Glassy freezing in relaxor ferroelectric lead magnesium niobate

Adrijan Levstik, Zdravko Kutnjak, Cene Filipič, and Raša Pirc
Jožef Stefan Institute, P.O. Box 3000, 1001 Ljubljana, Slovenia
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The freezing process in lead magnesium niobate (PMN) has been investigated by measurements of the frequency-dependent complex dielectric constant and its third harmonic component. The linear complex dielectric susceptibility was analyzed by a temperature-frequency plot in order to determine the temperature dependence of the dielectric relaxation spectrum and to identify the freezing temperature. It was found that both the shape of the relaxation spectrum and its temperature behavior in the PMN relaxor show remarkable similarities to dipolar glasses, i.e., the longest relaxation time diverges according to the Vogel-Fulcher law, while the bulk of the distribution of relaxation times remains finite even below the freezing temperature. The frequency and the temperature dependence of the third harmonic susceptibility, similar to the behavior observed in linear dielectric response, indicate that the same underlying relaxation spectrum and therefore the same slowing-down mechanism is controlling both linear and nonlinear dynamic response. The observed splitting between the field-cooled and zero-field-cooled dielectric constant—comparable to the one obtained in spin glasses—effectively demonstrates the occurrence of typical glassy nonergodic behavior in the vicinity of the transition temperature where the ferroelectric phase would appear above a threshold electric field. [S0163-1829(98)05718-X]

I. INTRODUCTION

Lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (abbreviated as PMN) is considered as a typical representative of ferroelectrics with diffuse phase transitions known as relaxor ferroelectrics. These are characterized by a broad frequency dispersion in the complex dielectric constant, slowing dynamics, and logarithmic polarization decay.[1,2]

Recently established electric-field–temperature (E-T) phase diagram[3,4] shows that by cooling PMN in a dc electric field higher than $E_C \approx 1.7$ kV/cm, a long-range ferroelectric phase is formed. Both ferroelectric hysteresis[5] and nanodomain structure[6] were observed in the PMN relaxor. Also, it was shown[7,16,19] that for values of the static external electric field below E_C, PMN undergoes a transition in the vicinity of $T_f = 220$ K into a nonergodic state without long-range ferroelectric order, which is similar to the dipolar glass state.[3,8,9]

In spite of intensive investigations, the mechanism responsible for the freezing process is not yet understood. For instance, it is well known that PMN shows a broad peak in the real part of the temperature-dependent dielectric constant, which grows and shifts to lower temperatures with decreasing frequency.[1] Dielectric permittivities of various dipolar glasses show similar behavior.[10] In addition, the slowing down of the characteristic relaxation time according to the Vogel-Fulcher law,[8] the observed critical behavior of dielectric nonlinearity,[9] and the E-T phase diagram seem to indicate that at low values of external dc electric-field PMN is a glasslike system.

While it is known that the relaxation spectrum in dipolar glasses undergoes a dramatic change in shape and width on cooling the system toward the freezing transition, only few attempts were made to address this question in case of the PMN relaxor. So far, the width of the distribution of relaxation times was indirectly estimated from a master plot.[9,3] In another turn, the assumption of asymmetric widening of the relaxation spectrum with decreasing temperature—based on the dielectric data obtained in rather narrow range of frequencies over five decades only—was made some time ago.[7] In contrast, another description of the relaxation spectrum—based on a symmetric Fröhlich ansatz—was very recently given in Ref. 11. However, a quantitative description of the temperature dependence of this important dynamic quantity based on a direct measurement has not yet been formulated.

It should be mentioned that the actual temperature dependence of the characteristic relaxation time itself is not yet firmly established. Previous works—based on a Vogel-Fulcher-type analysis of dielectric data, again obtained in rather narrow range of frequencies—suggest various possibilities including a simple Arrhenius behavior with deviations observed at low and high temperatures,[9,3] a more complicated Vogel-Fulcher law,[8] and the recently introduced ''power-modified'' Arrhenius ansatz.[12,11] The situation regarding the relaxation in PMN got even more confused by the discovery of two relaxation modes in the PMN ceramics.[13]

Furthermore, it was shown recently[14] that the widely accepted Vogel-Fulcher analysis of temperature shifts of ε' and ε'' peaks with changing frequency does not necessarily imply freezing, i.e., deviations from an Arrhenius behavior of the characteristic relaxation time could arise solely from the temperature variations in dielectric intensity and changes in the shape of the relaxation spectrum even in the case that the relaxation time behaves nondivergently according to the Arrhenius law. The above problem clearly calls for a different approach in dielectric data analysis than was used so far in the case of the PMN and some other relaxor systems. In addition, reports[9,3] of an activated temperature dependence of the relaxation time in the PMN—though obtained in rather narrow range of temperatures—are further indications that the question whether there is a glassy freezing in the PMN

relaxor at all is still waiting for an unambiguous answer.

The observed peaks in the temperature dependence of ε' and ε'' in case of high values of dc electric field (close to or above E_C)[15,3,16,17] and the existence of Barkhausen jumps of microdomains controlling the poling process below freezing temperature T_f (Ref. 16) should exclude glassiness in favor of a random-field mechanism of freezing into a domain state on a nanometric length scale.[16] However, as pointed out by Colla *et al.*[4] according to the model proposed by Westphal and co-workers,[16] neither history-dependent effects[19] nor nonlinear phenomena[18,9] were taken into account.

It has been known for some time that, in contrast to the linear susceptibility, the third harmonic component χ_3 should exhibit a critical singularity at freezing temperature T_f in spin glasses.[20,21] Moreover, a scaling behavior $\chi_3 \sim (T-T_f)^{-\gamma}$ was found in several glassy systems,[22,23] with γ ranging from 0.9 to 3.8. It should be noted that similar behavior—i.e., critical temperature dependence of the high-temperature side of the peak in third harmonic susceptibility—was observed in the PMN relaxor,[18,9,24] with $\gamma=2.86$. However, as recently noted[25] the situation in dipolar glasses is more complicated than in magnetic spin glasses due to the presence of random local electric fields. It was shown within the framework of a dynamic random-bond random-field model that in the experimentally relevant low-frequency limit, the quasistatic susceptibility χ_3 diverges on approaching the freezing temperature T_f.[25] This means that the nonlinear part of the susceptibility should be viewed as a dynamic quantity showing frequency-dependent effects, analogous to the behavior observed in the case of the linear susceptibility. Thus, an investigation of the dynamic effects in the nonlinear susceptibility—i.e., an identification of the relevant quasistatic limit—should be appropriate before any analysis of the critical behavior is attempted.

It is known that the response of the glassy system to an external field should depend on the history of the system. Specifically, if the system has been cooled in an external field, the corresponding field-cooled susceptibility χ_{FC} will differ from the zero-field-cooled susceptibility χ_{ZFC}, which is observed after cooling the sample in zero field. Such splitting between χ_{FC} and χ_{ZFC}—i.e., indication for nonergodic behavior—has been observed in many glassy systems,[10] including dipolar[26] and quadrupolar glasses.[27]

It should be noted that history-dependent effects such as the difference between FC and ZFC dependencies of neutron quasielastic scattering intensity[19] and the linear birefringence[16] were observed in the PMN relaxor. However, an experiment performed in the typical manner as is widely used in the case of dipolar glassy systems[26] and therefore a direct observation of the splitting between χ_{FC} and χ_{ZFC}—i.e., $\varepsilon_{\mathrm{FC}}$ and $\varepsilon_{\mathrm{ZFC}}$—is required in order to demonstrate the onset of the nonergodicity in the PMN relaxor.

In this work we present experimental results, which indicate specific glasslike freezing process in the PMN similar to the one observed in dipolar glasses. These results have been obtained by studying the quasistatic and frequency-dependent linear and nonlinear dielectric response at sufficiently low values of the external dc electric field in order to ensure that PMN remained during experiments in the glassy regime. In order to avoid the above shortcomings of the Vogel-Fulcher-type analysis, a recently introduced method of dielectric data analysis via the temperature-frequency plot[28] was adopted.

The experimental procedures are briefly summarized in Sec. II. The results and the analysis of the linear and nonlinear dielectric response are given in Sec. III. A discussion of the results are given in Sec. IV, which also includes a comment on the glassy nature of our data.

II. EXPERIMENTAL PROCEDURES

The platelet-shaped samples were cut and polished from a single crystal of the PMN. The silver electrodes were applied by evaporation technique on (001) faces, and therefore the dielectric response was always measured perpendicularly to the (001) plane.

The frequency-dependent complex dielectric constant $\varepsilon^*(\nu,T)=\varepsilon'-i\varepsilon''$ was measured between 190 and 400 K on a sample, which was 1 mm in diameter and 1 mm thick. The frequency range from 20 Hz to 20 GHz was covered by three different techniques: (a) Low-frequency measurements from 20 Hz to 1 MHz were carried out by using a HP4282 Precision LCR Meter. (b) The measurements in the frequency range from 1 MHz to 1 GHz were performed by the HP4291 RF Impedance Analyzer. Here the sample was fixed at the center of a radial line effectively terminating the coaxial reflectometer. (c) The data in the range of frequencies from 1 GHz to 20 GHz were taken by the HP 8510B Network Analyzer. The amplitude of the probing ac electric signal was for all measuring frequencies 20 V/cm. Having in mind that the history-dependent effects play an important role in the PMN relaxor, special attention was paid to the way the low-temperature phase was reached, i.e., all runs were performed in the same way starting at the same high temperature of 420 K and the dielectric constant was always determined on cooling the system with the same cooling rate of -0.5 K/min.

The temperature dependencies of the field-cooled P_{FC} and zero-field-cooled P_{ZFC} quasistatic dielectric polarization have been measured between 80 and 350 K by using the corresponding method as described in Ref. 26 on $4\times4\times0.41$ mm^3 sample. The zero-field-cooled dielectric constant $\varepsilon_{\mathrm{ZFC}}=\lim_{E\to0}P_{\mathrm{ZFC}}(E,T)/\varepsilon_0E$ was determined by cooling the system down in zero field $E=0$ by applying an external electric field $E=245$ V/cm at temperature $T=80$ K, and slowly heating the sample (0.5 K/min) up to 350 K while measuring the corresponding polarization charge by the Keithley 617 programmable electrometer. At temperature $T=350$ K, the scanning rate was reversed (-0.5 K/min) and the field-cooled dielectric constant $\varepsilon_{\mathrm{FC}}=\lim_{E\to0}P_{\mathrm{FC}}(E,T)/\varepsilon_0E$ was measured by cooling the system down to 80 K in the same external electric field $E=245$ V/cm. A long-living remanent polarization P_R has been observed at 80 K where the field E was switched off and monitored on heating (0.5 K/min) the sample in zero field again up to 350 K.

The nonlinear dielectric response, i.e., the third-order nonlinear susceptibility χ_3 was determined always on cooling the system (-0.5 K/min) between 330 and 190 K on the same sample as in the case of FC/ZFC experiments. Due to the weakness of the response signal, various experimental techniques have been tested ranging from simple lock-in to wave analyzer technique, but eventually, in all cases, the same reproducible results have been obtained. Measurements

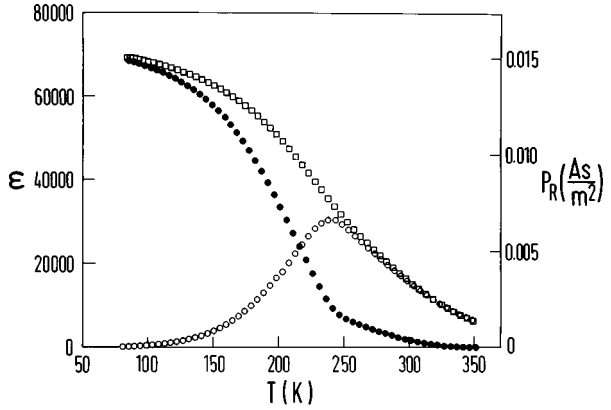

FIG. 1. Temperature dependence of the field-cooled (□) and zero-field-cooled (○) quasistatic dielectric constant ε' of the PMN measured perpendicularly to the (001) plane. Also shown is the remanent polarization P_r (●) obtained in a heating run.

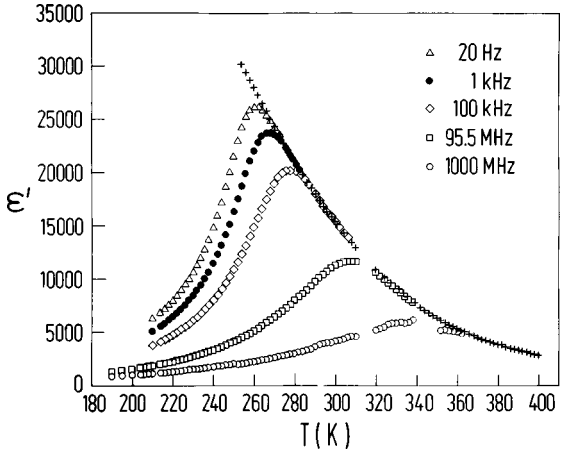

FIG. 2. Temperature dependence of the static dielectric constant ε_s (+) determined via standard Cole-Cole plots analysis. In order to demonstrate typical glasslike slowing down occurring in the PMN system, $\varepsilon'(\nu,T)$ is plotted at various frequencies ν.

in the range of frequencies between 1 Hz and 30 kHz, reported in this paper, have been performed by the HP 35665A dynamic signal analyzer. Here the amplitude $E=245$ V/cm of the probing ac electric signal—applied at the first-harmonic frequency—was equal for all measuring frequencies.

The temperature of the samples was stabilized and monitored to within ± 0.01 K in the temperature range from 80 to 400 K by using an ac bridge technique with the platinum resistor PT100 as a thermometer.

III. RESULTS AND ANALYSIS

This section is concerned with a description of the results obtained in linear and nonlinear dielectric experiments and with their analysis.

A. FC and ZFC dielectric susceptibility

One of the fundamental experiments in order to probe the glassy nature of the material under investigation is to measure the splitting between FC and ZFC susceptibility.[10] The results obtained on PMN system shown in Fig. 1 represent strong evidence that the nature of the state in low external electric field is indeed spin-glasslike. Namely, a splitting between field-cooled (□) and zero-field-cooled (○) dielectric constants—as a consequence of ergodicity breakdown—has indeed been observed.

This experiment can also provide an estimate for the freezing temperature T_f, i.e., the temperature where the splitting between $\varepsilon_{\rm FC}$ and $\varepsilon_{\rm ZFC}$ should occur. It should be noted, however, that the freezing temperature $T_f \approx 240$ K thus obtained is not a true static quantity, but rather depends on the experimental time scale $t_{\rm expt}$ connected with the rate of temperature scan in the zero-field-cooling experiment,[26,28] which in our case was $t_{\rm expt} \approx 300$ s.

Also, it should be noted that the splitting observed in the PMN relaxor is not as sharp as it was observed, for instance, in deuteron glasses.[26,29] Instead, FC and ZFC curves open gradually, thus making an estimate of $T_f(t_{\rm expt})$ more difficult. Since this effect was more pronounced at higher values of the external dc electric field applied in FC experiment (compare Figs. 1 and 2), one may argue that the result of the FC experiment would essentially depend on the actual trajectory in the E-T phase diagram,[4] i.e., gradually increasing gap can be viewed as a consequence of finite external electric field applied in the FC experiment that slightly changes the properties of the glass state toward properties characteristic of an induced ferroelectric phase.

A remanent polarization P_R (●) has been observed after the external field in FC experiment was switched off. Here, a small gap between $\varepsilon_{\rm FC}$ and P_R curves in Fig. 1, appearing immediately after removal of the external field at the lowest temperature, is a consequence of the fast high-frequency dielectric response. By measuring the size of this gap it was possible to make an additional and independent estimation of ε_∞.

At fixed low temperature, P_R was found to be indeed a long-living quantity remaining constant on time scales longer than several hours. On heating the sample P_R decreased with increasing temperature and the slow relaxation was observed at temperatures approaching the freezing temperature close to 220 K. This is in agreement with the previously reported observation of a long-living relaxing electric polarization created by cooling down PMN sample in the low-field regime.[3,9,7]

B. Complex dielectric constant

Direct information on the dynamic processes occurring in PMN relaxor was obtained via measurements of the linear part of the frequency-dependent complex dielectric constant. Figure 2 shows the temperature dependencies of the real part of the linear dielectric constant ε' measured at different frequencies.

Analogous to other dipolar glassy systems[10,29] lead magnesium niobate exhibits pronounced dispersion in ε', i.e., the real part of the linear dielectric constant starts to deviate from the static value (+) at temperatures, which shift to lower values with decreasing frequency. The result of this effect is broad peaks, which grow in size with increasing experimental time scale. It should be noted that the size and the position of peaks measured at frequencies in kHz region were in good agreement with previously published values.[1,8,7,9]

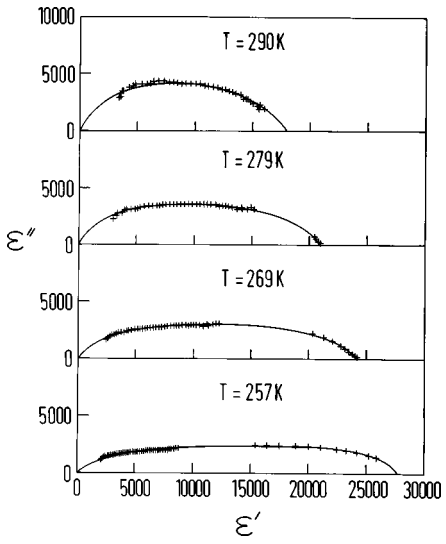

FIG. 3. Measured values of ε'' plotted vs ε' in the PMN at four temperatures. Solid lines are fits obtained via standard analysis using a particular ansatz for the relaxation spectrum.

1. Standard analysis via Cole-Cole plots

Although Fig. 2 is very effective in showing the dramatic slowing down of the relaxation process, it cannot provide unambiguous information about characteristic relaxation time[14] nor relaxation spectrum. As already mentioned in the Introduction, deviations from an Arrhenius behavior obtained via the Vogel-Fulcher analysis of temperature shifts of ε' and ε'' peaks measured at different frequencies could be a consequence of temperature variations in dielectric intensity and changes in the shape of the relaxation spectrum, and not necessarily of the divergent behavior of the characteristic relaxation time.

One standard way to overcome these problems is to analyze the so-called Cole-Cole plots where ε'' is plotted as a function of ε' by using some specific model for the distribution of relaxation times $g(\ln\tau)$. The general idea is that the complex dielectric constant can be described as a sum of Debye relaxations,

$$\varepsilon^*(\omega)-\varepsilon_\infty=(\varepsilon_S-\varepsilon_\infty)\int_{\tau_1}^{\tau_2}\frac{g(\ln\tau)d\ln\tau}{1+i\omega\tau}. \qquad (1)$$

Here, τ_1 and τ_2 are lower and upper cutoffs, respectively, and the distribution of relaxation times satisfies the normalization condition $\int_{\tau_1}^{\tau_2} g(\ln\tau)d\ln\tau=1$. Figure 3 shows a set of typical Cole-Cole diagrams for four different temperatures. Here, solid lines were obtained by numerical fit to a linear model for the distribution of relaxation times $g(\ln\tau)$,[28,29]

$$g(z)=2\frac{(z_2-z)}{(z_2-z_1)^2}, \quad z_1\leqslant z\leqslant z_2, \qquad (2)$$

where $z=\ln(\omega_a\tau)$ is the integration variable with ω_a as an arbitrary unit frequency, and again $g(z)$ is the distribution of relaxation times with lower and upper cutoffs z_1 and z_2. It should be stressed that no evidence was found suggesting an additional relaxation process in the single PMN crystal. On the other hand, the Cole-Cole diagrams show clearly that by lowering the temperature the dielectric relaxation becomes strongly polydispersive, i.e., the dielectric dispersion cannot be completely covered even with a ten decades wide range of frequencies, which was experimentally available. The above procedure can provide information about the temperature dependencies of important parameters ε_S, ε_∞, and τ. However, the results depend on the choice of $g(\ln\tau)$, i.e., some prior knowledge about the shape of the relaxation spectrum is needed. Therefore, the Cole-Cole plots cannot provide direct and independent information about the actual relaxation spectrum under investigation.[28,29]

2. Temperature-frequency plot

Recently, it was shown that the information about the behavior of the relaxation spectrum can be directly extracted by using a special representation for the real part of the dielectric constant in a so-called temperature-frequency plot.[28] This method was later effectively applied to various glassy systems such as deuteron glasses,[29] quasi-one-dimensional deuteron glasses,[30] spin-density-waves systems,[31] and other orientational glasses.[32]

A detailed description of this method is given in Refs. 28 and 29. Here we will only briefly summarize its essential steps in order to keep our focus on the results. In the first step, a reduced dielectric constant is defined as[28]

$$\delta=\frac{\varepsilon'(\nu,T)-\varepsilon_\infty}{\varepsilon_s-\varepsilon_\infty}=\int_{z_1}^{z_2}\frac{g(z)\,dz}{1+(\omega/\omega_a)^2\exp(2z)}. \qquad (3)$$

Again, a natural assumption is made that the distribution of relaxation times $g(z)$ is limited between lower and upper cutoffs z_1 and z_2. High-frequency dielectric constant ε_∞ was found to be a temperature-independent quantity. Its value—determined from Cole-Cole plots—is equal to 10. The low-frequency limit of the real part of the dielectric constant ε_s was obtained by extrapolation of the measured $\varepsilon'(\nu)$ to zero frequency.[29] It should be noted that similar to the case of deuteron glasses ε_s determined in the above way was found to be essentially equal to the independently measured FC dielectric constant.[28,29]

In the second step, by scanning δ—now playing the role of an experimentally adjustable parameter—between the values 1 and 0, ε' will vary between ε_s and ε_∞, and the filter in the second part of the Eq. (3) will scan the distribution of relaxation times $g(z)$, thus probing various segments of the relaxation spectrum.[29]

For each fixed value of δ a characteristic temperature-frequency profile was obtained in the (T,ν) plane. A typical (T,ν) plot for PMN is shown in Fig. 4. As pointed out in Refs. 28 and 29, the (T,ν) plot should provide a reliable qualitative description of the temperature variation of various segments of the relaxation spectrum. Consequently, the temperature dependence of the relaxation cutoffs $z_1(T)$ and $z_2(T)$ can be deduced from Fig. 4 before any analysis is made.

For instance, the data corresponding to the smallest value of δ lie nearly on a straight line. This, in turn, suggests a linear relationship between z_1 and $1/T$, which implies an Arrhenius-type behavior of the shortest relaxation time, namely, $\tau_1=\tau_{01}\exp(E/T)$. On the other hand, the dramatic bending of the lowest curves for δ close to 1 with decreasing

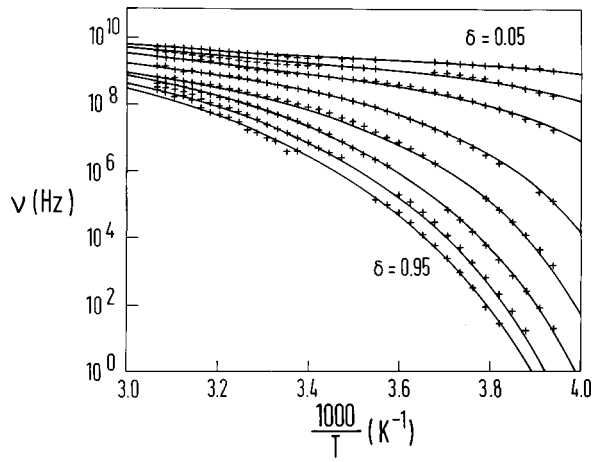

FIG. 4. Temperature-frequency plots for several fixed values of the reduced dielectric constant δ, top to bottom, 0.05, 0.10, 0.20, 0.40, 0.60, 0.80, 0.90, 0.95. Solid lines are fits obtained with a linear expression for the relaxation spectrum.

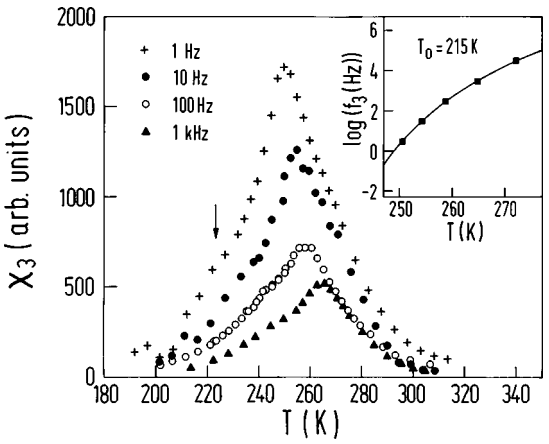

FIG. 5. Temperature dependencies of the third-order nonlinear dielectric susceptibility χ_3 measured at various frequencies ν. Inset shows that the temperature shift of χ_3 peaks with changing frequency is governed according to the Vogel-Fulcher law.

temperature indicates a possible divergent behavior of $z_2(T)$, therefore implying a Vogel-Fulcher-type behavior of τ_2, i.e.,

$$\tau_2 = \tau_{02}\exp[U/(T-T_0)]. \tag{4}$$

At this point, the parameters τ_{01}, τ_{02}, E, U, and T_0 can be extracted in two ways: (a) By a best-fit analysis of the data based on the exact numerical evaluation of the integral in Eq. (3). Though by using this method it is possible to describe entire (T,ν) plot in a unique way, one needs a specific model for the relaxation spectrum $g(z)$. (b) In another method one can simply use the generic Vogel-Fulcher-type ansatz given in Eq. (4) and fit separately each curve in Fig. 4. Extrapolation of the set of fitting parameters thus obtained towards $\delta = 1$ and $\delta = 0$ should than provide the parameter values for the relaxation cutoffs.[33,30] It should be mentioned that in the second method no model for $g(z)$ is needed, thus making the (T,ν) analysis completely free of any prior assumptions about the shape of the relaxation spectrum.

Both options have been tested. In the first method, the asymmetric linear ansatz given in Eq. (2) was used for $g(z)$, which, in turn, did not contain any additional parameters. The solid lines in Fig. 4 were obtained by fitting the data to the exact numerical evaluation of the integral in Eq. (3) for the function $g(z)$. It should be stressed that within the error of estimation both methods gave the same results for the fitting parameters: $T_0 = 224 \pm 6$ K, $f_{01} = 1/2\pi\tau_{01} = 6.4\times10^{12}$ Hz, $f_{02} = 1/2\pi\tau_{02} = 3.7\times10^{9}$ Hz, $E = 100 \pm 50$ K, and $U = 970 \pm 100$ K.

It is obvious that in this case there were no problems with the unrealistic values for fitting parameters as previously reported in the case of some other standard approaches.[12] Also, the value for T_0 is close to the previously reported Vogel-Fulcher temperature determined via Vogel-Fulcher-type analysis.[8] This suggests that in the PMN relaxor the divergence of the characteristic time has indeed its origin in the true divergence of the maximum relaxation time and is not merely a consequence of the temperature variations in the dielectric strength and the shape of the relaxation spectrum.

C. Third-order nonlinear dielectric susceptibility

It has been argued[20] that the analysis of the critical behavior of the third-order nonlinear susceptibility in the vicinity of the freezing transition can provide additional insight into the nature of the freezing process and specifically an independent information on the freezing temperature. However, the above expectations can be justified only for the nonlinear response measured at least on the quasistatic experimental time scale.[25]

In another turn, it is natural to expect that on all other finite experimental time scales one would observe the third-order nonlinear susceptibility influenced by the glassy dynamics in a similar way as it was observed in the case of linear susceptibility. Specifically, one can expect that the temperature dependence of the static χ_3 will play the role of an envelope for all other χ_3 curves obtained on a finite-time scale.[25] Figure 5 shows that similar behavior of the third-order nonlinear dielectric constant indeed takes place in the PMN relaxor. Here χ_3 measured at various frequencies is plotted as a function of temperature. Similar, as in the case of linear response, peaks shift to lower temperature and grow in size by decreasing the frequency.

The inset in Fig. 5 shows the results of the Vogel-Fulcher-type analysis applied to the third-order nonlinear data. The use of this method can be justified at this point by recalling the results of the temperature-frequency plot analysis, namely, actual freezing in the dynamics of the Vogel-Fulcher-type indeed takes place in the PMN relaxor. Here, the third harmonic frequency denoted as f_3 is plotted as a function of the temperature where the corresponding χ_3 curve reaches its maximum value. Clearly, the above behavior can be well described by the Vogel-Fulcher law with a corresponding freezing temperature $T_0 = 215$ K, which is between the temperature of the divergence of maximum relaxation time obtained via temperature-frequency plot and the temperature $T_C = 212$ K of the field-induced ferroelectric phase transition taking place when the external field above E_C is applied.

It should be noted that the analysis of the third harmonic data by a critical power-law ansatz $(T-T_f)^{-\gamma}$ was not successful due to the dynamic and rounding effects similar to

those, which were reported previously in the case of the linear susceptibility analysis.[2] Specifically, the fitting results were unstable on shrinking the temperature range in which fits were performed.

IV. DISCUSSION

Within the framework of macroscopic dielectric experiments performed in a small external electric field, the PMN relaxor system clearly shows a number of properties, which are widely accepted as typical for dipolar glasses.

A. Broken ergodicity

The existence of the splitting between the FC and ZFC static linear dielectric susceptibilities was observed on a quasistatic experimental time scale, indicating that ergodicity is broken below some apparent freezing temperature T_f. Consequently, a long-living remanent polarization P_R was found to exist below T_f. In contrast to dipolar glasses where P_R vanishes on approaching $T_f(t_{\mathrm{expt}})$,[26,29] a change of slope has been observed at the temperature of the peak in zero-field-cooled dielectric constant, and a long-living tail has been found extending up to ≈320 K, i.e., well above the freezing temperature. The same tailing was also reported in the case of PLZT-8 ceramics.[34] This behavior suggests that on heating part of the system remains in the nonergodic, i.e., frozen-state[34] even after crossing the freezing temperature, indicating a hysteresis effect in the glass transition line so far unknown to exist in dipolar glasses.

B. Divergence of the longest relaxation time

Analogous to the case of deuteron glasses, an asymmetric broadening of the relaxation spectrum and the divergence of its low-frequency limit were found to take place in the PMN relaxor. In particular, the divergence of the longest relaxation time implies a transition from the ergodic into a nonergodic state, i.e., ergodicity is effectively broken at the Vogel-Fulcher temperature T_0, which can be identified as the freezing temperature T_f. On the other hand, while the longest relaxation time diverges the bulk of the relaxation spectrum remains active even below the Vogel-Fulcher temperature T_0. This is in agreement with previous observations of slow polarization decay far below the freezing temperature.[34] It is interesting to note that this behavior of the relaxation spectrum is qualitatively in accordance with the predictions of the theory of hierarchically constrained dynamics.[35,36]

C. Slowing dynamics and the third-order nonlinear susceptibility

The third-order nonlinear dielectric constant behaves in a way similar as expected for a typical orientational glass system. The expression for χ_3 based on a soft-spin version of the random-bond–random-field Ising model

$$\beta H = -\frac{1}{2}\beta\sum_{ij} J_{ij}S_iS_j - \beta\sum_i (h_i+E)S_i \tag{5}$$

was derived in Ref. 25,

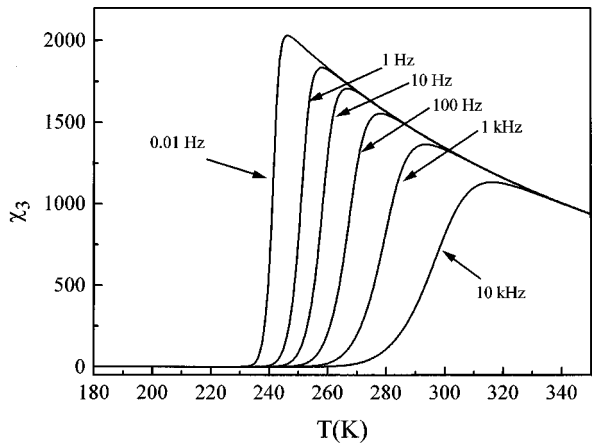

FIG. 6. The third-order nonlinear dielectric susceptibility $\chi_3(T,\omega)$ at various frequencies according to the random-bond–random-field model. Here, the Vogel-Fulcher law Eq. (4) was adopted for the temperature behavior of the characteristic relaxation time τ.

$$\chi_3(\omega) = \beta^3 \frac{[(1-3p^2)(1-p^2)]_x(1-i\omega\tau)}{(1-i3\omega\tau)(1-i\omega\tau)-\beta^2J^2[(1-p^2)^2]_x}, \tag{6}$$

implying that χ_3 is actually a dynamic quantity and therefore depends on the experimental time scale. Here ω is the frequency of the probing signal, i.e., the frequency of the first harmonic dielectric response, $\beta=1/T$ with Boltzmann constant set to 1. The random-bond interactions J_{ij} and the random local electric fields h_i are assumed to have a Gaussian probability distribution with zero mean and variances J^2/N and $J^2\tilde{\Delta}$, respectively. The local polarization p in a unit Gaussian random field x is given by $p=\tanh(\beta J\sqrt{q+\tilde{\Delta}}x)$, and the glass order parameter q is determined by the self-consistent equation $q=[p^2]_x$, where $[\cdots]_x$ means a Gaussian average $(2\pi)^{-1/2}\int dx\exp(-x^2/2)[\cdots]$. The quasistatic value of χ_3 is then

$$\chi_3 = \beta^3 \frac{[(1-3p^2)(1-p^2)]_x}{1-\beta^2J^2[(1-p^2)^2]_x}. \tag{7}$$

Although critical slowing down for the characteristic relaxation time τ is predicted by the above theory, it was already pointed out in Ref. 25 that the corresponding distribution of relaxation times—as deduced from linear dielectric data—should be included in a phenomenological model based on Eq. (6) in order to describe nonlinear measurements. Indeed, the divergent behavior of the characteristic relaxation time for χ_3 is actually—within the error of determination—the same as the behavior of the longest relaxation time in the relaxation spectrum of the linear dielectric response. The temperature behavior of $\chi_3(T,\omega)$ described by Eq. (6) for various frequencies is schematically shown in Fig. 6 with τ obeying the Vogel-Fulcher law (4).

While the above theory qualitatively reproduces the observed dynamic features in the third-order nonlinear susceptibility of PMN, there are clearly two distinct discrepancies. Similar to the linear data shown in Fig. 2, it is obvious from Fig. 6 that the static χ_3 should play the role of an envelope for other high-frequency curves, which start to deviate from

it at temperatures where the corresponding measuring frequency exceeds the lowest relaxation frequency in the relaxation spectrum. In contrast to this expected behavior, no limiting envelope can be deduced from the nonlinear data taken in the range of frequencies from 1 Hz to 30 kHz. Instead, a curve obtained at lower frequency always lies above any other curve taken at higher frequency.

The reason for this discrepancy may be the same as for the gradually increasing gap between FC and ZFC curves. Namely, in order to ensure a good signal to noise ratio, the amplitude ($E = 245$ V/cm) of the ac measuring signal used in nonlinear experiment was 10 times larger than in linear susceptibility measurements. Consequently, a finite external ac field may be more effective at lower frequencies in moving the system along the finite-field trajectory in the E-T phase diagram. This idea is supported by linear dielectric constant data that were taken simultaneously with the third-order nonlinear data. Curves taken at different frequencies do not form an envelope in contrast to Fig. 2, but behave in a way similar to the χ_3 data, thus indicating that the path of the approach toward the freezing is different for various measuring frequencies. Furthermore, it was shown recently that a similar increase in linear dielectric permittivity with increasing ac and dc external electric field can be viewed as a consequence of the ferroelectric domain-wall motion process.[38]

The second discrepancy, which also seems to be related to the above problem is the fact that the drop of χ_3 at different frequencies after reaching the maximum is not so pronounced as suggested by the theory. The shape of deviations and their appearance close to the transition temperature (denoted by an arrow in Fig. 5 for data at 1 Hz)—where even stronger anomalies were observed in linear susceptibility when ferroelectric state was induced by a strong bias electric field[15,3,16,17]—suggest that the same mechanism of field-induced ordering is responsible for both effects.

The fact that χ_3 is a dynamic quantity has another important consequence for the (E-T) phase diagram. Namely, the position of the transition line between the paraelectric and glassy phase obtained from the position in the peaks in χ_3 (Ref. 24) is not well defined since it depends on the measuring frequency, i.e., it will shift to much higher temperatures in case of higher measuring frequencies.

V. CONCLUSIONS

It is obvious that the state of the PMN relaxor in low-external electric field can be *empirically* described as the dipolar glass state. The underlying microscopical mechanism responsible for glasslike behavior of relaxors may be different than in other dipolar glass systems. Specifically, in the case of deuteron glass systems $Rb_{1-x}(ND_4)_xD_2PO_4$, the glass state is much more stable against an external electric field contrary to the metastable glasslike state in the PMN relaxor, i.e., no crossover towards a long-range order phase nor any significant influence on the linear dielectric constant could be observed in those systems, even for values of the bias field much larger than E_C in the case of the PMN relaxor.[26,33]

On the other hand, NMR measurements[39] suggest that a phase segregation between ferroelectric nanodomains and glassy regions occurs for ferroelectric-rich mixtures $0.2 < x < 0.3$ in $Rb_{1-x}(ND_4)_xD_2PO_4$ thus providing a possible conceptual link between dipolar glasses and relaxors. The question remains still open whether PMN relaxor glass phase is a dipolar glass state with randomly interacting polar microregions[34,37] in the presence of random fields or a ferroelectric state broken up into nanodomains under the constraint of quenched random fields.[16] It should be mentioned, however, that the qualitatively same experimental results were obtained on glassy mixtures $0.3 < x < 0.65$ in $Rb_{1-x}(ND_4)_xD_2PO_4$ in which case no nanodomains have been observed.[39] While our experiments seem to be *empirically* more in accordance with the dipolar glass picture, recent measurements studying the dielectric response of 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.[38] However, one would actually expect to observe various domain-type effects as for instance Barkhausen jumps while probing different glass-ferroelectric crossover states in the (E-T) phase diagram[3,4] induced by the finite dc bias fields typically used in such experiments. Clearly, additional experiments in the zero-field limit are needed to answer this question.

In summary, the investigation of the linear and the third-order nonlinear dielectric response shows that ergodicity is indeed effectively broken in the PMN relaxor due to the divergence of the longest relaxation time in the distribution of relaxation times. The glassy dynamics together with the splitting between the quasistatic FC-ZFC susceptibilities demonstrate that the nonergodic state can be at least empirically described as a dipolar glass state. This can be easily perturbed by an external electric field, which induces growth of the long-range ferroelectric order and consequently crossover effects can be observed in the quasistatic linear and nonlinear dielectric constants measured in a finite electric field.[4]

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