing to increasing temperature behavior when approaching the freezing transition from above was observed in both a_3 and $\hat{a}_3$. Such behavior is in accordance with the recently proposed spherical random-bond–random-field model of relaxor ferroelectrics. In a high enough bias electric field another crossover from the glasslike-increasing to the ferroelectriclike-decreasing temperature behavior in a_3 has been found, which agrees with the predictions of the SRBRF model as well. The above results support the idea that, on cooling in zero electric field, relaxor ferroelectrics undergo a transition to a random-bond-driven glass state, while above the critical electric field E_C they undergo a transition into an inhomogeneous random-field-modulated ferroelectric state.

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