# Electric-field–temperature phase diagram of the relaxor ferroelectric lanthanum-modified lead zirconate titanate

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Transition lines between various phases in the electric-field–temperature phase diagram of 9/65/35 lanthanum-modified lead zirconate titanate ceramics were determined by measurements of the temperature and electric-field-dependent dielectric constant. Above a critical field ($E_C$) the dc bias electric field induces a transition from the relaxor (R) to the long-range ferroelectric (FE) phase. In the temperature direction of the approach to the FE phase the R-FE transition line was determined from the field-cooled–field-heated dielectric susceptibilities, while depolarization temperatures were obtained from the field-cooled–zero-field-heated dielectric susceptibilities. A considerably large shift was found for the above two R-FE transition lines demonstrating the strong impact of the electric field on the stability of the FE phase with increasing temperature. It was found that below $E_C$ ergodicity is broken due to the divergence of the longest relaxation time at the freezing temperature $T_0 = 259$ K. Hence the system exhibits a transition line between the ergodic (ER) and nonergodic (NR) relaxor state. In the dc bias field direction of the approach to the FE phase, the temperature dependence of $E_C$, i.e., the transition lines between ER or NR and FE phases were studied by measurements of the complex dielectric constant as a function of a dc bias field at several fixed temperatures. The experimental results are compared with the results of a spherical random bond-random field model of relaxor ferroelectrics. [S0163-1829(99)00233-7]

## I. INTRODUCTION

Lanthanum-modified lead zirconate titanate ceramics $Pb_{1-x}La_x(Zr_yTi_{1-y})_{1-x/4}O_3$ (PLZT) is a very promising material for numerous applications. The compositional phase relations of this material were first explored by Haertling.[1] For certain compositions, including the one of $x = 0.09$ and $y = 0.65$ (denoted as 9/65/35 PLZT ceramics), it belongs to relaxor materials. PLZT ceramics thus allows studies of the relaxor properties, which are typically characterized by a broad frequency dispersion in the complex dielectric constant and slowing dynamics.[2–4]

The results of the dielectric experiments on the most studied relaxor system lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) show that no long-range ferroelectric order is established in zero dc bias field. However, by cooling the PMN monocrystal in an electric field higher than the critical field $E_C \approx 1.7$ kV/cm (Ref. 5) or the PMN ceramics in a field higher than $E_C \approx 4$ kV/cm[6] a long-range ferroelectric phase is formed. Evidence that a dc electric field can induce such a transition came from an x-ray study.[7] Later, the electric-field–temperature (E-T) phase diagram of the PMN relaxor was proposed,[5,8,9] based on the linear and nonlinear dielectric studies.

Similar investigations have already been initiated in the PLZT relaxor system. Behavior of the field-cooled–zero-field-heated (FC-ZFH) dielectric susceptibilities[10,11] has shown that by applying a dc bias field higher than $E_C \approx 5$ kV/cm a long-range ferroelectric order is established in 9/65/35 PLZT ceramics. In particular, this was confirmed by studies of the ferroelectric polarization and depolarization by means of the pyroelectric current measurements.[10]

Below $E_C$ no long-range order is formed in 9/65/35 PLZT ceramics at temperatures ranging between 723 and 90 K and only a broad dielectric peak typical of relaxors can be observed.[10] The relaxor freezing process has been studied both in the PMN system and in 9/65/35 PLZT ceramics.[12–17,5] Recent investigations[17] based on the temperature behavior of the frequency dependent complex dielectric constant, the quasistatic field-cooled (FC) and zero-field-cooled (ZFC) dielectric (linear and the third-order nonlinear) susceptibilities, and the pyroelectric current in zero dc electric field, indicate a glasslike freezing process similar to one observed in the PMN system and dipolar glasses. Here it should also be mentioned that nanometer-sized polar regions, which are often associated with relaxor behavior,[14,18] were observed in some *x*/65/35 PLZT ceramics using TEM microscopy.[19] Nanodomain structure has also been reported in PMN and lead stroncium tantalate relaxors.[20,21]

In spite of intensive investigations, the E-T phase diagram of PLZT ceramics has not been studied in detail yet. In particular, only depolarization temperatures at a few dc bias fields have been determined so far in 9/65/35 PLZT ceramics.[10,11] In this work we present three different sets of experimental results of the dielectric behavior in 9/65/35 PLZT ceramics in order to determine the E-T phase diagram: (i) temperature dependences of the complex dielectric constant measured at several dc bias fields higher than critical field $E_C$, (ii) the temperature dependence of the frequency-dependent complex dielectric constant, which allows studies of the freezing process in bias fields smaller than $E_C$, and (iii) the dielectric response vs dc bias field at several fixed temperatures.

The experimental procedures are summarized in Sec. II. The results and analysis of measurements are given in Sec. III. A discussion of the results is given in Sec. IV, in which the E-T phase diagram of 9/65/35 PLZT ceramics is also presented and compared to the results of the spherical random bond-random field model of relaxor ferroelectrics.

 

## II. EXPERIMENTAL PROCEDURES

The platelet-shaped sample was cut from the hot pressed 9/65/35 PLZT ceramics. After polishing, the thickness of the sample was 0.52 mm. Gold electrodes were applied to the surface area of $4.7\times3.5$ mm$^2$ by the evaporation technique.

Three different sets of measurements were performed in order to determine the phase transition temperatures in the E-T phase diagram. In all cases the complex dielectric constant was measured in the frequency range from 20 Hz–1 MHz by using HP4282 Precision LCR Meter. The amplitude of the probing ac electric signal was 1 V for all measuring frequencies.

The first set of measurements was designed to study the field induced transition from the ergodic relaxor phase to the long-range ferroelectric phase. The sample was first cooled from 410 K down to 150 K in a dc bias field. At 150 K the dc bias field was switched off and the sample was short circuited. Then, the sample was heated back to 410 K. The cooling and heating rates were $\pm1$ K/min. In both, cooling and heating run, the complex dielectric constant was measured at various frequencies. In this way, the measurement was repeated by applying several different dc bias fields ranging from 3–8.5 kV/cm. Since it is well known that the history-dependent effects play an important role in relaxor systems,[22,23,17] the sample was annealed at 410 K for one hour prior to each measurement run in order to ensure the equal conditions for all runs and to eliminate the effects of previous treatments.

The second set of measurements was performed in order to study the freezing process of the system, i.e., the transition from the ergodic to the nonergodic relaxor phase. Recently, it was shown that the aging effect strongly influences the dielectric data taken in the first few hours after annealing the PLZT ceramics.[17] In order to reduce the aging effect enough not to interfere with the regular dielectric dynamics, the sample was cooled from 410–345 K and aged for one day. However, it was found that the application of the dc bias electric field on the ZF aged sample induces again the aging of the ac dielectric constant. Thus before measuring the frequency dependent complex dielectric constant in a small dc bias field ($E<E_C$), the sample was aged at 345 K for one day in this particular field. After that, the frequency dependent complex dielectric constant was measured during cooling the sample from 345 K down to 200 K. In this way, the freezing dynamics was studied subsequently in the dc bias fields of 0, 1, and 2.5 kV/cm.

In the third set of measurements, the dielectric response was studied as a function of the dc bias field at several fixed temperatures. In this case, the transition line between the ergodic or nonergodic relaxor phase and the induced FE phase was probed. The sample was cooled down in a zero bias field after being annealed at 410 K to a given fixed temperature. Then, the dc bias field with an increasing rate of 10 V/cms was applied to the sample, hence the complex dielectric constant was measured at various frequencies as a function of the dc bias field. The whole procedure was repeated at various temperatures between 195 and 310 K. The temperature was stabilized within $\pm0.01$ K by using lock-in bridge technique with a platinum resistor Pt1000 as a thermometer.

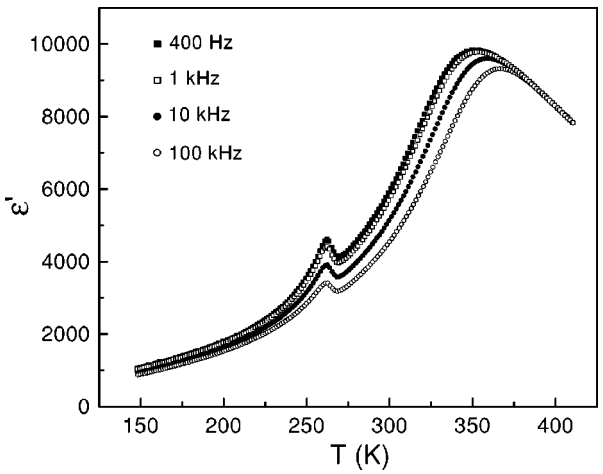


FIG. 1. Temperature dependence of the real part of the complex dielectric constant measured in the FC-ZFH run at the dc bias field of 8.5 kV/cm.

## III. RESULTS AND ANALYSIS

This section gives a description of the dielectric results and their analysis measured as a function of the temperature at several fixed dc bias fields as well as the dielectric results measured as a function of the dc bias field at several fixed temperatures.

### A. Temperature dependence of the dielectric response above $E_C$

Several measurements of the temperature dependent complex dielectric constant in relaxor materials[5,6,8,10,17,23] revealed that below the critical dc bias field $E_C$ no anomalies can be detected in the dielectric response. However, if the dc bias field is higher than $E_C$, additional peaks in the dielectric response can be observed.[5,6,8,10,23] These anomalies were explained as a consequence of the electric-field induced phase transition into the long-range-order ferroelectric phase.[5,8,10,11] Several measurements of the temperature dependent dielectric response in the dc bias field have been performed in PLZT ceramics.[24–27] Nevertheless, the FC-ZFH ac dielectric measurements together with the pyroelectric measurements have established the value of the critical electric field $E_C\approx5$ kV/cm in the 9/65/35 PLZT ceramics.[10,11]

In the temperature direction of the approach to the FE ordered state the FE-ER phase transition temperatures were determined from the temperature dependence of the complex dielectric constant measured in several fixed dc bias fields. In this subsection only the determination of the depolarization temperatures, i.e., the temperatures of the FE-ER phase transition measured in a zero-field-heating run following the field-cooling run (FC-ZFH), will be presented. The other dc bias field sequences (FC and FC-FH) will be discussed in Sec. IV. Figure 1 shows the real part of the complex dielectric constant obtained in the ZFH run on the sample cooled in a dc bias field of 8.5 kV/cm. Besides the broad dispersive dielectric maximum, typical for relaxors, also a peak at $\approx260$ K can be observed. The maximum value of the peak was found to be frequency dependent. Its temperature position, however, did not depend on the frequency, contrary to the broad peaks associated with the ergodic relaxor phase.

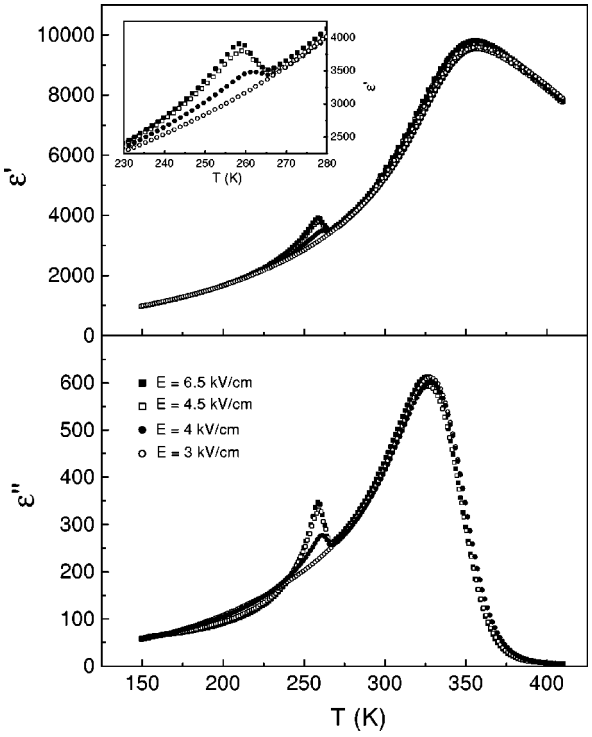


FIG. 2. Temperature dependence of the real and imaginary parts of the complex dielectric constant measured at 10 kHz in the FC-ZFH run at several dc bias fields. The inset shows peaks indicating the ferroelectric to relaxor phase transition.

The real and imaginary parts of the complex dielectric constant obtained during FC-ZFH measurements in different dc bias fields are shown in Fig. 2. For simplicity, only results obtained at one frequency (10 kHz) and in four different bias fields are shown. While at $E=3$ kV/cm no peaks were observed, at $E=4$ kV/cm rounded peaks appear at the same temperature in both, the real and imaginary part of the complex dielectric constant. Above $E=4.5$ kV/cm these rounded peaks become sharper, thus indicating the ferroelectric to ergodic relaxor phase transition. Similar results have been reported in 8/65/35 PLZT ceramics.[11] In addition, the observed hysteresis loops prove the FE nature of the field induced low- temperature phase with the typical value for the remanent polarization of $5\mu C/cm^2$.

The depolarization temperatures were determined from the temperature positions of peaks, obtained after the subtraction of the dielectric background coming from the broad relaxor dielectric peak. Two of the resulting peaks, obtained during FC-ZFH measurements in two different dc bias fields, are shown in Fig. 3. On the low-temperature side, FE-ER peaks can be rather well fitted to the Curie-Weiss law. On the other hand, the decay on the high-temperature side of the peak is too sharp for the continuous mean-field behavior, thus indicating that the transition between the field induced long-range ferroelectric and the ergodic relaxor phase could be weakly first order.

### B. Temperature dependence of the dielectric response below $E_C$

Similar to the other relaxor materials, no transition anomaly in the dielectric response of the 9/65/35 PLZT ceramics can be detected below the threshold field $E_C$.[10,11] Here, the relaxor system undergoes a transition from the ergodic into the low-temperature nonergodic state.[17] The freezing process in the 9/65/35 PLZT ceramics[17] is qualitatively similar to that observed in the PMN system[16] and deuteron glasses,[28] in which the divergence of the longest relaxation time effectively breaks ergodicity at a Vogel-Fulcher freezing temperature $T_0$. Similar to the PMN system,[5,6] the freezing temperature in 9/65/35 PLZT ceramics was found to be nearly the same as the depolarization temperature obtained at $E>E_C$.[17] However, the freezing process in 9/65/35 PLZT ceramics has been studied only in zero dc bias field, i.e., in the regime of the pure relaxor state. Here we report results of measurements of the dielectric dynamics obtained in various dc bias fields smaller than $E_C$, i.e., in the relaxor to ferroelectric crossover regime.

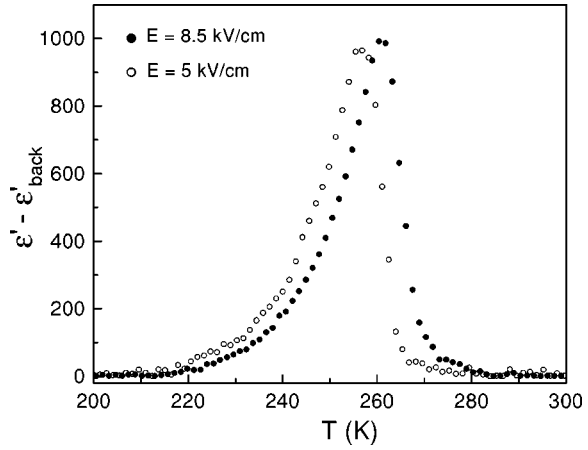


FIG. 3. Real part of the complex dielectric constant obtained in the FC-ZFH run for two different dc bias fields after subtraction of the background. The depolarization temperatures of the ferroelectric to ergodic relaxor phase transition were determined from the peak positions.

The information about the behavior of the relaxation spectrum and thus about the dynamic process was directly extracted by using a so-called temperature-frequency plot.[28] This method has already been successfully applied to various glassy systems,[28–31] and recently also to the 9/65/35 PLZT ceramics[17] in zero dc bias field. The extended description of this method is given in Refs. 28 and 32. The essential point is that by varying the reduced dielectric constant

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

different segments of the relaxation spectrum $g(z)$ are being probed. Here, the distribution of relaxation times is limited by the lower and upper cutoffs $z_1$ and $z_2$. In this procedure, the knowledge of the parameters $\varepsilon_s$ and $\varepsilon_\infty$ is necessary. As pointed out in (Ref. 17), the aging process substantially reduces the value of $\varepsilon_s$ in the first few hours after annealing. Therefore it is necessary to study the dynamics on the sample, which was previously aged in a particular dc bias field. Typical aging time was one day.

The temperature-frequency plot obtained from measurements in the dc bias field of 1 kV/cm is shown in Fig. 4. Since the aim of our work was determination of the transi-

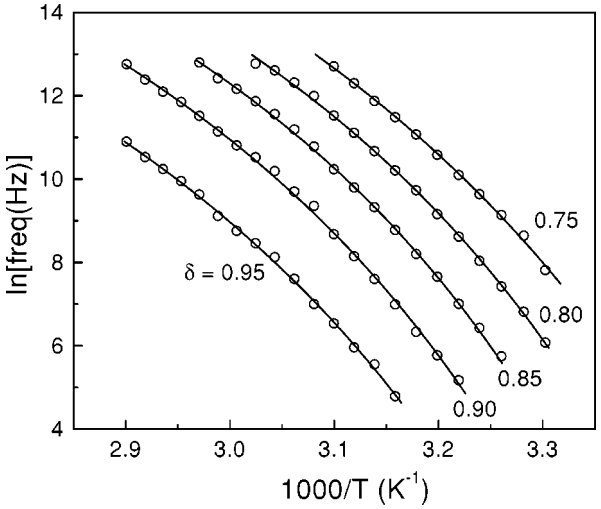


FIG. 4. Temperature-frequency plots for several fixed values of the reduced dielectric constant $\delta$ determined at the dc bias field of 1 kV/cm. Solid lines are fits obtained with a generic Vogel-Fulcher expression.

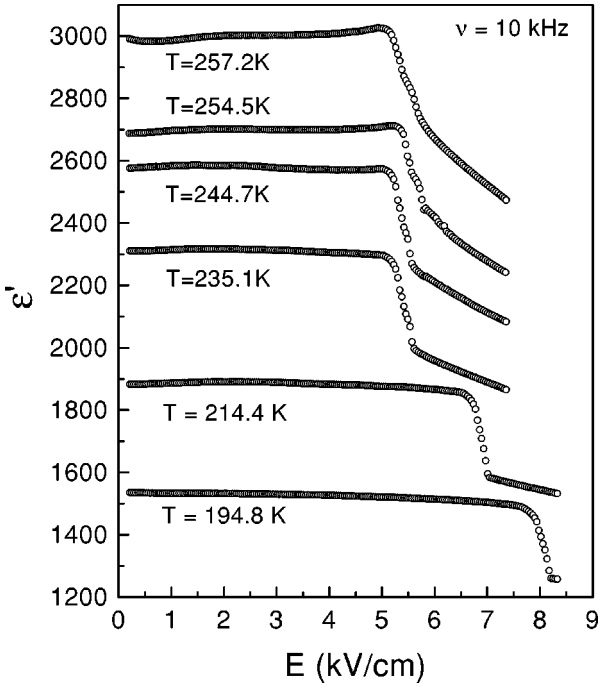


FIG. 5. Real part of the complex dielectric constant as a function of the dc bias field measured at several fixed temperatures below the freezing temperature $T_0$.

tion temperatures, only values of $\delta$ close to 1 are shown. The results are very much similar to the ones observed under zero-field conditions.[17] Bent curves indicate the divergence of the longest relaxation time that can be described by the Vogel-Fulcher law

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

Each $\delta$ curve in Fig. 4 was fitted separately to Eq. (2). Then fitting parameters were extrapolated to $\delta = 1$ giving values of $T_0 = 259 \pm 4$ K, $f_{02} = 1/2\pi\tau_{02} = (9.7 \pm 0.6) \times 10^9$ Hz, and $U = 1100 \pm 200$ K. In the same way, the frequency-temperature plot in the zero dc bias field gives $T_0 = 259 \pm 4$ K, $f_{02} = (6.5 \pm 0.5) \times 10^9$ Hz, and $U = 1000 \pm 100$ K, and for the dc bias field of 2.5 kV/cm $T_0 = 258 \pm 8$ K, $f_{02} = (5.3 \pm 0.8) \times 10^{13}$ Hz, and $U = 1800 \pm 400$ K. It is interesting to note that by increasing the dc bias field the activation energy and the frequency $f_{02}$ increase. The freezing temperature was found to be independent of the magnitude of the dc bias field and within the error of determination it coincides with the depolarization temperature at $E_C$. The analysis described above was performed only in the temperature range where $\varepsilon_s$ was exactly known, while $\varepsilon_\infty$ was estimated to be very small in comparison to $\varepsilon'$ and could thus be neglected (see details in Ref. 17).

### C. Dielectric response as a function of a dc bias field measured at fixed temperatures

In order to study the R-FE phase transition in the field direction of the approach to the FE ordered state the complex dielectric constant as a function of the dc bias field was measured at several constant temperatures. The electric-field dependence of the real part of the complex dielectric constant obtained at several temperatures below the freezing temperature $T_0$ is shown in Fig. 5. Due to the similarity of the results obtained at different frequencies in the range from 100 Hz–100 kHz only those obtained at frequency of 10 kHz are shown. It can be seen that the real part of the complex dielectric constant starts to decrease very steeply above some threshold field. Such dependence is the result of a first-order transition from the nonergodic relaxor state to a long-range ferroelectric order.[9,17] However, even at fields above the critical one, the real part of the dielectric constant is still decreasing, indicating that the long-range ferroelectric phase is still incompletely ordered. The persistence of the logarithmic relaxation process in such a field induced phase transition has been clearly shown in the PMN relaxor.[9]

In the temperature range from 259 K down to 235 K the critical bias field is almost independent of the temperature, however for temperatures below 235 K $E_C$ starts to increase (see Fig. 5). Above $T_0$, $E_C$ is increasing with increasing temperature, as shown in Fig. 6. By comparing Figs. 5 and 6 different behavior of the real part of the dielectric constant below $E_C$ can be seen. Below $T_0$, in the nonergodic relaxor phase, $\varepsilon'$ was more or less constant, while above $T_0$ the real part of the dielectric constant is increasing with increasing dc bias field all the way up to the critical field. Similar behavior in the ergodic relaxor phase has already been reported in the PMN crystal[33,34] and 9/65/35 PLZT ceramics,[35] and has been explained as being a consequence of the dc bias field induced reorientation of the polar nanoregions, favoring their alignment in the direction of the field.[34]

Figure 7 shows the imaginary part of the complex dielectric constant. Its dependence on the dc bias field is very similar to the dependence of the real part. At temperatures above $T_0$, the initial decrease at low fields in both, the real and imaginary parts is probably a result of the interfering aging process, since the measurement was initiated immediately after the sample was cooled from 410 K to a particular fixed temperature.

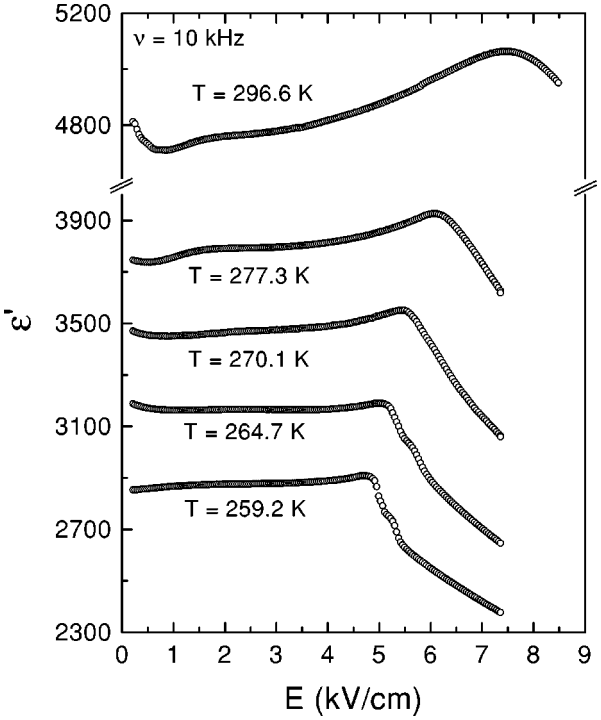


FIG. 6. Real part of the complex dielectric constant as a function of the dc bias field measured at several fixed temperatures above the freezing temperature $T_0$.

## IV. ELECTRIC-FIELD–TEMPERATURE PHASE DIAGRAM

The experiments described in the previous section enable construction of the E-T phase diagram of 9/65/35 PLZT ceramics shown in Fig. 8. The transition lines separating various phases are drawn through the experimental points indicating phase-transition temperatures. Since the transition lines were found to depend on the way of the approach to the FE phase, the phase diagram is shown for each of these two directions — the temperature and the dc bias field direction. In both Figs. 8(a) and 8(b) arrows indicate the direction of the crossing over the specific transition line.

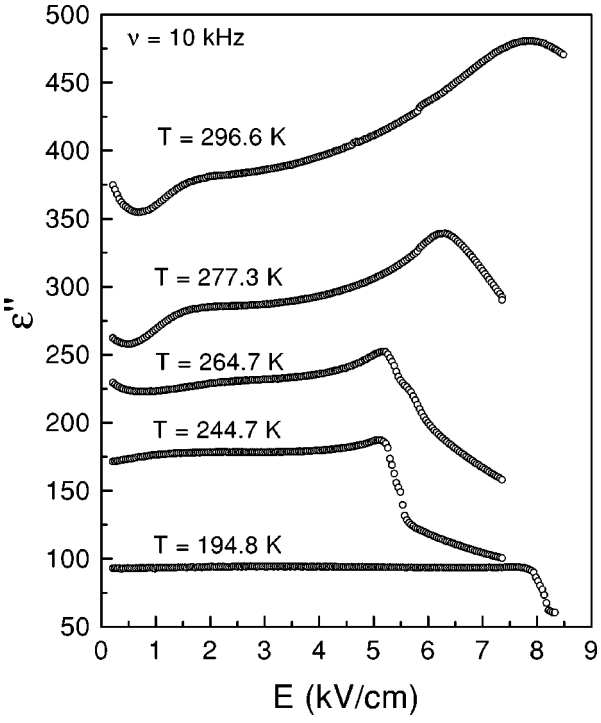


FIG. 7. Imaginary part of the complex dielectric constant as a function of the dc bias field measured at several fixed temperatures.

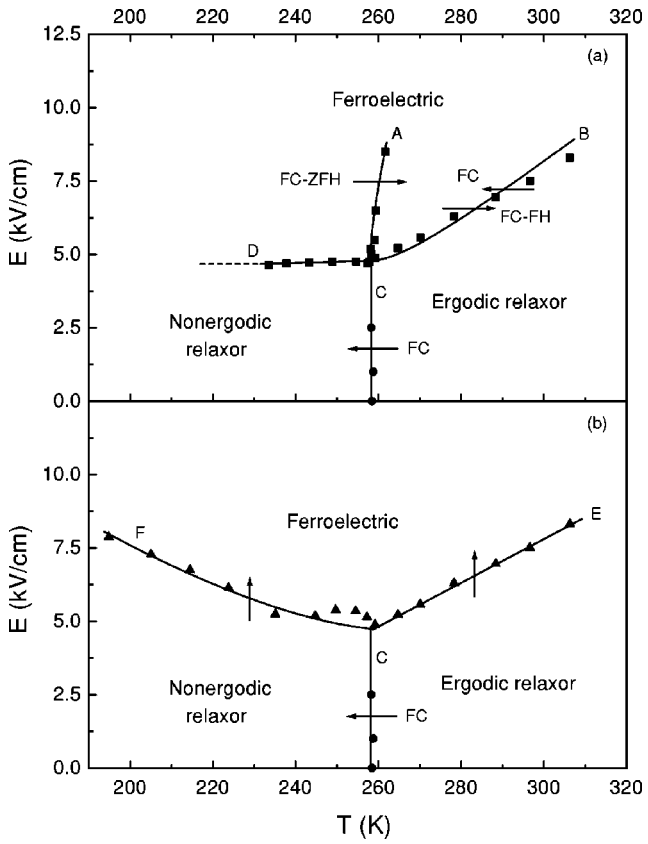


FIG. 8. E-T phase diagram of 9/65/35 PLZT ceramics, when (a) FE phase is approached in the temperature direction or (b) in the dc bias field direction. The transition lines between various phases were determined on the basis of three different types of measurements: (i) squares denote transition temperatures determined from the FC-ZFH and FC-FH complex dielectric constant, (ii) circles denote freezing temperatures determined from temperature-frequency plots, and (iii) triangles denote critical field, which was obtained from the dc bias field dependent dielectric response measured at fixed temperatures. Arrows indicate the direction of the crossing over the specific transition line.

### A. The temperature direction of the approach to the ferroelectric phase

The phase diagram, constructed on the basis of the temperature dependent complex dielectric constant measured at several fixed dc bias fields, is shown in Fig. 8(a). The line A indicates temperatures (denoted by squares) of the ferroelectric to ergodic relaxor phase transition, determined from FC-ZFH measurements described in the Sec. III A. Line C indicates the freezing transition line separating the ergodic from the nonergodic relaxor state. Freezing temperatures determined from frequency-temperature plots (see Sec. III B) in different dc bias fields are denoted by circles. They nearly

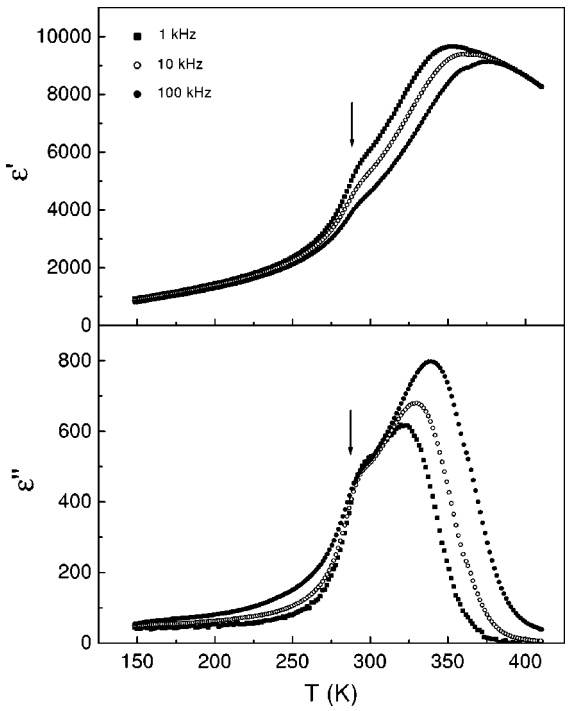


FIG. 9. Temperature dependence of the real and imaginary parts of the complex dielectric constant measured at several frequencies in a FC-FH run. Arrows indicate the position of the anomalies corresponding to the transition from the field induced ferroelectric to ergodic relaxor phase, which in this particular dc bias field sequence of 6.5 kV/cm occurs at $\approx 25$ K higher temperature than in the case of the FC-ZFH run.

coincide with the depolarization temperature at $E_C$, similar to the case observed in the PMN system.[5,6]

The temperature dependence of the $E_C$ above $T_0$ [line E in Fig. 8(b), which will be discussed in the next subsection], suggests that one should enter the ferroelectric phase by crossing this line during cooling the sample under the dc bias field, i.e., at much higher temperatures than suggested by the depolarization line A. Indeed, anomalies in the temperature dependence of the FC and FC-FH complex dielectric constant exist at temperatures determined by line E, thus indicating the field induced relaxor to ferroelectric transition. The results of the FC-FH run obtained in the dc bias field of 6.5 kV/cm are shown in Fig. 9. Distinctive change in slopes of both the real and imaginary part of the complex dielectric constant (denoted by arrows) marks the FE-ER phase transition, which takes place at higher temperatures than in the FC-ZFH run. Therefore on the basis of the FC and FC-FH complex dielectric constant (results are denoted by squares) a new line B indicating the ER-FE and FE-ER field induced phase transitions was drawn. As already pointed out, this transition line coincides with the line E shown in Fig. 8(b). It should be stressed, however, that hysteresis in transition temperatures of 5 K for the FC and FC-FH measurements was found, perhaps indicating a weak first-order character of the field induced ER-FE transition.

### B. Random bond-random field model of relaxor ferroelectrics

We now discuss the properties of PLZT ceramics in terms of the recently proposed spherical random bond-random field (SRBRF) model of relaxor ferroelectrics,[36] which was initially developed for PMN. In analogy to PMN the glassy behavior of the system is expected to be due to reorientable polar clusters embedded in a random array of chemically ordered nanodomains. We introduce a dimensionless order parameter field $\vec{S}_i$, related to the dipole moment of the polar cluster $C_i$. The vector $\vec{S}_i$ has a large number of equilibrium orientations lying on a quasispherical shell of radius $|\vec{S}_i|$, which scales with the number of unit cells $n_i$ in $C_i$. Here $i=1,2,\ldots,N$, where $N$ is the total number of reorientable clusters. Going over to the continuous limit we assume that each component $S_{i\mu}$ $(\mu=x,y,z)$ varies in the range $-\infty<S_{i\mu}<+\infty$, and that the set of all fields is subject to the spherical constraint

$$\sum_{i=1}^{N} \vec{S}_i^2 = 3N. \tag{3}$$

The Hamiltonian of a relaxor ferroelectric is written in the form

$$H=-\frac{1}{2}\sum_{ij} J_{ij}\vec{S}_i\cdot\vec{S}_j-\sum_i \vec{h}_i\cdot\vec{S}_i-\sum_i \vec{E}\cdot\vec{S}_i, \tag{4}$$

where $J_{ij}$ represents a set of randomly frustrated interactions or bonds, which are infinitely ranged and are characterized by the mean value of the coupling $[J_{ij}]_{av}=J_0/N$ and the variance $[J_{ij}^2]_{av}^c=J^2/N$. The random fields $\vec{h}_i$ are similarly characterized by the variance $[h_{i\mu}h_{j\nu}]_{av}=\delta_{ij}\delta_{\mu\nu}\Delta$.[37] There are in general two order parameters in the system, namely, the polarization $\vec{P}$ with components

$$P_\mu=\frac{1}{N}\sum_{i=1}^{N}\langle S_{i\mu}\rangle, \tag{5}$$

and the glass order parameter

$$q_\mu=\frac{1}{N}\sum_{i=1}^{N}\langle S_{i\mu}\rangle^2. \tag{6}$$

In an isotropic system or a pseudocubic system with $\vec{E}\|[111]$, both order parameters are $\mu$ independent, i.e., $P_\mu=P$ and $q_\mu=q$. Since in a ceramic system all orientations are represented with the same average probability, we will in the following limit ourselves to the above isotropic case with only two order parameters $P$ and $q$.

After applying the replica trick and imposing the spherical constraint (3) (Ref. 38) the average free energy can be calculated leading to the following coupled equations for the order parameters:

$$q=\beta^2J^2(q+\Delta/J^2)(1-q)^2+P^2, \tag{7}$$

$$P=\beta(1-q)(J_0P+E). \tag{8}$$

By analyzing the solutions of these equations we are led to the following conclusions: For $E=0$ and $J_0<J_{0c}\equiv(J^2+\Delta)^{1/2}$ a spherical glass state $(q\neq 0)$ without long-range order $(P=0)$ is formed. If $E=0$ and $J_0>J_{0c}$, an inhomogeneous ferroelectric state with a nonzero polarization $(P\neq 0)$ becomes stable for $T<T_c$, where

$$kT_c = J_0\left(1 - \frac{\Delta}{J_0^2 - J^2}\right). \tag{9}$$

In case of a nonzero electric field ($E \neq 0$), Eqs. (7) and (8) can easily be solved numerically, yielding $q = q(E,T)$ and $P = P(E,T)$, from which the derivatives such as the dielectric susceptibility $\chi(E,T) = \partial P/\partial E$ can be obtained.

Returning to the E-T phase diagram, we realize that a change from a glassy phase to a ferroelectric one in a field $E$ can occur if the parameter $J_0$ is $E$ dependent, i.e., $J_0 = J_0(E)$, which can be explained, in principle, by the field induced polarization-strain coupling.[39] Thus a critical field $E_C$ may exist such that for $E > E_C$ one has $J_0(E) > J_{0c}$. We can express $J_0(E)$ as a power series to leading term in $E$,

$$J_0(E,T) = J_{0c} + J_1\left[\left(\frac{E}{E_C(T)}\right)^2 - 1\right]. \tag{10}$$

As long as $J_0 < J$ one can draw a vertical transition line C in the E-T phase diagram between the ergodic and nonergodic relaxor phases at a freezing temperature

$$kT_0 = \sqrt{J^2 + \Delta}, \tag{11}$$

which is independent of the applied dc bias field $E$. For $E$ above $E_C$ and $J_0 > J_{0c}$, the temperature of the relaxor to ferroelectric phase transition can be determined from the temperature position of the peak in the dielectric susceptibility

$$\chi = \frac{\beta(1-q)(1 + 2J_1 PE/E_C)}{1 - \beta J_0(1-q) + 2\beta P(J_0 P + E)G}, \tag{12}$$

where $1/G \equiv 1 + 2\beta^2 J^2(q + \Delta/J^2)(1-q) - \beta^2 J^2(1-q)^2$. This can be done formally, since the observed weakly first-order transition seems to be close to the predicted continuous mean-field behavior.

Using $J/k = 258.4$ K, $J_{0c}/J = 1.01$, $J_1/J = 0.04$, and $\Delta/J^2 = 0.0058$, the temperature dependences of $q$ and $P$ in various dc bias fields were determined by simultaneous solution of Eqs. (7) and (8). Temperature position of the peaks in the dielectric susceptibility were then determined from Eq. (12), resulting in transition line B [solid line in Fig. 8(a)], which agrees well with experimental results.

In the case of the temperature direction of the approach to the FE phase in a FC-ZFH run, one can draw another phase transition line D separating FE and nonergodic relaxor phases. This critical field line of $4.8 \pm 0.1$ kV/cm was determined as the dc bias field, at which the real part $\varepsilon'$ of the FE peaks (see inset to Fig. 2) becomes saturated. The procedure was performed in a way, such that the value of $\varepsilon'$ obtained at a specific temperature during FC-ZFH runs was plotted as a function of the fixed dc bias field, which had been applied during cooling. The results of this procedure performed at 243.3 K are shown in Fig. 10. In this manner, the critical field separating FE and NR phases (denoted by squares) was determined as a function of the temperature.

### C. The dc bias field direction of the approach to the ferroelectric phase

Figure 8(b) shows the phase diagram obtained in the case of the approach to the ordered FE phase in the dc bias field direction. Lines E and F indicate the critical dc bias field, at which the long-range ferroelectric order is induced. Line E indicates transition temperatures between ER and FE phases, and line F divides NR and FE phases. These two lines (denoted by triangles) were determined from measurements of the complex dielectric constant as a function of the dc bias field at constant temperatures as described in Sec III C. For orientation, the transition line C which separates the ergodic from the nonergodic relaxor state is plotted again.

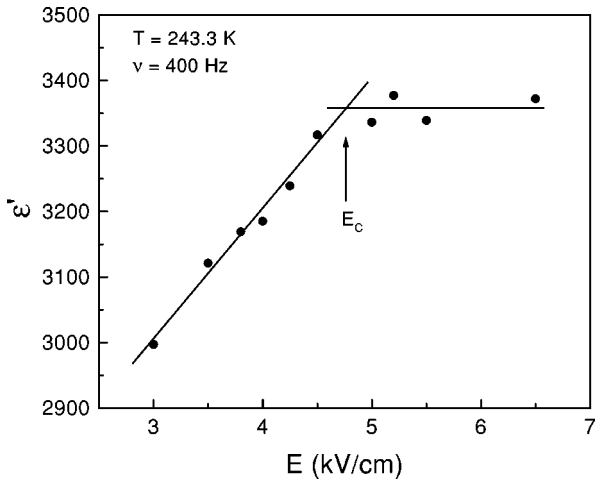


FIG. 10. Real part of the complex dielectric constant obtained at 243.3 K during FC-ZFH runs as a function of the fixed dc bias field applied during cooling. The critical field of 4.8 kV/cm (indicated by arrow) was determined as a dc bias field, at which the value of $\varepsilon'$ becomes saturated.

While line E in Fig. 8(b) coincides with line B in Fig. 8(a), which means that the transition temperatures between ER and FE phase are independent of the way of the approach to the FE phase, it is interesting to note that the temperature dependence of the line F in Fig. 8(b) differs considerably from line D in Fig. 8(a). Obviously, when the system is cooled in zero dc bias field conditions and undergoes a transition into the nonergodic relaxor phase, a higher dc bias field is needed to induce the FE phase than in case, when the system is cooled down in the dc bias field. Similar to line B, the experimental transition line E was approximated by using Eq. (12). Here, the transition temperatures were determined from the field position of the peaks in the dielectric susceptibility calculated as a function of the dc bias field at fixed temperatures.

It should be mentioned that transition lines A and F are dynamic quantities dependent on the experimental time scale. Therefore they cannot be in principle described by the results of the static spherical random bond-random field model. The solid lines A and F in Fig. 8 are thus just guides to the eye.

## V. CONCLUSIONS

On the basis of the dielectric response measured in two different ways of approach to the FE phase, the temperature and dc bias field directions, the E-T phase diagram of the 9/65/35 PLZT ceramics was constructed. In the temperature direction, by cooling the system in the dc bias field above $E_C$ a relaxor to ferroelectric phase transition was induced, while

by cooling below $E_C$ the system undergoes the transition from the ergodic to the nonergodic relaxor state at a freezing temperature $T_0$, at which the divergence of the longest relaxation time effectively breaks ergodicity. It was found that the freezing temperature $T_0$ is independent of the magnitude of the dc bias field and it coincides with the depolarization temperature determined at $E_C$.

In the field direction of the approach to the FE phase the temperature dependence of the critical field $E_C$ was determined. It was found that above $T_0$ the critical field is increasing with increasing temperature, while $\approx 25$ K below $T_0$ it starts to increase again with decreasing temperature. This behavior was not observed in the FC-ZFH run, thus suggesting that higher dc bias field is needed to induce the FE phase when the system is cooled in zero dc bias field conditions from ER into NR phase than in the case, when the system is cooled down in the ER phase in a dc bias field. The ER-NR and ER-FE transition lines can be well described by a spherical random bond-random field model of relaxor ferroelectrics.

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