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Dielectric behavior of lead magnesium niobate relaxors

Z.-Y. Cheng* and R. S. Katiyar
Department of Physics, P.O. Box 23343, University of Puerto Rico, San Juan, Puerto Rico 00931-3343

X. Yao
Electronic Materials Research Laboratory (EMRL), Xi'an Jiaotong University, Xi'an 710049, China

Aqiang Guo
Department of Technological Physics, P.O. Box 207, Xidian University, Xian 710071, China

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The dielectric behavior of a solid solution, 10 mol % lead titanate in lead magnesium niobate, is measured at different frequencies from 100 Hz to 100 kHz in the temperature range from −100 to 120 °C. A standardizing method is introduced to analyze the curve of the dielectric constant vs temperature. It results a master curve behavior between the dielectric constant and temperature at temperatures higher than the temperature of the dielectric constant maximum. The dielectric relaxation behavior is analyzed with various models. The best way to characterize the degree of the dielectric relaxation for relaxor ferroelectrics is established using the experimental data. It is indicated that the temperature dependence of the static dielectric constant can be well described by an exponential function, while the temperature dependence of the relaxation time is described by a superexponential function. Based on the specialty of the relaxor ferroelectrics, a distribution function for the relaxation times is introduced and a model is introduced to simulate the dielectric behavior of the relaxor ferroelectrics. The model can express well both the temperature and frequency dependence of the dielectric behavior for a relaxor ferroelectrics. All of the parameters in the fitting formula can be experimentally determined. The model shows that in the low-temperature range, there are two simple relationships about the dielectric frequency spectrum: $\varepsilon''(\omega,T)=(-\pi/2)\partial\varepsilon'(\omega,T)/\partial\ln\omega$ and $\varepsilon'=B(T)*(\ln\omega_0-\ln\omega)$. These relationships are verified by the experimental results. A way to obtain the accurate value of ε_∞ in the low-temperature range is described. [S0163-1829(97)06713-1]

I. INTRODUCTION

Since the discovery of dielectric relaxation behavior in lead magnesium niobate (PMN) by Smolensky and Agranovskaya,[1] the studies on the relaxor ferroelectrics (RFE), especially with $\mathrm{Pb}(B'_{1/3}B''_{2/3})\mathrm{O}_3$-type and its solid-solution-type perovskites, have been intensified due to their excellent dielectric and electromechanical properties, on the one hand, and to their strange polarization mechanism on the other.[2] Therefore research on the RFE has two objects. One is to find high-performance materials for applications, and the other is to understand its polarization mechanism in theory. Many physical models have been proposed to explain the behavior of the RFE, for example, the inhomogeneous microregion model,[3,4] the micro-macro domain transition model,[5,6] the superparaelectric model,[2] the dipolar glass model and the glass model,[7,8] the order-disorder model,[9,10,11] the local electric field model,[12] etc. Although it is widely accepted that the behavior of the polar region (cluster) in the material is a key to the behavior of the RFE, a full understanding of the RFE's behavior does not exist yet.

The characterization of the dielectric behavior of a RFE is important for both applications and theoretical research. The main characteristic of the RFE is that a broad peak appears in the temperature dependence of the dielectric behavior, and so research on the characterization of the dielectric behavior of the RFE is focused on the relation between the dielectric constant and temperature. A great amount of work, which can be divided into three kinds, has been done on the characterization of the dielectric relaxation behavior of the RFE. The first kind is that which focuses on the characterization of the relationship between the dielectric constant and the temperature at temperatures higher than the temperature (T_m) of the dielectric constant maximum;[3,13] the second one is on the characterization of the frequency dependence of T_m,[7,8] and the last one is about the fitting of the temperature dependence of the dielectric constant.[14–16] However, there are some indeterminacy and some contradictions in the characterization.[15,17] Therefore, the characterization of the RFE's dielectric behavior is still an open problem.

The solid solution of PMN with the lead titanate (PT) is a typical system with perovskite structure, in which the phase transition behavior can change from a diffused phase transition to a typical ferroelectric phase transition.[18] It is, therefore, a very interesting system for research on the RFE. In this paper, we carefully measure the dielectric behavior of a solid solution in the PMN-PT system with a diffused phase transition. The experimental results and the general features of the RFE are given in Sec. II. Based on the experimental data, the characterization of the dielectric relaxation behavior of the RFE is investigated. The advantage and disadvantage of various characterizing methods are discussed. The temperature dependence of the static dielectric constant is given in Sec. III A based on the characterization study of the dielectric behavior at the temperatures much higher than T_m. The temperature dependence of the relaxation time and its

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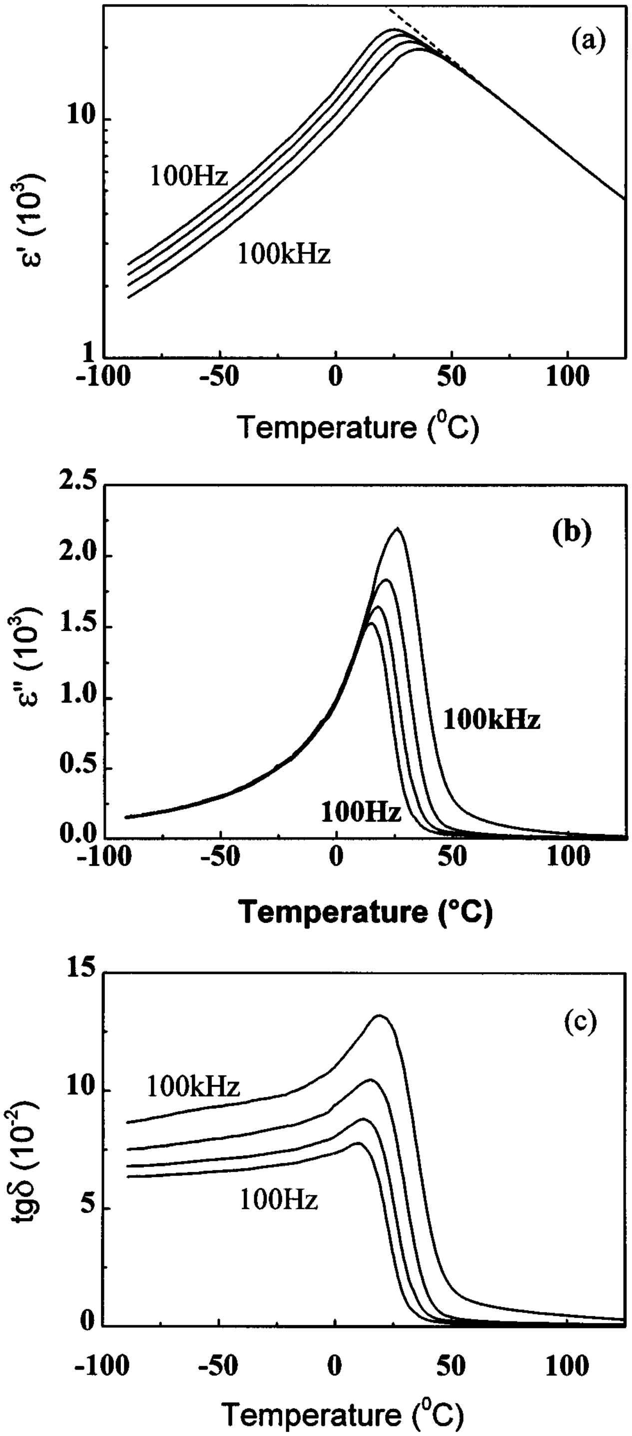

FIG. 1. Dielectric behavior as a function of temperature at measured frequency (0.1, 1, 10, and 100 kHz) for 0.9 PMN–0.1 PT with a cooling rate 0.8 °C/min. (a) Dielectric constant (ε') (solid line) and fitted results (dotted line) of Eq. (3) with $\alpha=10.70$ and $\beta=0.0182$. (b) Dielectric absorption (ε''). (c) Loss tangent ($\tan\delta$).

distribution are given in Sec. III B. A characterizing method is introduced based on it. The formula to simulate the dielectric behavior of the RFE is given in Sec. III C. In Sec. III D, the experimental results are used to verify the model. The discussion and comparison of our present model with the existing ones are given in Sec. IV, and finally the conclusions are given in Sec. V.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The starting materials of ultrahigh purity are used to prepare a solid solution ceramic of 10 mol % PT in PMN (0.9 PMN–0.1 PT). The perovskite-phase powders were synthesized through the columbite-precursor method as described in Ref. 19. The samples were prepared by the conventional ceramic processing. The gold electrodes were deposited on the surfaces of the disk-type samples by the dc sputtering. The capacitance and loss tangent were measured in the temperature range from 120 to −100 °C with a cooling rate of 0.8 °C per minute using an HP4274A LCR meter with a high-resolution function at the frequencies of 0.1, 0.12, 0.2, 0.4, 1, 2, 4, 10, 20, 40, and 100 kHz. The oscillating level of the signal was about 0.5 V/mm. The four test leads, which were connected directly to the electrodes of the sample, were used to increase the measuring accuracy. Before the measurement, a standard calibration was performed to remove any stray capacitance, lead, and contact resistance. The dielectric constant was calculated from the measured capacitance, with the geometric parameters of the sample, and using a parallel-plate capacitance model. The temperature was measured using an HP3455A multimeter via a 100-Ω platinum resistance thermometer. To increase the measuring accuracy of the temperature, a four-wire configuration was used to measure the resistance of the 100-Ω platinum resistance thermometer. The temperature controller, HP3455A, and HP4274A were interfaced to a computer.

Some measured dielectric constant (ε'), dielectric absorption (ε''), and loss tangent ($\tan\delta$) data versus temperature are shown in Fig. 1. It demonstrates a typical dielectric behavior of a RFE. The basic features of the dielectric behavior are the following.

(1) There is a broad peak in the dielectric constant as a function of temperature. With increasing frequency, T_m increases, while the magnitude of the peak decreases.

(2) There is a strong dielectric dispersion in radio frequency region around and below T_m. This dielectric dispersion does not obey the Debye theory.[8]

(3) At temperatures around and above its peak temperature (T'_m) of the dielectric absorption, the dielectric absorption exhibits a strong frequency dependence, i.e., the dielectric absorption increases with increasing frequency.

(4) The value of T'_m is much lower than that of T_m at the same frequency.

(5) With increasing frequency, T'_m shifts to higher temperature and the magnitude of the dielectric absorption peak increases.

(6) With decreasing temperature, the dielectric absorption increases rapidly in the temperature region around T_m.

(7) The dielectric absorption is nearly independent of the frequency (in fact, the dielectric absorption shows only a very small decrease with the increase of the frequency) at a temperature much lower than T'_m.

(8) With decreasing temperature in the lower-temperature range, although both the dielectric constant and the dielectric absorption rapidly decrease, the loss tangent decreases very little.

The maximum dielectric constant of the sample at 100 Hz is about 2.4×10^4 at T_m. Based on research on lead scandium tantalate relaxors,[20] the relaxor with the stoichiometric compound has the highest dielectric constant to compare with the nonstoichiometric compound. Thus a higher dielectric constant of the sample reflects the fact that the sample is of stoichiometric compound and is, therefore, an ideal candidate for research on basic behavior of the RFE.

III. CHARACTERIZATION AND MODEL OF DIELECTRIC RELAXATION FOR THE RFE

A. Temperature dependence of dielectric constant at temperatures higher than T_m

Since Smolenky's work,[3] the characterization of the temperature dependence of the dielectric constant, above T_m, has been widely studied with various models as an important feature to characterize the dielectric relaxation behavior of a RFE. There are mainly two methods, which have been widely used in research on the RFE, to characterize it. The first one is a quadratic relation, which was given by Smolensky as follows:[3]

$$\frac{1}{\varepsilon'(T,\omega)}=\frac{1}{\varepsilon_{\max}(\omega)}\left[1+\frac{[T-T_m(\omega)]^2}{2\delta^2}\right], \tag{1}$$

where ω is the angular frequency, T is the temperature, $\varepsilon_{\max}$ is the magnitude of the dielectric peak, and δ is a constant which was used to express the degree of the dielectric relaxation in a RFE. The second one is a power relation, which was given by Martirena and Burfoot as follows:[13]

$$\frac{1}{\varepsilon'(\omega,T)}=\frac{1}{\varepsilon_{\max}(\omega)}\left[1+\frac{[T-T_m(\omega)]^\gamma}{2\delta_\gamma^2}\right], \tag{2}$$

where δ_γ and γ are constants. The value of γ ($1\leqslant\gamma\leqslant 2$) is the expression of the degree of dielectric relaxation in a RFE. When $\gamma=1$, Eq. (2) expresses the Curie-Weiss behavior of the ferroelectrics, while for $\gamma=2$, Eq. (2) is identical to Eq. (1).

To find the most accurately experimental values of T_m and $\varepsilon_{\max}$, the curves of the dielectric constant vs the temperature for each frequency were smoothed and interpolated in a narrow temperature range around T_m. When Eq. (1) is used to fit the experimental results with the experimental values of both T_m and $\varepsilon_{\max}$, we find that the value of δ is indeed nearly a constant, provided that the fitting temperature range is far from T_m. But the fitted relation strongly deviates from the experimental point (T_m,$\varepsilon_{\max}$). Meanwhile, as the fitting temperature range is close to T_m, the value of δ is strongly dependent on the choice of both the frequency and temperature ranges used in the fitting process. As an example, the relation between $\varepsilon_{\max}(\omega)/\varepsilon'(\omega,T)$ and $(T-T_m)^2$ at 1 kHz for 0.9 PMN–0.1 PT is shown in Fig. 2.

The form of Eq. (1) can be also written as

$$\frac{1}{\varepsilon'(T,\omega)}=a+bT+cT^2, \tag{1$'$}$$

where a, b, and c are constants. All of T_m, $\varepsilon_{\max}(\omega)$, and δ are uniquely decided by the values of a, b, and c. Therefore all the values of T_m, $\varepsilon_{\max}(\omega)$, and δ can be directly given by using Eq. (1′) to fit the experimental relation between T and $\varepsilon'(T,\omega)$. When Eq. (1′) is used to fit the experimental results, for the temperature range far from T_m, even though the value of δ is indeed nearly a constant, the fitted values of T_m and $\varepsilon_{\max}(\omega)$ strongly deviate from their experimental values. For the fitting temperature range close to T_m, all of the values of T_m, $\varepsilon_{\max}(\omega)$, and δ are strongly dependent on both the frequency and temperature ranges used in the fitting process. As an example, the results of 1 and 100 kHz for 0.9 PMN–0.1 PT are shown in Table I.

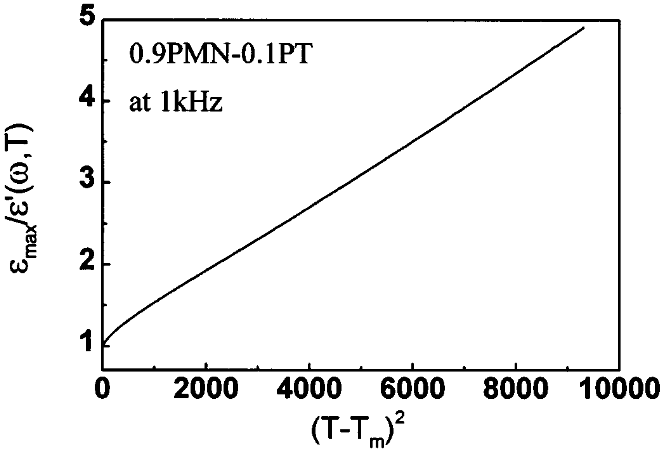

FIG. 2. $\varepsilon_{\max}/\varepsilon'(T)$ vs $(T-T_m)^2$ for 0.9 PMN–0.1 PT at 1 kHz at temperatures higher than T_m, where T_m and $\varepsilon_{\max}$ are the experimental results.

The above results indicate that the quadratic relation cannot characterize well the dielectric behavior of 0.9 PMN–0.1 PT at temperatures above T_m. Since the value of δ is dependent on the choice of the frequency and temperature ranges, there is indeterminacy in characterizing relaxation behavior of a RFE. For the power relation, the form of Eq. (2) can be changed to Eq. (2′) to fit the experimental results when the experimental values of both T_m and $\varepsilon_{\max}$ are used:

$$\begin{aligned} y&=\ln[\varepsilon_{\max}(\omega)/\varepsilon'(\omega,T)^{-1}]\\ &=\gamma\ln[T-T_m(\omega)]-\ln(2\delta_\gamma^2). \end{aligned} \tag{2$'$}$$

So a linear relation will be expected between y and $\ln(T-T_m)$. However, as shown in Fig. 3, the relation between y and $\ln(T-T_m)$ cannot describe correctly a linear function, even though the relation is nearly a linear function in the temperature range from T_m to about T_m+10 °C. Moreover, the power function cannot characterize well the experimental results adequately. Thus it is very difficult to use the value of γ to characterize the degree of the dielectric relaxation behavior in a RFE. Therefore the characterization of the dielectric constant at the temperatures above T_m is still an open problem for the research on the RFE.

Based on the dielectric relaxation theory,[21] for a material with a relaxation polarization, when the temperature is very high, the relaxation time (τ) of the relaxation polarization is very small, and so the measured dielectric constant at radio frequency equals the static dielectric constant (ε_s). On decreasing the temperature, both ε_s and τ monotonically increase, and the measured dielectric constant deviates from ε_s to a lower value. Therefore the dielectric relaxation behavior of a material with a relaxation polarization is dependent on two factors, vs the temperature dependence of ε_s and that of τ. Here ε_s is dependent on both the dipole moment and the

TABLE I. Fitted results of T_m, $\varepsilon_{\max}$, and δ using the experimental results at 1 and 100 kHz with Eq. (1a) in different temperature range at temperatures above T_m.

Temperature range (°C)	1 kHz			10 kHz		
	δ (K)	T_m (°C)	$\varepsilon_{\max}$	δ (K)	T_m (°C)	$\varepsilon_{\max}$
Measured[a]		28.077	22 690		35.758	19 781
T_m–50	36.2	18.983	23 652	29.6	33.218	15 827
T_m–70	40.6	12.294	24 852	38.1	24.587	21 004
30–60	40.8	11.211	25 204			
40–70	41.1	10.467	25 392	39.7	20.038	22 058
50–80	39.7	18.721	22 689	39.8	20.144	22 002
60–90	38.8	26.488	20 179	38.9	27.111	19 850
70–100	38.3	32.801	18 146	38.4	33.228	17 962
80–110	38.3	38.867	16 289	38.3	39.218	16 134
90–120	38.6	45.258	14 381	38.6	44.095	14 659

[a] Measured results of both T_m and $\varepsilon_{\max}$ are obtained by fitting the curve of the dielectric constant vs temperature in a small temperature range around T_m.

concentration of the dipoles in the material, and the dipole orientations under an external electric field, while τ is the orientational relaxation time of the dipoles under external electric field, which is dependent on both the activation energy and the infinite relaxation time (τ_0) of the dipoles. Therefore it needs at least two sets of parameters to characterize the dielectric relaxation behavior of a material system with a relaxation polarization process.

It is widely known that the dielectric relaxation behavior of the RFE originates from the polar regions (clusters) in the material.[2,3,5–8] A polar region is something like a dipole; i.e., a RFE is a material with a special kind of the relaxation polarization. Thus the measured dielectric constant of a RFE at temperatures much higher than T_m can be used to estimate its ε_s and to characterize the temperature dependence of ε_s. It was experimentally found that the relation, between ε' and T at temperatures much higher than T_m in the RFE, can be expressed as follows:[8,22]

$$\varepsilon'(T)=\exp[\alpha-\beta(T-273.15)], \tag{3}$$

where α and β are the constants, and they are larger than zero. The fitted results for 0.9 PMN–0.1 PT are shown in Fig. 1, where $\alpha=10.70$ and $\beta=0.0182$/°C. The stability of the fitted parameters, with the change of both the temperature range and the frequency used in the fitting process, is shown in Table II. The results in Table II clearly show that Eq. (3) can describe well the dielectric behavior of the material at temperatures much higher than T_m. Based on the general dielectric relaxation theory,[21] the orientational polarizability of the dipole is proportional to the inverse of the absolute temperature. Thus, to express the static dielectric constant of the RFE, we can modify Eq. (3) to Eq. (3a):

$$\varepsilon_s=\frac{1}{T}\exp[\alpha'-\beta'(T-273.15)], \tag{3a}$$

where T is the absolute temperature and α' and β' are the constants. We can use the value of β' in Eq. (3a) as a parameter to characterize the producing process of the polar regions in the RFE. The fitted results are $\alpha'=16.356$ and $\beta'=0.0156$ for 0.9 PMN–0.1 PT.

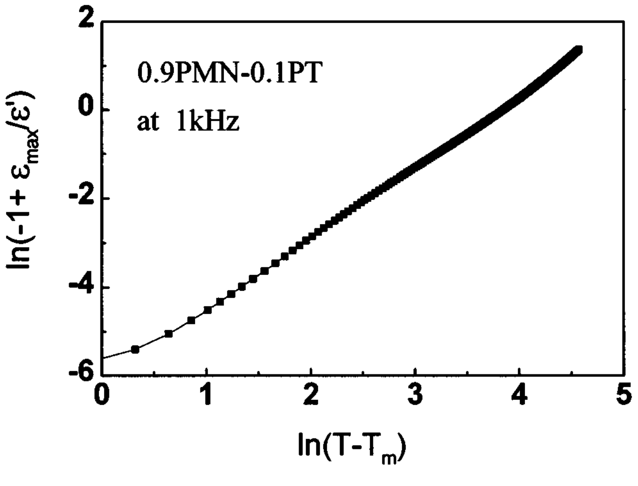

FIG. 3. $y=\ln(\varepsilon_{\max}/\varepsilon'(T)^{-1})$ vs $\ln(T-T_m)$ for 0.9 PMN–0.1 PT at 1 kHz at temperatures higher than T_m, where T_m and $\varepsilon_{\max}$ are the experimental results.

It is very interesting to compare Eqs. (1), (2), and (3) for the degree of characterization of the dielectric relaxation behavior in a RFE. Both Eqs. (1) and (2) attempt to describe the degree of the dielectric relaxation behavior at temperatures higher than T_m with only one set of parameter: there-

TABLE II. Fitted results of α and β using the experimental results at 1 and 100 kHz with Eq. (3) in different temperature ranges at temperatures above T_m.

Temperature range (°C)	1 kHz		100 kHz	
	α	β (1/°C)	α	β (1/°C)
40–70	10.58	0.0164	10.53	0.0157
50–80	10.63	0.0173	10.62	0.0171
60–90	10.67	0.0179	10.67	0.0178
70–100	10.70	0.0183	10.70	0.0182
80–110	10.71	0.0183	10.71	0.0183
90–120	10.69	0.0182	10.69	0.0181

fore, they have some intrinsic shortcomings to characterize the dielectric relaxation behavior of a RFE. In addition, as indicated in the above discussion, they cannot fit well the experimental results. Meanwhile, it was also found that there was not a good corresponding relation between the value of either δ or γ and the degree of the dielectric relaxation in the RFE.[17,23] Thus either δ or γ in Eqs. (1) and (2), respectively, is not a good parameter to completely characterize the degree of dielectric relaxation behavior of a RFE. Moreover, it is widely known that in the RFE the volume fraction of the polar regions monotonically increases with decreasing temperature. Equation (1) is not a monotonic function of temperature. Thus, although Eq. (1) may be used to describe the dielectric behavior of the material at high temperature, it cannot be used to describe the temperature dependence of ε_s for a RFE. Equation (3), though it can well describe the temperature dependence of ε_s for a RFE, requires another parameter to characterize the temperature dependence of the relaxation time in the material to adequately describe the degree of dielectric relaxation for the material, because as discussed above the degree of dielectric relaxation (or the width of the peak) is dependent on the temperature dependence of both ε_s and τ. In addition, Eqs. (1) and (2) have three and four parameters, respectively, in the fitting process, but Eq. (3) has only two parameters. Thus the good fitted results indicate the reasonability and correctness of Eq. (3). By the way, all of δ, γ, and β' (or β) have a common advantage, which is error free from the geometric parameters of the sample, since the geometry parameters only affect $\varepsilon_{\max}$ in Eqs. (1) and (2) and α in Eq. (3), respectively.

To find more information from the temperature dependence of the dielectric constant at temperatures higher than T_m, the dielectric constants at different frequencies are compared with a standardizing method which is somewhat analogous to the method used by Jonscher *et al.* to analyze the frequency dependence of the dielectric absorption;[21] i.e., the dielectric constant at a frequency is divided by its experimental maximum value ($\varepsilon'_{\max}$) to get the normal dielectric constant, while the normal temperature is equal to the real temperature minus experimental value of T_m. The results for 0.9 PMN–0.1 PT at 11 frequencies from 100 Hz to 100 kHz are shown in Fig. 4, which clearly indicates that there is a master curve between the normal dielectric constant and the normal temperature for the dielectric constant of the material at the temperatures higher than T_m. The existence of a master curve confirms the correctness in using Eq. (3a) to express ε_s.

B. Temperature dependence of the relaxation time and distribution of relaxation times

Based on the above discussion, the relaxation time increases with decreasing temperature. The larger the relaxation time is, the more the measured dielectric constant deviates from ε_s. Thus the peak of the dielectric constant is dependent on the temperature dependence of both ε_s and τ. That is, the peak of the dielectric constant contains information of both ε_s and τ. The master curve in Fig. 4 also shows that the peaks of the dielectric constant at different frequencies for the materials originate from only one mechanism. Thus we can use the frequency dependence of T_m to get insight into the temperature dependence of the relaxation time. Because the Debye relationship cannot describe the relationship,[7,8] two models have been introduced to characterize the relationship. One is the Vogel-Fulcher (VF) relationship based on considering the concept of a polar glass.[7] It shows that the relaxation time (τ_{VP}) in the Vogel-Fulcher model is dependent on T as given below:

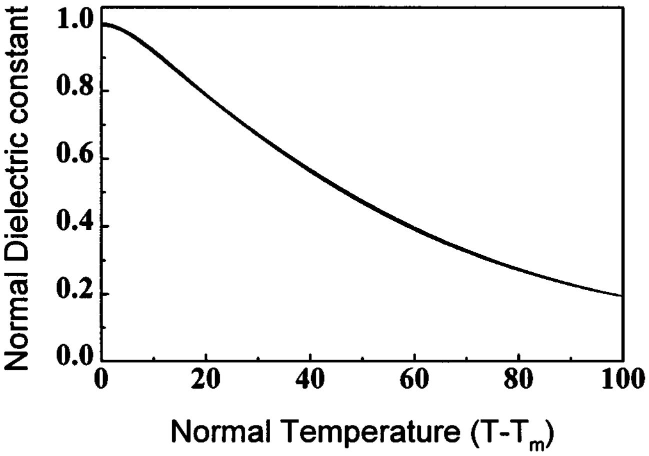

FIG. 4. Master curve for 0.9 PMN–0.1 PT at temperatures higher than T_m. There are 11 curves with different frequencies from 100 Hz to 100 kHz, where T_m and $\varepsilon_{\max}$ are the experimental results.

$$\tau_{\mathrm{VP}}=\frac{1}{\omega_0}\exp\left(\frac{T_0}{T-T_f}\right), \qquad (4)$$

where ω_0 is the attempt frequency of a microdipole (or the Debye frequency), T_0 is the equivalent temperature of the activation energy of the relaxation process, and T_f is the freezing temperature of the polar regions in a RFE.

Because Eq. (4) is singular at T_f, it cannot continuously describe the dielectric behavior of a RFE in the whole temperature range. In addition, there are some intrinsic shortcomings in Eq. (4) when it is used for the RFE.[8] A more reasonable model was proposed by Cheng *et al.*, which is based on the special features of the RFE. It shows that the temperature dependence of the relaxation time (τ_C) can be expressed as a super exponential function given below:[8]

$$\tau_C=\frac{1}{\omega_0}\exp[(T_0/T_m)^p], \qquad (5)$$

where $p(>1)$ is a constant, which connects with the degree of dielectric relaxation in a RFE.

To describe the dielectric behavior of a RFE, we can use Eq. (5) to express the temperature dependence of the relaxation time. Thus the degree of the dielectric relaxation can be characterized well with both parameter β' in Eq. (3a) and p in Eq. (5), where β' determines the high-temperature side of the dielectric constant peak, while p determines the low-temperature side of the dielectric constant profile. In any case, it is impossible for all of the polar regions in a RFE to have the same relaxation time. Thus, although Eq. (5) can describe the main characteristics of the relaxation time, a distribution function of the relaxation times is also needed to completely describe the dielectric behavior of the material. The distribution of the relaxation times cannot be directly

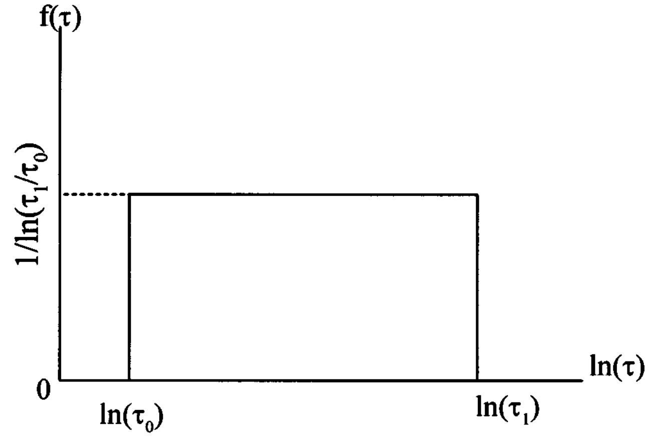

FIG. 5. Distribution function of the relaxation times for the RFE.

determined by experiment, because it is very broad in the RFE. And there is no prior analysis which is widely accepted. In the RFE, the polar region cannot be infinitely small and would have at least the volume of a crystalline cell. Thus the value of the relaxation times must have a limit at the short end and the value of the short limit is nearly independent of the temperature. The polar region cannot be also infinitely large as the RFE cannot reach the ferroelectric phase at low temperatures when there is no external electric field to induce it. Thus the value of the relaxation times must also have a limit at the long end. With decreasing temperature, it is widely known that the size of the polar regions increases. Thus the value of the long limit should increase with decreasing temperature. Meanwhile, new polar regions appear in some nonpolar regions. Therefore it is assumed that the distribution $[f(\tau)]$ of τ is a constant from the short end (τ_0) to the long end (τ_1) in the logarithmic scale as shown in Fig. 5. Based on the above discussion, it is reasonable to assume $\tau_0 = 1/\omega_0$ and τ_1 equals the value of τ_C in Eq. (5). Thus the distribution of τ can be expressed as follows:

$$f(\ln(\tau)) = \begin{cases} 0 & (\tau < \tau_0,\quad \tau > \tau_1), \\ \dfrac{1}{\ln(\tau_1/\tau_0)} & (\tau_0 \leq \tau \leq \tau_1), \end{cases} \tag{6}$$

where

$$\tau_1(T) = \tau_0 \exp[(T_0/T)^p]. \tag{7}$$

C. Model to simulate the dielectric response for the RFE

The dielectric relaxation response of each polar region can be described with the following Debye relation:

$$\Delta\varepsilon^* = \varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}, \tag{8}$$

where $\varepsilon^* = (\varepsilon' - i\varepsilon'')$ represents the total complex dielectric constant and ε_∞ is the dielectric constant at high frequency, which results from the electron polarization, ionic polarization, and other polarization in the material with a rapid response time.

For the RFE, the value of ε_s is generally of the order of 10^4 or higher and the value of ε' is generally of the order of 10^3–10^4. These can be clearly seen from the above results of 0.9 PMN–0.1 PT. The value of ε_∞ is generally smaller than a few hundreds. Thus Eq. (8) can be written as

$$\varepsilon^*(\omega, T) \approx \frac{\varepsilon_s(T)}{1 + i\omega\tau(T)}. \tag{8a}$$

Now let us consider with the dielectric relaxation response of the RFE with a constant distribution of the relaxation times as shown in Eq. (6). Using Eqs. (6) and (8a), we get the total dielectric response of the RFE as follows:

$$\varepsilon^* = \int_{\tau_0}^{\tau_1} \frac{\varepsilon_s}{\ln(\tau_1/\tau_0)} \frac{1}{1 + i\omega\tau}\, d\ln(\tau). \tag{9}$$

After integrating Eq. (9), we get the final results for both the dielectric constant and the dielectric absorption of the RFE as

$$\varepsilon' = \frac{\varepsilon_s}{2\ln(\tau_1/\tau_0)} \ln\left(\frac{\tau_1^2}{\tau_0^2} \frac{1 + \omega^2\tau_0^2}{1 + \omega^2\tau_1^2} \right), \tag{10}$$

$$\varepsilon'' = \frac{\varepsilon_s}{\ln(\tau_1/\tau_0)} [\tan^{-1}(\omega\tau_1) - \tan^{-1}(\omega\tau_0)]. \tag{11}$$

As discussed above, the value of ε_s for the RFE can be expressed as

$$\varepsilon_s(T) = \frac{1}{T} \exp[\alpha' - \beta'(T - 273.15)]. \tag{12}$$

Thus, using Eqs. (7), (10), (11), and (12), we can calculate both the temperature dependence and the frequency dependence of both the dielectric constant and the dielectric absorption for the RFE. For 0.9 PMN–0.1 PT, the frequency dependence of T_m had been analyzed with the model based on Eq. (5). It shows that the parameters in Eq. (7) are $p = 8.81$, $\omega_0 = 1.16 \times 10^{13}$ Hz, and $T_0 = 430$ K. With these parameters, the simulated temperature dependence of both the dielectric constant and the dielectric absorption at different frequencies are shown in Fig. 6. All of the basic dielectric features of a typical RFE, described in Sec. II, clearly appear in Fig. 6. Although the contribution of ε_∞ to the dielectric constant is overlooked, the dielectric behavior in the low-temperature range is extrapolated by the dielectric behavior at the temperature around and higher than T_m, and the value of ω_0 determined by the frequency dependence of T_m is of some derivation from real ω_0,[8] Fig. 6 clearly shows that the estimated dielectric response is very similar to the experimental results in Fig. 1. It strongly suggests that the present model can be used to describe the dielectric behavior of the RFE.

D. Verification of the present model

For the dielectric behavior of the RFE, what is the most difficult to understand is its dielectric behavior in the low-temperature range. Thus the dielectric relaxation behavior of the material in the low-temperature range is a good object to verify the present model. For a material with a temperature dependence of the relaxation time, as expressed in Eq. (5), it was shown that $\omega\tau \approx 1$ at T_m.[8] With decreasing the temperature from T_m, the relaxation time increases rapidly. That is,

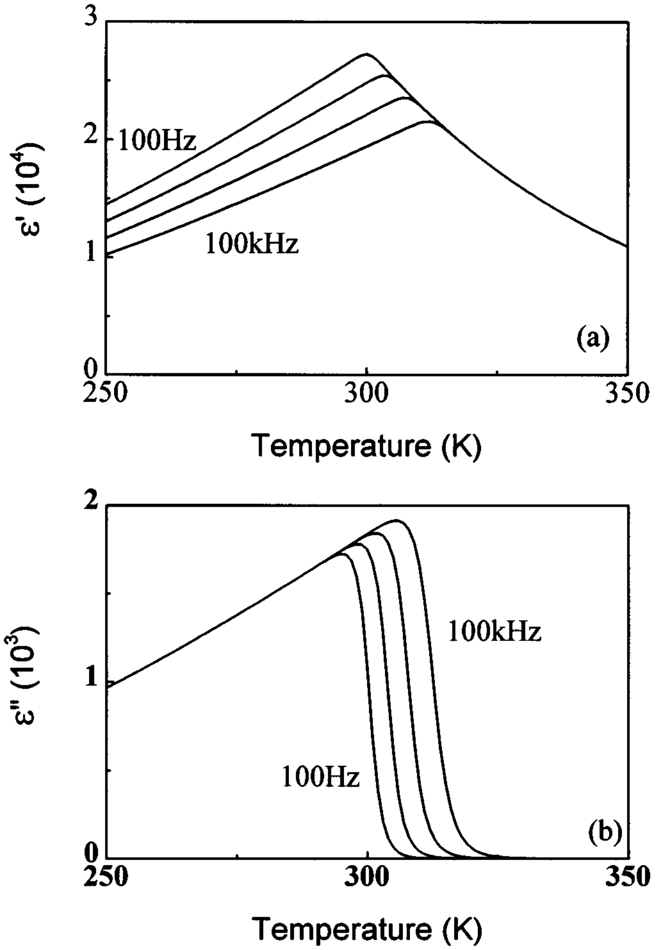

FIG. 6. Simulated dielectric response of 0.9 PMN–0.1 PT by Eqs. (10) and (11) with parameters of $\alpha'=16.356$, $\beta'=0.0156$ °C, $p=8.8$, $T_0=430$ K, and $\tau_0=10^{-13}$ s. The frequencies are 0.1, 1, 10, and 100 kHz, respectively.

in the low-temperature range, we have $\omega^2\tau_1^2 \gg 1$. Meanwhile, $\omega^2\tau_0^2 \ll 1$. For example, $\tau_0 \approx 10^{-13}$ for 0.9 PMN–0.1 PT; therefore, $\omega\tau_0 < 10^{-6}$ for frequencies lower than 10 MHz. Thus Eqs. (10) and (11) can be simplified as follows:

$$\varepsilon' = \frac{\varepsilon_s}{\ln(\tau_1/\tau_0)} \ln(\omega_0/\omega), \tag{13}$$

$$\begin{aligned}\varepsilon'' &= \frac{\varepsilon_s}{\ln(\tau_1/\tau_0)} \left(\frac{\pi}{2} - [\omega\tau_1 + (\omega\tau_2)^{-1}] \right) \\ &= \frac{\varepsilon_s}{\ln(\tau_1/\tau_0)} \frac{\pi}{2}.\end{aligned} \tag{14}$$

Hence,

$$\frac{\partial \varepsilon'(\omega)}{\partial \ln\omega} = -\frac{\pi}{2} \varepsilon''. \tag{15}$$

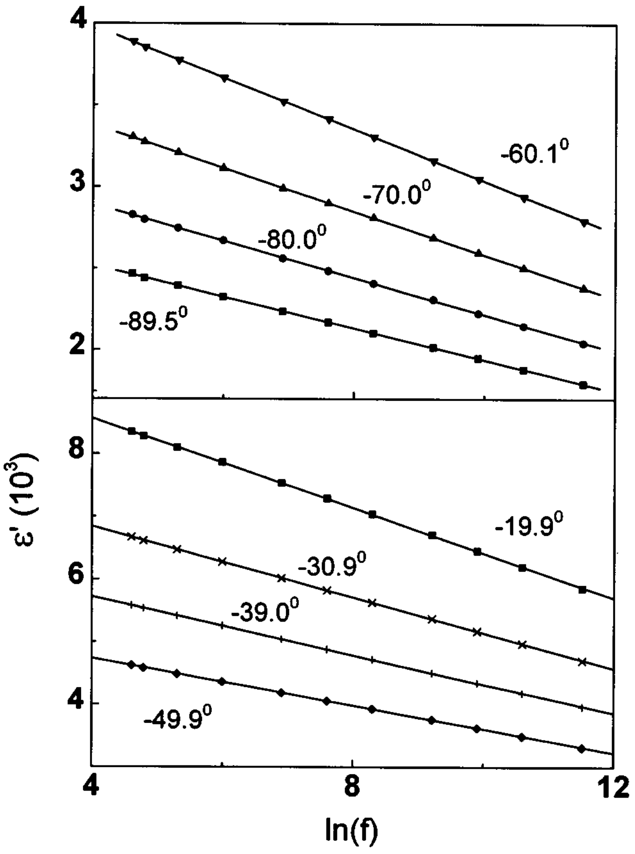

FIG. 7. Frequency dependence of the dielectric constant at some temperatures in the low-temperature range for 0.9 PMN–0.1 PT.

From Eq. (14), it can be noticed that although the dielectric absorption is nearly a constant, the dielectric absorption has a small decrease with increasing frequency when τ_2 is so large that $\omega\tau_1 > 1/(\omega\tau_2)$. Figure 7 shows the frequency dependence of the dielectric constant for 0.9 PMN–0.1 PT at temperatures in the low-temperature range. As expected, it indicates that there is indeed a linear relationship between the dielectric constant and the logarithm of the frequency. Equation (13) can be rewritten as follows:

$$\varepsilon' = A(T) - B(T)\ln\omega, \tag{16}$$

where

$$A(T) = \frac{\varepsilon_s}{\ln(\tau_1/\tau_0)} \ln\omega_0, \quad B(T) = \frac{\varepsilon_s}{\ln(\tau_1/\tau_0)}.$$

Thus,

$$\frac{A(T)}{B(T)} = \ln\omega_0, \quad B(T) = \frac{2}{\pi} \varepsilon''(T).$$

The frequency dependence of the dielectric constant at some temperatures in the low-temperature range is fitted with Eq. (16). The best-fitted parameters $[A(T)$ and $B(T)]$ and the measured dielectric absorption at the temperatures are shown in Table III. It is clearly shown that the ratio of the fitted parameter $A(T)$ to $B(T)$ is very close to the value of $\ln \omega_0$, which was obtained by fitting the frequency dependence of T_m based on Eq. (5).[8] It can also be seen from Table III that the ratio of the measured ε'' to the fitted parameter $B(T)$ is very close to the expected value of 1.57 for the present model. All of these good agreements strongly confirm the correctness of the present model. Thus, based on

TABLE III. Fitted results of $A(T)$ and $B(T)$ using the experimental results at low temperatures with Eq. (16).

Temperature (°C)	$A(T)$	$B(T)$	$A(T)/B(T)$	$\varepsilon''(T)$	$\varepsilon''(T)/B(T)$	$\frac{A(T)}{B(T)\ln\omega_0}$
−89.5	2909.3	96.945	30.009	151.98	1.568	0.998
−80.0	3345.2	112.73	29.674	174.28	1.546	0.986
−70.0	3909.0	132.48	29.506	206.70	1.560	0.981
−60.1	4613.2	157.64	29.264	246.40	1.563	0.973
−49.9	5502.2	189.55	29.027	297.03	1.567	0.965
−39.9	6649.2	232.07	28.652	361.60	1.558	0.952
−30.9	7973.3	282.43	28.231	440.76	1.561	0.938

Eqs. (13), (14), and (15) of the present model, it is very easy to understand the dielectric relaxation behavior of a RFE in the low-temperature range.

IV. DISCUSSION

The temperature dependence of the relaxation time expressed by Eq. (5) can be interpreted as a Debye relationship with a temperature dependence activation energy. Thus the equivalent temperature (T_{eff}) of activation energy increases on decreasing temperature with a power function of the inverse of the temperature as follows:

$$T_{\mathrm{eff}}=T_0(T_0/T)^{p-1}. \tag{17}$$

It is generally believed that the activation energy for the thermal fluctuation of a polar region is proportional to its volume (V).[7,23,24] That is,

$$T_{\mathrm{eff}}=QV, \tag{18}$$

where Q is an equivalent temperature of anisotropical energy, which is dependent on the material. Thus the distribution function of the relaxation times in Eq. (6) results in a constant distribution of the size of the polar regions and a strong temperature dependence of the size of the largest polar region. Unfortunately, the value of Q cannot be obtained directly from the experimental measurement. It is assumed that the activation energy of the polar regions in the material and the transition enthalpy of the paraelectric-ferroelectric phase transition in the material have the same origin. Thus we can use the transition enthalpy to estimate the value of Q. The transition enthalpy of the ferroelectic-paraelectric phase transition in the perovskite compound is generally in the order of 100 J/mol. For example, it is 209, 364, and 75 J/mol for $BaTiO_3$, ordered $Pb(Sc_{1/2}Ta_{1/2})O_3$, and PLZT 11/30/70, respectively.[25,26] Thus the equivalent temperature of the activation energy of a unit cell is about 10–30 K (the transition enthalpy divided by the Avogadro's number), i.e., $Q=10$–30 K per unit cell. Thus the number (N) of the unit cells in a largest polar region is dependent on the temperature by

$$N(T)=\frac{T_0}{Q}(T_0/T)^{p-1}, \tag{19}$$

so that $N\approx300$–700 for a largest polar region in 0.9 PMN–0.1 PT at the temperature of 300 K, which is in the temperature range of T_m; i.e., the size is about 3–4 nm, while its size is about 5–9 nm at the temperature of 250 K. These results are close to the experimental results in PMN, PMN-PT, and PLZT.[27–29] Anyway, it seems difficult to explain the continuous growth of individual polar regions in the low-temperature range. Such behavior can be explained as follows: In the low-temperature state, a high concentration of the polar regions increases the interaction among them, thereby increasing the relaxation time of each polar region. Therefore, even though the size growth of individual polar region is slow with decreasing temperature in the low-temperature range, the increase of relaxation time of the polar regions is much stronger than their size growth; i.e., in the low-temperature range, the activation energy of the polar region is not proportional to its volume. If the interaction among the polar regions is very strong, it can result in a phase transition in the materials. It is known as the spontaneous relaxor-normal ferroelectric transition. Such a behavior has been found in PST and PNN-PT-PZ.[30,31]

Based on Eqs. (10) and (11), either the peak of the dielectric constant or the peak of the dielectric absorption does not correlate with any phase transition in the materials. The peak only reflects the fact that the relaxation time of the largest polar region in the material increases to a value which is approximately the inverse of the frequency. These agree with the experimental results. For example, studies by neutron and x-ray diffraction on PMN and its solid solution have revealed a mean cubic structure even at the temperature down to 5 K, but there are some nanometeric polar regions with rhombohedral distortion.[32,33]

It is very interesting to compare the present model with the other models reported earlier. For the fitting of the temperature dependence of the dielectric constant, a great deal of work, in which it was assumed that the dielectric constant of the polar region in the ferroelectric phase was a constant and that the dielectric constant of the polar region in the paraelectric phase was dependent on the Curie-Weiss law, has been done based on the inhomogeneous microregion model.[15–17] The results cannot describe accurately the temperature dependence of the dielectric constant. In addition, there was no way to get both the frequency dependence of the dielectric constant and the behavior of the dielectric absorption. However, there were two models proposed based on consideration of relaxation behavior of the polar regions in the materials. One was introduced by Bell based on ideal superparaelectrics.[24] A logarithmic Gaussian distribution of the polar region size in the material was assumed in the model. The results of this model cannot give the basic feature Nos. (7) and (8) of the RFE in Sec. II. Another one was

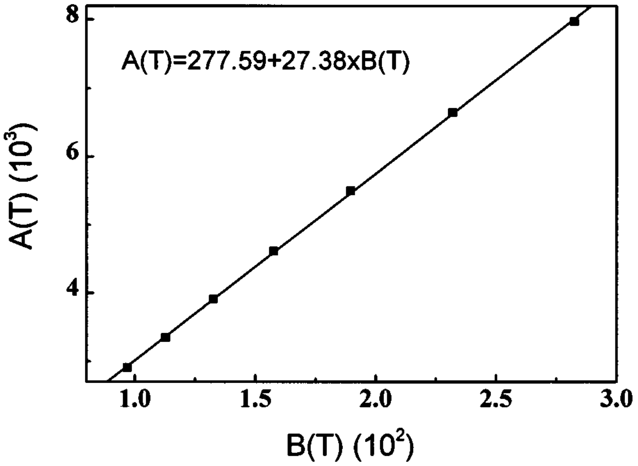

FIG. 8. Relation between the $A(T)$ and $B(T)$ in Table III. The solid line is the fitted result by Eq. (20) with the parameters $\varepsilon_\infty=278$ and $\omega_0=7.9\times10^{11}$ Hz. ■ is the data.

introduced by Lu and Valvarin.[34] An exponential distribution of the polar region sizes was assumed in the model. The results of the latter model are better than that of the Bell's model, but it predicts that the dielectric absorption always increases with increasing frequency, which contradicts the experimental results in the low-temperature range. Compared with these models, the advantage of the present model is that the simulated dielectric behavior in the present model can characterize all of the basic features of the RFE. In addition, all of the parameters used in the fitting process are experimentally determined in the present model, whereas there are some artificial parameters in both Bell's and Lu and Calvarin's models. Both these latter models were based on a strong inhomogeneous distribution of the polar region sizes, while the present model is based on a homogeneous distribution in some limited range. Thus the advantage of the present model indicates that the distribution of the polar region size in the RFE is very smooth in a limited range.

For present model, the distribution function of the relaxation times expresses the fact that the distribution of the volume of the polar regions is constant from the volume of a unit cell to that of the largest polar region, which is dependent on the temperature. In any case, the distribution of the volume of the polar region cannot strictly be a step function at the limit value. Based on Eq. (10), the dielectric constant maximum for a frequency appears where the long end of the relaxation time is equal to the inverse of the frequency. It results in the simulated frequency dependence of the dielectric behavior, at the temperature around T_m, having a little deviation from experimental results. Since the relaxation time of a polar region contained only one unit cell, it must be dependent on the temperature, which is different from the assumed τ_0 in Eq. (6). As discussed above, the activation energy of a polar region containing one unit cell is very small. Thus its change is very small, and we still have $\omega\tau_0 \ll 1$. Therefore we get the same result when the temperature dependence of τ_0 is considered in the present model. Although the ratio of the fitted $A(T)$ to $B(T)$ in Eq. (16) is nearly a constant, it can be noticed from Table III that the ratio increases a bit with decreasing temperature. It can be explained due to the effect of ε_∞ as follows: If ε_∞ is not neglected in Eq. (10), the parameters $A(T)$ and $B(T)$ in Eq. (16) will have a following relation:

$$A(T)=\varepsilon_\infty+B(T)\ln\omega_0. \tag{20}$$

It is known that the value of ε_∞ is nearly independent of the temperature. Thus there is a linear relationship between the fitted $A(T)$ and $B(T)$ at different temperatures in the low-temperature range. The data in Table III are plotted in Fig. 8, which clearly shows that the value of $A(T)$ is, as expected, dependent on $B(T)$ by a linear relation. Fitting the data in Fig. 8 with Eq. (20), we get $\varepsilon_\infty=278$, $\ln\omega_0=27.4$, i.e., $\omega_0=7.9\times10^{11}$ Hz. It is difficult to get the accurate value of ω_0 by fitting the frequency dependence of T_m.[8] Therefore, besides the value of ε_∞, Eq. (20) also gives us an easy way to obtain an accurate value for ω_0.

V. CONCLUSIONS

The dielectric behavior of 0.9 PMN–0.1 PT at temperatures higher than the temperature of the dielectric constant maximum is analyzed with various characterization methods. A standardizing method is introduced to analyze the dielectric constant for temperatures higher than T_m. It results in a master curve behavior for the RFE. The shortcomings of both the quadratic relation and the power relation are indicated. It is shown that the exponential function can characterize well the static dielectric constant of a RFE. A superexponential function is used to characterize the temperature dependence of the relaxation time. It is indicated that the degree of the dielectric relaxation behavior is dependent on two parameters: One, the parameter β' in Eq. (12), determines the high-temperature side of the dielectric peak; second, the parameter p in Eq. (7) determines the low-temperature side of the dielectric peak. A constant distribution function of the logarithmic relaxation times from the short end to the long end is assumed. The value of the short end is independent of the temperature, while that of the long end is strongly dependent on the temperature with the superexponential function. Based on it, the formula to calculate the dielectric behavior of the RFE is given. All of the basic features of the RFE can be computed with the formula. Both the temperature dependence and the frequency dependence of the dielectric behavior are simulated using the parameters, which can be determined by the experimental results of the material in the temperature around and higher than T_m. The simulated result is very similar to the experimental results. The present model is rigorously verified with the dielectric behavior of 0.9 PMN–0.1 PT in the lower-temperature range. The way to obtain the accurate value of ε_∞ in the low-temperature range is given. It is indicated that $\varepsilon_\infty=278$ for 0.9 PMN–0.1 PT in the low-temperature range.

Based on our model, both the dielectric constant peak and the dielectric absorption peak do not correlate with any phase transition in the materials. When the relaxation time of the largest polar region in the material increases to the inverse of a frequency with decreasing temperature, the dielectric constant at that frequency reaches its peak and the dielectric absorption at the frequency strongly increases. It appears that the present constant distribution model is certainly an idealized model. In fact, the distribution cannot be a strict step function at the long end. It should be mentioned that the distribution smoothly decreases to zero at the long end. It results in the simulated frequency dependence of the dielectric constant at the temperatures around T_m having a little deviation from the experimental results.

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[*] Author to whom correspondence should be addressed. Electronic address: cheng@upracd.upr.clu.edu

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