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Slow dynamics and ergodicity breaking in a lanthanum-modified lead zirconate titanate relaxor system

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The freezing of the dynamic process in a 9/65/35 lanthanum lead zirconate-titanate (PLZT) ceramics has been investigated by measurements of the frequency-dependent complex dielectric constant and the quasistatic field-cooled (FC) and zero-field-cooled (ZFC) dielectric susceptibilities. It was found that the aging process is responsible for the difference in temperature variations of the FC static dielectric constant and the static dielectric constant determined in the dynamic ZFC experiment. Analysis of the complex dielectric susceptibility by a temperature-frequency plot has revealed that for an aged PLZT sample the ergodicity is broken due to the divergence of the longest relaxation time in the vicinity of 249 K, i.e., the temperature where the ferroelectric phase can also be induced by applying sufficiently high electric field. However, the bulk of the distribution of relaxation times was found to remain finite even below the freezing temperature. It is shown that the behavior of the relaxation spectrum and the splitting between the field-cooled and zero-field-cooled dielectric constants in PLZT relaxor is qualitatively similar to what was observed in the lead magnesium niobate (PMN) relaxor and is reminiscent of the nonergodic behavior reported in various spin glasses. Moreover, the temperature dependence of the third order nonlinear susceptibility indicates a glassy rather than ferroelectric multidomain nature of the nonergodic relaxor state in both PMN and PLZT systems. [S0163-1829(99)01101-7]

I. INTRODUCTION

For certain compositions, lanthanum-modified lead zirconate titanate ceramics $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ (abbreviated as PLZT) belongs to relaxor ferroelectrics. These are characterized by a broad frequency dispersion in the complex dielectric constant, slowing dynamics, and a logarithmic polarization decay.[1–5] Although in these systems no transition is observed down to very low temperatures in zero electric field, a long-range ferroelectric order can be stabilized by applying an electric field above a certain threshold level,[6–9] thus effectively inducing a relaxor-to-ferroelectric transition.[10,5,11] For instance, Fig. 1 shows a schematic electric-field–temperature ($E-T$) phase diagram for the PLZT composition $x=0.09$, $y=0.65$ labeled as 9/65/35, which is probably the most studied PLZT composition. It can be seen that by cooling 9/65/35 PLZT ceramics in a dc electric field higher than $E_C \approx 5$ kV/cm a long-range ferroelectric phase is formed. The ferroelectric polarization was indeed observed through pyroelectric current[5] and hysteresis loop measurements.

Below the threshold field E_C, only a typical relaxor behavior could be observed and no transition anomaly was detected between 723 K and 90 K.[5] The nanodomain structure, which can typically be associated with relaxor behavior[10,12] was observed in x/65/35 PLZT ceramics by using transmission electron microscopy.[13]

In spite of intensive investigations, the mechanism responsible for the relaxor freezing process is not yet understood. Several earlier experimental results such as the slowing down of the characteristic relaxation time according to the Vogel-Fulcher law,[14] the observed critical behavior of the dielectric nonlinearity,[15,16] and the $E-T$ phase diagram[8] have favored the interpretation that at low values of external dc electric field the relaxor state may be a glassy state. In fact, it was suggested that relaxor systems could be considered as a dipolar glass based on the freezing of superparaelectric clusters.[17,18]

Contrary to this, various experiments[19,7,10,20] have later suggested that glassiness should be excluded in favor of a

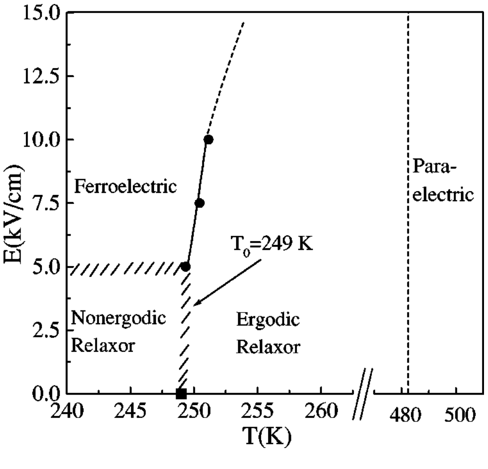

FIG. 1. Schematic electric-field–temperature ($E-T$) phase diagram. Data represented by solid circles were obtained from pyroelectric current measurements and dielectric susceptibility experiments (see Refs. 5,9), while the freezing transition represented by a solid box was determined from the temperature-frequency plot.

random field mechanism of freezing into a domain state on a nanometric length scale.[10] For example, measurements studying the dielectric response of lead magnesium niobate (PMN) ceramics in high ac and dc electric fields have shown that the observed dynamics in the ergodic phase may be explained as a domain-wall motion process.[21,22] However, it should be pointed out that random fields have been demonstrated to result in glassy states as well.[23,24]

Several more recent experiments point toward the existence of the qualitative equivalence between the nonergodic relaxor state and the dipolar glass state. Specifically, investigations of PLZT ceramics by micro-Raman scattering have shown that for lanthanum contents above $x=0.08$ in rhombohedral compositions x/65/35, the relaxor behavior is associated with the observation of second order Raman selection rules down to very low temperatures which is, in turn, in agreement with the glassy character of the low temperature relaxor state.[12] In addition, recent investigations of the linear and the third-order nonlinear dielectric response in the PMN relaxor[25] have shown that ergodicity is effectively broken due to the divergence of the longest relaxation time. Also, it has been shown that the splitting between the quasistatic FC-ZFC susceptibilities occurs in that system. Furthermore, it has been demonstrated that in both rhombohedral 9/65/35 PLZT ceramics and in the PMN system the third order nonlinear dielectric constant behaves in a way similar as expected of a typical orientational glass system.[16,25]

It seems, however, that many of these rather contradictory interpretations are actually due to experimental results being obtained in much different bias electric field regimes, i.e., different regions of the $E-T$ phase diagram. Clearly, this calls for a set of experiments in a low field region of the $E-T$ phase diagram in order to provide an insight into the nature of the nonergodic relaxor state.

It has been known for some time that the temperature behavior of the relaxation spectrum in dipolar glasses undergoes a dramatic change in shape and width on cooling the system toward the freezing transition.[26,27] While similar behavior was found to exist in the PMN relaxor,[25] only a few attempts were made to address the question of slowing dynamics in PLZT ceramics, which is probably the least studied among relaxor systems. So far, the width of the distribution of relaxation times and the average relaxation time were estimated from frequency dependent linear dielectric susceptibility data in 9/65/35 PLZT ceramics.[4] It was found that rather far away from the temperature of the field induced relaxor-to-ferroelectric transition, i.e., in the temperature range from 360 K to 480 K the average relaxation time follows the nondivergent Arrhenius law.

Later, the analysis of the third order nonlinear dielectric susceptibility has shown that the typical relaxation time of the nonlinear dynamics is governed by divergent Vogel-Fulcher law[16] with the freezing temperature close to the temperature of the field induced relaxor-to-ferroelectric transition. It should be mentioned that similar behavior in third order nonlinear dielectric constant was recently reported to exist in the PMN relaxor.[25]

The observation of the splitting between the field-cooled susceptibility χ_{FC} and the zero-field-cooled susceptibility χ_{ZFC} in both the PMN crystal and 8/65/35 PLZT ceramics[25,28] provides additional indication of nonergodic behavior similar to the one observed in many glassy systems,[29] including dipolar[30] and quadrupolar glasses.[32] It should be noted, however, that the FC-ZFC experiment depends strongly on the experimental time scale and on various history effects such as aging, which is a particularly strong effect in the PLZT relaxor. These similarities lead to the question whether ergodicity breaking takes place also in 9/65/35 PLZT ceramics in zero bias electric field as reported for PMN single crystal system. Some hints at such a phenomenon were already observed from the saturation of the Raman intensity below the freezing temperature.[5] A confirming answer would strengthen the idea that the slowing dynamics and subsequently broken ergodicity (empirically similar to that observed in dipolar glasses) places these two chemically and structurally different relaxor systems in the same category.

In this work we present experimental results, which indicate a specific glasslike freezing process in 9/65/35 PLZT similar to the one observed in the PMN system and dipolar glasses. Quantitative results have been obtained by studying the quasistatic and frequency-dependent dielectric responses in the zero-limit of the external dc electric field in order to ensure that no relaxor-to-ferroelectric transition is induced in the PLZT system. In order to keep the dielectric data analysis free of any model, a method of dielectric data representation via the temperature-frequency plot[26] was adopted. Additionally, pyroelectric current determinations at zero field have been made, which confirm the above mentioned analysis.

The experimental procedures are briefly outlined in Sec. II. The results and the analysis of the dielectric response are given in Sec. III. A discussion of the results is given in Sec. IV.

II. EXPERIMENTAL PROCEDURES

The platelet-shaped sample of $1.9\times4\times5\ \mathrm{mm}^3$ was cut and polished from a block of 9/65/35 hot pressed PLZT ceramics previously used in Raman studies.[5] The golden electrodes were applied by evaporation technique.

The frequency-dependent complex dielectric constant $\varepsilon^*(\omega,T)=\varepsilon'-i\varepsilon''$ was measured between 79 and 415 K and in the frequency range from 0.01 Hz to 1 MHz. The frequency range was covered by two different techniques: (a) low frequency measurements from 0.01 Hz to 1 kHz were carried out by using a Schlumberger 1250 Impedance Meter. (b) The measurements in the frequency range from 20 Hz to 1 MHz were performed by the HP4282 Precision LCR Meter. The amplitude of the probing ac electric signal was 5 V/cm for all measuring frequencies.

It was found that the history-dependent effects (including aging) play an important role in the PLZT relaxor.[31] Specifically, Fig. 2 shows the dielectric constant measured at two different frequencies at given fixed temperature as a function of waiting time as described below. It is obvious that the aging effect can strongly influence the temperature dependence of the dielectric data taken within first few hours after the annealing. However, for waiting times longer than one day, changes in the dielectric constant due to aging become negligible within the experimental window of a few hours. No significant aging effect was detected in dc field experiments (see Sec. III A).

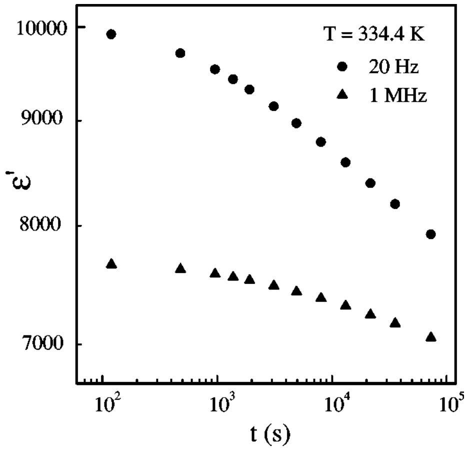

FIG. 2. Aging effect on the real part of the complex dielectric constant taken at two different frequencies represented in a log-log plot.

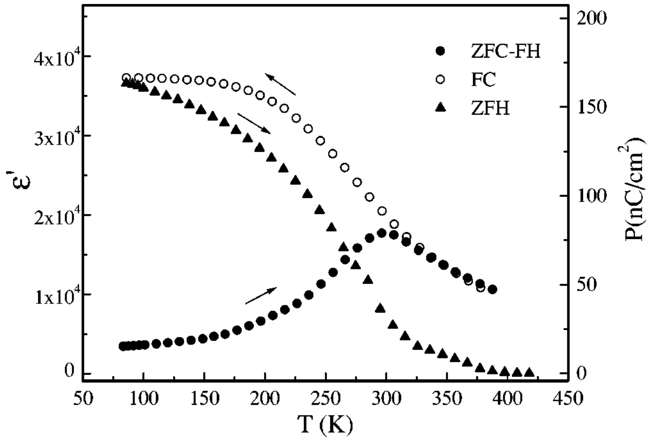

FIG. 3. Temperature dependence of the field-cooled (○) and zero-field-cooled–field-heat (●) quasistatic dielectric constant ε' of 9/65/35 PLZT ceramics. Also shown is remanent polarization P_r (solid triangle) obtained in a heating run.

Due to this important effect, special attention was paid to the way the low temperature relaxor phase was reached. The frequency dependent dielectric constant was measured in two different runs. In both runs the sample was first annealed at 415 K for one hour, then in the first cooling run the data were taken immediately after annealing. In this case, the dynamics of the sample within the initially rapid aging regime was studied. In the second run the sample was first cooled down to 345 K, i.e., in the vicinity of the broad dielectric constant maximum. There the temperature was stabilized and the sample was aged for one day. In this way the aging effect was reduced so that it did not interfere anymore with regular dielectric dynamics. The dielectric constant was always determined on cooling the system with the same cooling rate of -1 K/min.

The temperature variations of the field-cooled, $P_{\rm FC}$, and zero-field-cooled, $P_{\rm ZFC}$, quasistatic dielectric polarization were measured between 80 and 425 K by using the corresponding method as described in Ref. 30. The zero-field-cooled dielectric constant $\varepsilon_{\rm ZFC}=\lim_{E\rightarrow 0}P_{\rm ZFC}(E,T)/\varepsilon_0 E$ was determined by cooling an annealed sample down to 80 K in zero field $E=0$. There an external electric field of $E=50$ V/cm was applied and the sample was slowly heated (1 K/min) up to 400 K while the corresponding polarization charge was measured by the Keithley 617 programmable electrometer. At temperature $T=400$ K the scanning rate was reversed (-1 K/min) and the field-cooled dielectric constant $\varepsilon_{\rm FC}=\lim_{E\rightarrow 0}P_{\rm FC}(E,T)/\varepsilon_0 E$ was measured by cooling the system down to 80 K in the same external electric field $E=50$ V/cm. After the electric field E was switched off at 80 K, a long-living remanent polarization P_R was observed and monitored on heating (1 K/min) the sample in zero field again up to 425 K. In the second run, both $\varepsilon_{\rm FC}$ and P_R were also measured by applying a ten times smaller electric field $E=5$ V/cm.

The original third order nonlinear susceptibility data which will be analyzed in the last section have been published together with the corresponding measuring methods in Refs. 16 and 25 for 9/65/35 PLZT ceramics and for the PMN single crystal, respectively.

Pyroelectric current measurements were performed in a zero field heating (after zero field cooling) run at a heating rate of 1 K/min using the same Keithley electrometer.

The temperature of the samples was stabilized and monitored to within ± 0.01 K in the temperature range from 80 to 425 K by using a lock-in bridge technique with a platinum resistor PT100 as thermometer.

III. RESULTS AND ANALYSIS

This section gives a description of the results obtained in FC/ZFC quasistatic and spectroscopic dielectric experiments and their analysis.

A. FC and ZFC dielectric susceptibility

Quasistatic measurements of the splitting between FC and ZFC susceptibilities is one of the fundamental experiments to probe the onset of nonergodic behavior in the material under investigation.[29] The results obtained on 9/65/35 PLZT ceramics are shown in Fig. 3 and are very similar to those obtained on the 8/65/35 PLZT sample[28] and PMN relaxor.[25] They provide a strong indication that the nature of the low temperature state is qualitatively similar to the one reported in various orientational glasses,[30,32] where the observed splitting between field-cooled (○) and zero-field-cooled (●) dielectric constants indicates the onset of ergodicity breaking. It should be mentioned, however, that in contrast to the above data and the data taken on the PMN system, which were obtained in low-field limit in order to stay away from the relaxor-to-ferroelectric transition line, the FC/ZFC data obtained on 8/65/35 PLZT ceramics were obtained in rather high dc bias fields (3–5 kV/cm), thus moving the system into the vicinity of the transition line.

It should be stressed that an estimate of the freezing temperature T_f, i.e., the temperature where the splitting between $\varepsilon_{\rm FC}$ and $\varepsilon_{\rm ZFC}$ should occur is not a true static quantity, but depends strongly on the experimental time scale in the zero-field-cooling experiment,[30,26] which was in our case $t_{\rm expt}\approx 300$ s. In principle, the limit $T_f(t_{\rm expt}\rightarrow\infty)$ should provide the temperature of static ergodicity breaking, however, an

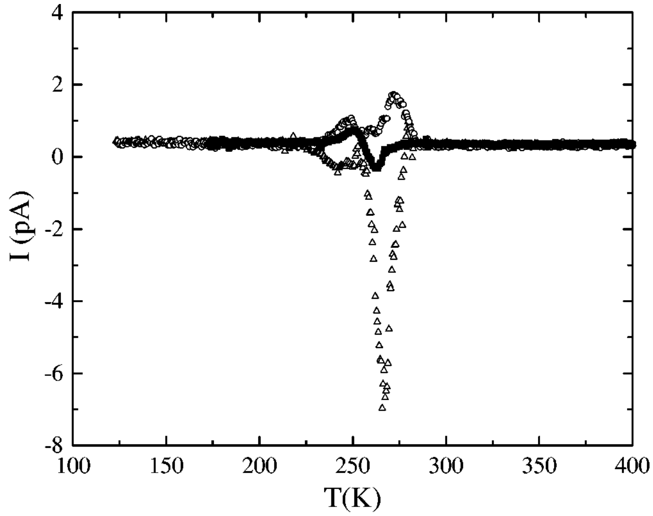

FIG. 4. Pyroelectric current I obtained in a zero field heating run after zero field cooling experiments. Note randomness in pyroelectric current peaks.

experiment of this kind is very time consuming and the results thus obtained would suffer from a rather high level of noise.

A frozen remanent polarization P_R is observed after the external field in FC experiment is removed. The small gap between $\varepsilon_{\mathrm{FC}}$ and P_R curves in Fig. 3 is due to the very fast high-frequency dielectric response and can in principle provide an independent estimate of ε_∞.

At temperatures below 100 K, P_R was found to be time independent on time scales longer than several hours. On heating the sample, P_R was decreasing with increasing temperature and the slow relaxation was observed at temperatures above 150 K. Qualitatively, this is in agreement with the previously reported observation of a long-living relaxing electric polarization created by cooling down 8/65/35 PLZT ceramics[28] and PMN sample in the low-field regime.[25] The temperature of the inflection point of the $P_R(T)$ plot is 250 K, i.e., it coincides with the already determined freezing temperature in 9/65/35 PLZT (see Fig. 1 and Ref. 5).

Another hint at ergodicity breaking is provided by the zero field cooling weak pyroelectric current peaks which appear in the vicinity of the freezing temperature T_f on heating (Fig. 4). Their sign and amplitude are at random, and differ from one run to another. This reflects the nonreproducibility of the low temperature ground state, as expected for a nonergodic system.

B. Complex dielectric constant

The frequency-dependent complex dielectric constant can provide a direct information on the dynamic processes occurring in PLZT relaxor.

Figure 5 shows a set of dielectric data taken at several temperatures in a Cole-Cole diagram. Analogous to the PMN system[25] and to other dipolar glassy systems,[29,27] 9/65/35 PLZT ceramics exhibits pronounced dispersion in the dielectric constant, i.e., the Cole-Cole plots start to deviate from the ideal monodispersive or Debye semicircles at temperatures below 350 K. With decreasing temperature, the relaxation becomes extremely polydispersive, in fact much more than it was observed in PMN or some dipolar glasses.[27] As shown in Fig. 6, it manifests itself in a rather small and very flat, i.e., almost frequency independent imaginary part of the complex dielectric constant. This, in turn, leads at low temperatures to the very strongly suppressed Cole-Cole plots.[1,33,34]

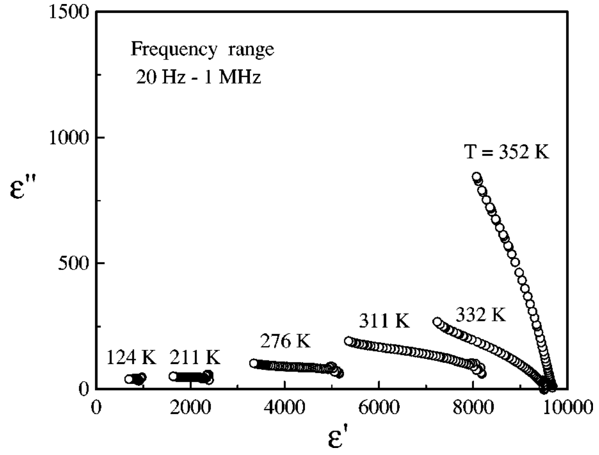

FIG. 5. Measured values of ε'' plotted vs ε' in an unaged 9/65/35 PLZT ceramics at five temperatures.

The standard analysis of Cole-Cole plots could in principle provide information about the temperature variations of important parameters such as the static dielectric constant ε_s, the dielectric constant at very high frequencies ε_∞, and the characteristic relaxation time τ. However, these results would strongly depend on the choice of the distribution of relaxation times $g(\ln \tau)$, i.e., some prior knowledge is required about the shape of the relaxation spectrum. This means that Cole-Cole plots cannot provide direct and independent information about the actual relaxation spectrum under investigation.[26,27] In addition, the rapidly increasing polydispersivity of the relaxation that cannot be completely covered even by an eight decades wide range of frequencies at any temperature, makes the above analysis practically impossible.

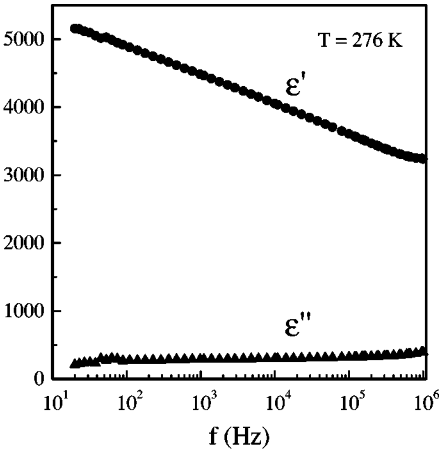

FIG. 6. Frequency dependence of the real and imaginary parts of the complex dielectric constant at given temperature. Note the very suppressed and almost flat imaginary dielectric constant, which indicates very broad distribution of relaxation times.

C. Temperature-frequency plot

In this method, which was recently successfully applied to various glassy and relaxor systems,[26,27,35–37,25] the special representation of the real part of the dielectric constant in the so-called temperature-frequency plot[26] allows a direct extraction of the information on the behavior of the relaxation spectrum.

Since an extensive description of this method was already given in Refs. 26 and 27, we will keep focus on its results after some basic definitions. Here a natural assumption is made that the distribution of relaxation times $g(z)$ is limited by the lower and upper cutoffs z_1 and z_2, respectively, where $z_i = \ln(\omega_a \tau_i)$ with ω_a as an arbitrary unit frequency. By being varied between the values 1 and 0, a reduced dielectric constant[26]

$$\delta \equiv \frac{\varepsilon'(\omega,T)-\varepsilon_\infty}{\varepsilon_s-\varepsilon_\infty} = \int_{z_1}^{z_2} \frac{g(z)\,dz}{1+(\omega/\omega_a)^2\exp(2z)}, \qquad (1)$$

is probing various segments of the relaxation spectrum. Here, by scanning the δ, the filter in the second part of Eq. (1) is actually probing the distribution of relaxation times $g(z)$ by shifting its position in ω space.[27] In practice, this is achieved by finding within the set of the dielectric data at given temperature T a frequency $\omega = 2\pi f$ at which the prescribed value of δ is reached.

Obviously, a prior knowledge about the temperature behavior of the two required parameters ε_s and ε_∞ is needed. The high frequency dielectric constant ε_∞ was found to be negligible small in comparison to the large static dielectric constant ε_s. As already mentioned and shown in Fig. 2, the static dielectric constant ε_s, which itself is required in this method, was found to be strongly affected by the aging process during a ZFC ac dielectric measurement run. Specifically, during the first few hours of cooling the sample down from the annealing temperature, ε_s was gradually reducing its value by as much as 20%, regardless of the rate of cooling. Due to this effect, the static limit of the ac dielectric data differs from the quasistatic value of the independently measured FC dielectric susceptibility, contrary to what was observed in PMN system, in which the aging effect was negligibly small.[25] As a consequence, the static value of the dielectric constant becomes uncertain at lower temperatures.

In order to avoid this problem, the dielectric dispersion was analyzed only in the sample, which was first aged for the period of one day. In this way, the aging effect was slowed down so that it did not interfere any more with the slow regular dielectric dynamics. As shown in Fig. 7, it was found that the Cole-Cole extracted static dielectric constant ε_s of the sample aged for one day was temperature independent in the whole temperature range, where ε_s could be determined. Thus one may conclude that the static dielectric constant remains constant down to very low temperatures.

A characteristic temperature-frequency profile for each fixed value of the reduced dielectric constant δ represented in the (T,f) plane is shown in Fig. 8. As pointed out in Refs. 26 and 27, the temperature dependence of the relaxation cutoffs $z_1(T)$ and $z_2(T)$ can be deduced from Fig. 8 without any model-based assumptions about the relaxation spectrum.

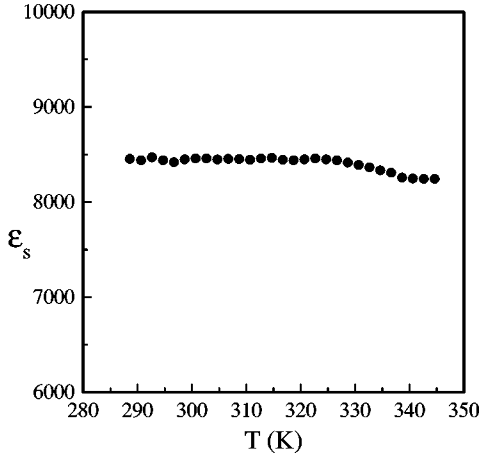

FIG. 7. Temperature dependence of the static dielectric constant obtained on the 9/65/35 PLZT sample after being aged for one day. The static dielectric constant remains temperature independent in an experiment in which the dielectric dispersion is measured immediately after each change of temperature.

In particular, the straight lines for low values of δ in Fig. 8 suggest a linear relationship between z_1 and $1/T$, which implies an activated or Arrhenius-type behavior $\tau_1 = \tau_{01}\exp(E/T)$ for the shortest relaxation time. Further, bent curves for δ close to 1 indicate a divergent behavior of $\tau_2(T)$ that can be effectively described by a Vogel-Fulcher law,

$$\tau_2 = \tau_{02}\exp[U/(T-T_0)]. \qquad (2)$$

It is interesting to mention that the same asymmetric behavior of the relaxation spectrum was very recently reported for PMN relaxor.[25] The parameters τ_{01}, τ_{02}, E, U, and T_0 were extracted by fitting each curve in Fig. 8 separately to the generic Vogel-Fulcher ansatz given by Eq. (2) and extrapolating the set of fitting parameters thus obtained towards $\delta = 1$ and $\delta = 0$. The solid lines in Fig. 8 are results of the above fitting procedure with the following fitting parameters: $T_0 = 249 \pm 4$ K, $f_{01} = 1/2\pi\tau_{01} = 3.8\times 10^{14}$ Hz, $f_{02} = 1/2\pi\tau_{02} = 7.2\times 10^{10}$ Hz, $E = 200 \pm 150$ K, and $U = 1400 \pm 100$ K. It is worth mentioning that up to this point no model for $g(z)$ was needed, therefore making the (T,f)

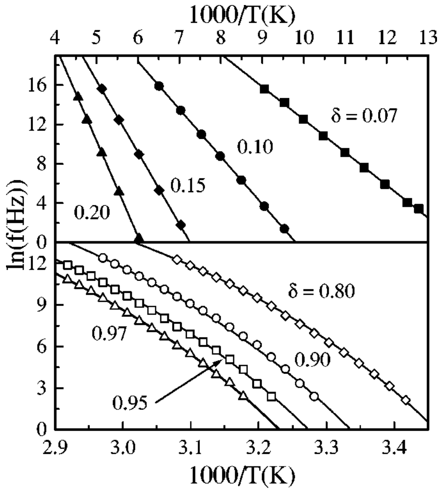

FIG. 8. Temperature-frequency plots for several fixed values of the reduced dielectric constant δ. Solid lines are fits obtained with a generic Vogel-Fulcher expression.

analysis completely free of any prior assumptions about the shape of the relaxation spectrum. In addition, the analysis of τ_2 was performed only in the temperature range where the static dielectric constant ε_s was exactly known.

The value for T_0 thus obtained is in fact very close to the previously reported Vogel-Fulcher temperature determined from the third order nonlinear dielectric data[16] and to the freezing temperature indicated by Raman scattering experiments.[5] Moreover, within the experimental error T_0 is equal to the temperature at which the relaxor-to-ferroelectric transition could be induced by applying a sufficiently high electric field.[5]

IV. DISCUSSION

The above results clearly indicate that the low temperature state in 9/65/35 PLZT ceramics possesses a number of empirical properties, which are characteristic for dipolar glasses.

In particular, the existence of the splitting between the FC and ZFC static linear dielectric susceptibilities observed on a quasistatic experimental time scale in both 9/65/35 PLZT ceramics and the PMN crystal, indicates the onset of broken ergodicity below some apparent freezing temperature T_f. The same behavior together with a long-living remanent polarization P_R was previously found in various orientational glasses.[30,32] In addition to this, an asymmetric broadening of the relaxation spectrum and the divergence of the maximum relaxation time in both 9/65/35 PLZT ceramics and the PMN relaxor is analogous to the behavior reported in several glassy systems.[26,27,35,37] Here, the divergence of the longest relaxation time implies a transition from the ergodic into a nonergodic relaxor state at the Vogel-Fulcher temperature T_0, which, in turn, can be identified as the freezing temperature T_f.

Nevertheless, while the longest relaxation time diverges the bulk of the relaxation spectrum remains active even below the Vogel-Fulcher temperature T_0 as clearly shown in Fig. 5. This behavior is in agreement with the observation of the slow polarization decay far below the freezing temperature and with previously reported behavior in PMN crystal[25] and $\mathrm{Rb}_{1-x}(\mathrm{ND}_4)_x\mathrm{D}_2\mathrm{PO}_4$ deuteron glass system.[26,27] Furthermore, the rather small activation energy of the high frequency limit of the relaxation spectrum obtained in 9/65/35 PLZT ceramics has—within the experimental error—the same order of magnitude as reported in PMN relaxor. It should be noted, however, that the existence of an ''unfrozen'' part of the relaxation spectrum is qualitatively in accordance with the predictions of the theory of hierarchically constrained dynamics.[38,39] For the linear ansatz $g(z)=2(z-z_1)/(z_2-z_1)^2$,[26] the width of the relaxation spectrum $\Delta z=z_1-z_2=2(\varepsilon_s-\varepsilon_\infty)(1-\delta)^{1/2}/\varepsilon''$ can be deduced from the result of the integral evaluation for ε^* [cf. Eq. (2) of Ref. 27] with the assumption that $\Delta z \gg 1$. The width of the unfrozen relaxation spectrum (estimated by using the above ansatz) continuously grows with decreasing temperature. It soon exceeds one hundred decades, thus demonstrating that a large part of the material is effectively frozen (see Fig. 9 for details).

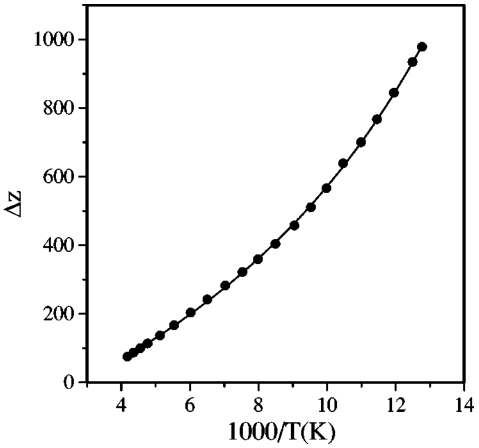

FIG. 9. Temperature dependence of the effective width Δz of the relaxation spectrum, which remains active even below the temperature at which the maximum relaxation time diverges, i.e., ergodicity is broken. Here, ε_s was assumed to remain temperature independent even at low temperatures as suggested by the behavior shown in Fig. 7.

These results qualitatively agree with the results recently reported on PMN relaxor[25] and with Raman scattering results that were already indicating glasslike freezing in 9/65/35 PLZT ceramics.[5,12] Moreover, the relaxor dynamics behavior empirically agree with the behavior reported on some dipolar glasses.[26,35]

The significance of the third order nonlinear susceptibility χ_3 in characterizing orientational glasses was discussed in various theoretical and experimental works.[40,35] Recently, it was suggested that χ_3 should be considered as a dynamic quantity in these systems.[40] Within the Ising random-bond random-field model it was shown that the quasistatic limit of a dynamic χ_3 reflects the critical behavior of the glass order parameter and therefore should diverge in the vicinity of the Almeida-Thouless line, i.e., the freezing temperature T_f.

Indeed, such behavior was very recently confirmed to exists in betaine deuteron glass system D-BP:BPI (40:60).[35] Furthermore, it was shown in both 9/65/35 PLZT ceramics[16] and PMN relaxor[25] that the third order nonlinear dielectric constant behaves in a way similar as expected for a typical orientational glass system. Specifically, in both systems χ_3 was found to be a dynamic quantity reflecting the slowing dynamics similar to the dynamic behavior in linear dielectric constant.[25,16] With decreasing temperature, the quasistatic limit of χ_3 was found to increase in both relaxors more rapidly than the linear susceptibility. For various reasons, a critical analysis of this quantity was not possible in the PMN relaxor[25] thus preventing a characterization of the critical behavior. However, at least a qualitative approach is possible.

In a system with average cubic symmetry and $n=3$ components of the order parameter, the relation between the polarization $\vec{P}$ and electric field $\vec{E}$ can be written as a power series $P_1=\chi_1E_1-\chi_{12}E_1(E_2^2+E_3^2)-\chi_3E_1^3+\cdots$. This can be inverted to give the equation of state

$$E_1=a_1P_1+a_{12}P_1(P_2^2+P_3^2)+a_3P_1^3+\cdots, \tag{3}$$

where $a_1=1/\chi_1$, $a_{12}=\chi_{12}/\chi_1^4$, and $a_3=\chi_3/\chi_1^4$.

To characterize the nonlinear dielectric response let us consider the temperature dependence of the coefficients a_3

and a_{12}. Specifically, for a ferroelectric (FE) system the scaling theory of second order phase transitions gives[41]

$$a_3^{FE} \propto (T-T_c)^{\gamma-2\beta}, \tag{4}$$

where γ is defined by $\chi_1 \propto (T-T_c)^{-\gamma}$ and β is the order-parameter critical exponent. It should be noted that in general $\gamma-2\beta>0$ for cubic systems at spatial dimensionality d=3, and hence the coefficient a_3^{FE} should vanish at T_c.

In a spin glass (SG) or dipolar glass (DG), however, χ_3 behaves according to[42,35]

$$\chi_3 \propto (T-T_f)^{-\gamma_3} \tag{5}$$

with $\gamma_3>0$, whereas χ_1 remains finite at T_f. Thus,

$$a_3^{SG} = \frac{\chi_3}{\chi_1^4} \propto (T-T_f)^{-\gamma_3}, \tag{6}$$

i.e., the third order coefficient diverges at the freezing transition. An analogous analysis can be made for the coefficient a_{12}.

As shown in Fig. 10, the ratio χ_3/χ_1^4 in both 9/65/35 PLZT and PMN relaxor increases sharply on approaching the freezing transition and thus its behavior is consistent with the one expected of a glassy rather than pure ferroelectric system. Moreover, the data obtained in 9/65/35 PLZT relaxor can be reasonably well fitted to the above SG ansatz with $\gamma_3=1$, which is the value expected from a mean-field theory of dipolar glasses[40] and with $T_f=253$ K, which is very close to the value $T_0=249$ K obtained from the temperature-frequency plot. Although, as discussed in Ref. 25, no critical fits of χ_3 data in PMN were possible in a strict statistical sense, it is obvious from Fig. 10 that the temperature behavior of χ_3/χ_1^4 is qualitatively closer to the glassy than the ferroelectric case.[43] It should be stressed again that the above results were obtained in zero bias field limit far below the threshold field, above which the ferroelectric microdomain multistate is observed.[12,8]

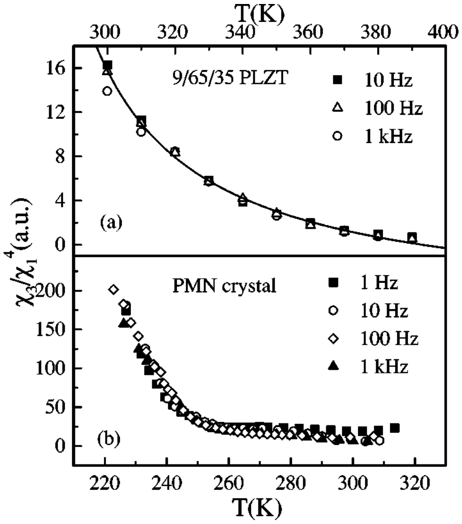

FIG. 10. Temperature dependences of the χ_3/χ_1^4 for (a) 9/65/35 PLZT ceramics and (b) PMN single crystal. Solid line through 9/65/35 PLZT data is a tentative fit with critical exponent $\gamma_3=1$.

In summary, the investigation of the linear and the third-order nonlinear dielectric response in zero electric field shows the onset of nonergodic behavior in the 9/65/35 PLZT ceramics. In the same way as in PMN single crystal the divergence of the longest relaxation time in the distribution of relaxation times effectively breaks ergodicity. The glassy dynamics together with the splitting between the quasistatic FC-ZFC susceptibilities and the critical behavior of χ_3/χ_1^4 demonstrate that the nonergodic state can be at least empirically described as a dipolar glass state.

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