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Temperature dependence of the dielectric constant of relaxor ferroelectrics

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The temperature dependence of the dielectric constant under different frequencies is measured and analyzed for two different relaxor ferroelectrics, the solid solution ceramics of lead magnesium niobate and lead zinc niobate, respectively. Compared with the experimental results, the disadvantage of simulated results from different methods about the temperature dependence of the dielectric constant for relaxors is given. Based on this and the general behavior of the temperature dependence of the dielectric constant at both high and low temperatures, it is assumed that there are two kinds of polarization processes in the relaxor ferroelectrics. One of the polarization processes is associated with the thermally activated flips of the polar regions in the materials. Thus, a set of formulas is proposed to fit the temperature dependence of the dielectric constant at different frequencies. The formulas are strictly certified with the measured data of both materials. The formulas can fit the measured relation with high precision. The fitted results confirm and/or show the following: (1) The dielectric behavior at high temperatures is mainly contributed from a relaxation polarization process, which is associated with the thermally activated flips of polar regions in relaxor ferroelectrics. (2) The dielectric behavior at low temperatures is mainly contributed from the other polarization process. The frequency dependence of the dielectric constant shows that this process is something like a resonance polarization in the materials. (3) The dielectric behavior at temperatures around the temperatures of the dielectric constant maximum is determined with both polarization processes. The micro-origin of the resonance polarization is discussed with the breathing of frozen polar region in the materials. Based on the breathing model, all of the characteristics of the resonance polarization are explained. The amplitude dependence of the dielectric constant for relaxor ferroelectrics is also explained with the breathing model. [S0163-1829(98)03514-0]

I. INTRODUCTION

A great deal of attention has been given to ferroelectrics with diffuse phase transition (DPT), with relaxor characteristics. These materials have high dielectric constants, high electrostriction coefficients, and switchable pyroelectric and piezoelectric properties.[1–3] All these useful properties of relaxor ferroelectrics (RFE's) have their origin in the strange polarization mechanism that is associated with the relaxor-type DPT. Although various models, such as the inhomogeneous microregion model,[4] the micro-macro domain transition model,[5,6] the superparaelectric model,[1] the dipolar glass models,[7,8] the order-disorder model,[9–11] and the local electric-field model,[12] have been proposed to explain the polarization mechanism, the polarization mechanism has not been fully clarified so far. However, it is widely accepted that the polarization is associated with the behavior of the polar regions in the materials.

The most important feature of the RFE is a broad peak that appears in the dielectric constant as a function of temperature. From both theoretical and application points of view, what is most important is the value of dielectric constant and both the temperature and frequency dependence of the dielectric constant. Thus, a lot of work has been reported on these characteristics of RFE.[7,8,13–18]

In order to characterize the dielectric constant peak, two relationships, one the Vogel-Fulcher relationship and the other a superexponential function, have been proposed to describe the frequency dependence of the dielectric constant maximum temperature (T_m) for RFE.[7,8] Both relationships are based on the consideration that the experimental result on the material has only one relaxation process. Although both relationships can well describe T_m and the frequency at radio frequency, only the results of the superexponential function are in the range of its physical significance.[8,19] However, the physical origin of the superexponential function is not clear.

To describe the temperature dependence of the dielectric constant in a larger temperature range, there are at least four methods reported in the literature. The first one is based on the inhomogeneous microregion model.[13–15] Although the method is widely used, it can only determine the behavior of the static dielectric constant. Therefore, the dielectric absorption and the frequency dependence of the dielectric constant cannot be described with this method. The other three methods are based on the superparaelectric model, with different considerations of the size distribution of the polar regions in the material.[16–18] In the superparaelectric model, it is thought that the dielectric behavior of RFE has its origin in the thermal flips of polar regions (superparaelectrics) in the material. Thus, the size distribution of the polar regions and its temperature dependence determine both the distribution of the relaxation times and the static dielectric constant, which are the key parameters to describe the dielectric behavior of the RFE. In all these three methods, the temperature dependence of the static dielectric constant, the size distribution of the polar regions, and the temperature dependence of the size distribution were assumed based on the experimental results. All three methods can simulate both the frequency dependence and temperature dependence of both the dielectric constant and dielectric absorption. The method reported by Cheng *et al.*, in which a homogeneous distribution of the polar region sizes in some limited range was assumed, can describe all the dielectric features of the RFE.[18]

It is interesting to compare the experimental results with the simulated results derived from the above methods. For the frequency dependence of the dielectric constant, Lu and Valvarin's method, in which an exponential distribution of the size of polar regions was assumed, can well fit the measured results at the temperatures near T_m. However, their method gives incorrect frequency dependence of the dielectric absorption at low temperatures. Meanwhile, although Cheng's method can well fit the measured results at temperatures lower than T_m, its fitted results at temperature near T_m have a little deviation from the experimental results. For the temperature dependence of the dielectric constant, if the simulated results are close to the experimental data at the temperatures higher than T_m, it is found that the simulated dielectric constant at the temperatures lower than T_m is always much smaller than the experimental data.[16–18] In all three methods, every possible distribution of the polar region's size has been included, and different relations between the static dielectric constant and temperature have been used. Therefore, the above results strongly indicate that, besides the contribution of the thermally activated flips of the polar regions, there may be other contributions to the dielectric behavior of the materials at low temperatures. In addition, with regard to the dielectric constant at the temperatures far away from T_m, two different general relations have been found to describe the experimental results at low temperatures and high temperatures, respectively.[20] That is, an exponential function for the dielectric behavior at temperatures much higher than T_m,[8,18,20] and a superexponential function for it at temperatures much lower than T_m.[19,20] All these results strongly indicate that RFE should have two polarization mechanisms.[21]

Based on the above results and the general dielectric theory, a set of formulas is proposed to describe the relation between the temperature and the dielectric constant at different frequency for RFE in this paper. The formulas are tested with the measured data on two different materials. The results show that the formulas can fit the experimental data with high precision. The fitted results suggest that one of the polarization mechanisms in these materials is resonance. The micro-origin of the resonance polarization is discussed with the breathing model of the frozen polar regions in the material.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The materials used in this study were two solid solution ceramics with perovskite structure: (i) 10 mol % $PbTiO_3$ in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN-PT), which is a widely studied typical RFE,[18,22,23] (ii) PZN-PT-BT with composition of $0.87\,(Pb_{1-x}La_{x/2}K_{x/2})(Zn_{1/3}Nb_{2/3})O_3-0.08\,PbTiO_3-0.05\,BaTiO_3$, $x=0.04$, which is also a typical RFE.[19,24,25] Both the samples, which were in disk forms and about 1 mm in thickness, were prepared with the starting materials of ultrahigh purity. Both samples were of pure perovskite phase as identified by x-ray diffraction.

The gold electrodes were deposited on the two sample surfaces by dc sputtering. An HP4274A *LCR* meter was used to measure the temperature dependence of both the capacitance and loss tangent with a cooling rate of about 0.8 °C per minute at 11 frequencies: 0.1, 0.12, 0.2, 0.4, 1.0, 2.0, 4.0, 10, 20, 40, and 100 kHz. The four test leads were connected directly to the electrodes on the sample to increase the measuring accuracy. Before the measurement, the samples had been thermally treated at temperatures much higher than T_m to remove the effect of electric history. The oscillating level of the measuring signal was about 0.5 V/mm to ensure the measured results are the small-signal dielectric properties. In addition, before each measurement a standard calibration was performed to remove any stray capacitance, lead, and contact resistance. The high-resolution function of the HP4274A meter was applied in the measurement. 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 dielectric constant was calculated from the measured capacitance using a parallel-plate capacitance model with the geometric parameters of the sample.

The measured temperature dependence of the dielectric constant at different frequencies for both materials is shown in Fig. 1. They demonstrate the typical dielectric behavior of RFE.[1,18] At high temperatures the temperature dependence of the dielectric constant is much stronger than that for the Debye medium. It was found that the temperature dependence of the dielectric constant for RFE at temperatures much higher than T_m obeys the following relation:[8,18]

$$\varepsilon_H(T)=\exp(\alpha-\beta T), \tag{1}$$

where α and β are the constants, T is the temperature in Kelvin, and $\varepsilon_H(T)$ is the measured dielectric constant at high temperatures. The value of β is associated with the product rate of the polar regions in the materials.

Fitting the measured results with Eq. (1), we get the values of both parameters α and β for PMN-PT and PZN-PT-BT, which are shown in Table I.[8,19] It can be seen that the product rate of polar regions in PMN-PT is larger than that in PZN-PT-BT.

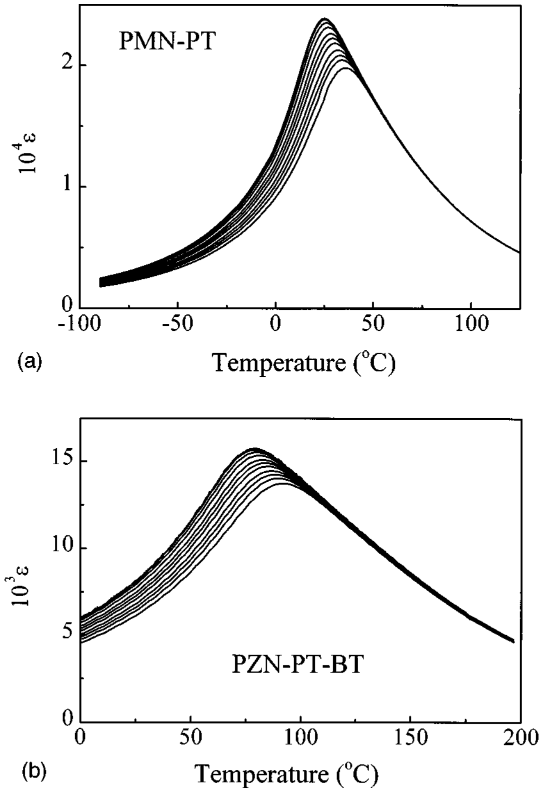

FIG. 1. Dielectric constant (ε) as a function of temperature at frequencies of 0.1, 0.12, 0.2, 0.4, 1, 2, 4, 10, 20, 40, and 100 kHz for PMN-PT: $0.9\,\mathrm{Pb(Mg_{1/3}Nb_{2/3})O_3}-0.1\,\mathrm{PbTiO_3}$ (a) and PZN-PT-BT: $0.87\,\mathrm{(Pb_{1-x}La_{x/2}K_{x/2})(Zn_{1/3}Nb_{2/3})O_3}-0.08\,\mathrm{PbTiO_3}$ $-0.05\,\mathrm{BaTiO_3}$ with $x=0.04$ (b). The largest dielectric constant is for the 100 Hz, the smallest for the 100 kHz, and the other curves in between are in the order of increasing frequency.

If the temperature is much lower than T_m, it was found that the frequency dependence of the dielectric constant can be described with the following relation:[18]

$$\varepsilon_L(\omega,T)=\varepsilon_\infty+A(T)(\ln\omega_0-\ln\omega), \tag{2}$$

where ε_∞ is the dielectric constant at the infinite frequency, ω_0 is the relaxation frequency of a polar unit cell that is independent of the temperature, $\varepsilon_L(\omega,T)$ is the measured dielectric constant at temperature (T) and frequency (ω in Hz), and $A(T)$ is an intrinsic parameter of the material.

TABLE I. The parameters in Eqs. (1) and (2) for PMN-PT and PZN-PT-BT.

Parameter	PMN-PT	PZN-PT-BT
α	15.67	14.48
β (10^{-3} K^{-1})	18.20	12.85
α_1	3.11	2.47
β_1 (K)	151.1	121.9
δ	0.950	0.304
ε_∞ (10^2)	2.8	4.5
ω_0 (Hz)	7.9×10^{11}	3.24×10^{13}
m	2.874	3.016
n	3.849	3.573

ε_∞ is determined by the electronic and ionic polarization.[19] Thus, it should be nearly independent of the temperature as the RFE does not show any observable phase transition. Therefore, the temperature dependence of the value of $A(T)$ is the key to describe the temperature dependence of the dielectric constant at low temperatures. It was found that $A(T)$, at temperatures much lower than the T_m, can be expressed as follows:[19,20]

$$A(T)=\exp[\alpha_1+(T/\beta_1)^{1+\delta}], \tag{3}$$

where $\alpha_1(>0)$, $\beta_1(>0)$ and $\delta(>0)$ are constants. The value of δ is associated with the frozen rate of polar regions in the material.

Fitting the measured results with Eqs. (2) and (3), we get the value of the parameters in Eqs. (2) and (3) for PMN-PT and PZN-PT-BT, which are shown in Table I.[19] It shows that the frozen rate of polar regions in PMN-PT is larger than that in PZN-PT-BT.

For the dielectric relaxation properties of both materials, from Fig. 1 and Table I, it can be seen that the dielectric relaxation strength of PMN-PT is much smaller than that of PZN-PT-BT. The value of T_m for PMN-PT is much lower than that for PZN-PT-BT. From the structure point of view, in PMN-PT only the B site of the perovskite (ABO_3) is occupied by different atoms, while in the case of PZN-PT-BT, both A and B sites are occupied by different atoms. Thus, PMN-PT and PZN-PT-BT represent two kinds of the RFE with perovskite structure. In addition, La enhances the relaxor behavior and decreases the T_m of the sample. The maximum dielectric constant of both materials at 100 Hz is about 2.4×10^4 and 1.6×10^4, respectively. Higher dielectric constant of the samples reflects that both samples are of good stoichiometry.[26] Therefore, both samples are suitable for the present studies.

III. ANALYSIS AND FORMULA TO SIMULATE THE DIELECTRIC BEHAVIOR OF RFE

A. Formula to simulate dielectric constant of RFE

For an RFE, as discussed in the Introduction, it is very difficult to simulate the dielectric behavior in a broad temperature range with only one relaxation polarization process. The temperature dependence of the dielectric behavior at temperatures much higher and much lower than the T_m follows a different mathematical approach. Thus, it is concluded that the RFE should at least have two polarization mechanisms contributing to the dielectric behavior of the material. In addition, the simulated results based on one relaxation polarization can describe the dielectric behavior at high temperatures. In other words, one of the polarization processes, which is associated with the thermally activated flips of the polar regions in the materials, determines the dielectric behavior of the materials at high temperatures. On the other hand, at temperatures much lower than the T_m, the simulated dielectric constants based on one relaxation process are always much smaller than the measured results. We can assume, as an extreme case, that the dielectric behavior of the RFE at temperatures much lower than the T_m is governed by some different polarization process in the material. The measured dielectric behavior of the RFE is the sum of the contributions of these two polarization processes, i.e. the dielectric constant of RFE can be expressed as

$$\varepsilon_m(\omega,T)=\varepsilon_1(\omega,T)+\varepsilon_2(\omega,T), \tag{4}$$

where ε_1 and ε_2 are the dielectric responses of two polarization processes, respectively; ε_m, the measured dielectric behavior of the material, represents the total dielectric response of the material. Like ε_m, both ε_1 and ε_2 are dependent on both the temperature (T) and frequency (ω). If ε_1 represents the dielectric constant contribution from the relaxation polarization process, which originates from the thermally activated flips of the polar regions, then ε_2 represents the contribution from the other polarization process.

Based on the general dielectric theory,[20,27] the dielectric response of both ε_1 and ε_2 can simply be written as

$$\varepsilon_i(\omega,T)=\frac{B_i(\omega,T)}{1+C_i(\omega,T)} \quad (i=1,2), \tag{5}$$

where both $B_i(\omega,T)$ and $C_i(\omega,T)$, respectively, are the function of both T and ω. The function forms of $B_i(\omega,T)$ and $C_i(\omega,T)$ are dependent on both the polarization mechanism and the material.

As discussed above, if the temperature is very high, $\varepsilon_1 \gg \varepsilon_2$ and $\varepsilon_m \cong \varepsilon_1$. When the temperature is very low, $\varepsilon_1 \ll \varepsilon_2$ and $\varepsilon_m \cong \varepsilon_2$. Therefore, the measured dielectric constant at very high temperature can be used to determine some features of ε_1, and that at very low temperature can be used to determine some features of ε_2.

For ε_1, the dielectric behavior at high temperatures can be used to describe its static dielectric constant. If one uses Eq. (1) to express B_1, which increases with decreasing temperature, C_1 should be very small at high temperatures and increases with decreasing temperature. At low temperatures, C_1 should be larger than B_1, so that ε_1 is much smaller than ε_m. Considering the general dielectric theory, both B_1 and C_1 are dependent on the intrinsic properties of the materials, such as the dipole moment and concentration of the polar regions, the size and distribution of the polar regions, the interaction among the polar regions, and the interaction between the polar and nonpolar regions. Therefore, C_1 is related to B_1.

For ε_2, the dielectric behavior is not clear. Based on the above discussion, it is known that the dielectric behavior at low temperature can be well described with Eqs. (2) and (3). Thus, if one uses Eq. (2) to express B_2, which increases with increasing temperature, C_2 should be very small at low temperatures and it increases with increasing temperature. At high temperatures, C_2 should be larger than B_2, so that ε_2 is much smaller than ε_m. B_2 and C_2 reflect the different features of the polarization process. Both B_2 and C_2 are dependent on the intrinsic properties of the polarization process. Thus, C_2 is related to B_2.

All of the measured relations between the temperature and dielectric constant for RFE are smooth in the whole temperature range. Therefore, for the RFE, although there are two different polarization processes, the weight of either ε_1 or ε_2 in ε_m changes with the temperature smoothering. This indicates that both of them should have some intrinsic relationship. That is also why the noticeable master curve behavior was found in RFE.[18] Therefore, C_2 is also related to B_1, and C_1 is related to B_2.

Based on both the characteristics and physical signification of C_1 and C_2, both C_1 and C_2 are dependent on both the temperature and frequency. Considering the above discussion, the temperature dependence of both C_1 and C_2 should be determined from Eqs. (1) and (3). Thus, Eq. (5) can be written as

$$\varepsilon_1(\omega,T)=\frac{\varepsilon_H(T)}{1+D_1(\varepsilon_H(T)/A(T)\ln\,\omega_0)^m}, \tag{6a}$$

$$\varepsilon_2(\omega,T)=\frac{\varepsilon_L(\omega,T)}{1+D_2(A(T)\ln\,\omega_0/\varepsilon_H(T))^n}, \tag{6b}$$

where $m(>1)$ and $n(>1)$ are constants that should be independent of both the temperature and frequency; while D_1 and D_2 should be independent of the temperature, but dependent on the frequency, i.e., $D_1=D_1(\omega)$ and $D_2=D_2(\omega)$.

In conclusion, we can use Eqs. (1)–(4), and Eqs. (6) to fit the measured dielectric constant of the RFE. The fitted results will be helpful to verify the correctness of Eqs. (6). If Eqs. (6) can fit well the measured curve, the results will provide a clue about the frequency dependence of both D_1 and D_2, which will be useful to study the polarization mechanism in the material. This is of great interest and importance to the study of RFE.

B. Verification of formula

With the parameters in Table I, we can fit the measured relation between the dielectric constant and temperature at each frequency using Eqs. (4) and (6). In this case, for each frequency there are four parameters to be determined through the fitting process, i.e., m, n, D_1, and D_2. Based on Eqs. (4) and (6), for each material there is a special temperature (T_e) at which the measured dielectric constant is only related to the value of both D_1 and D_2. The value of T_e is determined by the following relation:

$$\exp(\alpha-\beta T_e)=\ln\,\omega_0 \exp[\alpha_1+(T_e/\beta_1)^{1+\delta}]. \tag{7}$$

The value of T_e is 26.4 °C and 81.2 °C for PMN-PT and PZN-PT-BT, respectively. Compared with the results in Fig. 1, one can find that T_e is in the range of T_m. The relation between D_1 and D_2 at T_e is

$$\frac{\varepsilon_H(\omega,T_e)}{1+D_1(\omega)}+\frac{\varepsilon_L(\omega,T_e)}{1+D_2(\omega)}=\varepsilon_m(\omega,T_e). \tag{8}$$

Using Eq. (8), we can fit the measured relation between the dielectric constant and temperature at each frequency with three independent parameters. The fitted results at 11 frequencies for the studied materials show the following features:

(1) Equations (6) do fit well the measured data.

(2) Both D_1 and D_2 are strongly dependent on the frequency. With increasing frequency, the value of D_1 increases and that of D_2 decreases.

(3) There is no regular pattern between the frequency and the value of either m or n.

TABLE II. The fitted value of D_1 and D_2 at different frequency for PMN-PT and PZN-PT-BT, respectively.

Frequency (Hz)	PMN-PT		PZN-PT-BT	
	D_1	D_2	D_1	D_2
100	1.3122	0.9411	4.6750	0.4745
120	1.3541	0.9040	4.7650	0.4648
200	1.4801	0.8069	5.0624	0.4322
400	1.6661	0.6955	5.4392	0.3943
1000	1.9653	0.5662	6.1543	0.3408
2000	2.2371	0.4809	6.6357	0.3084
4000	2.5708	0.4053	7.1617	0.2790
10 000	3.1589	0.3152	7.9249	0.2437
20 000	3.7599	0.2561	8.6236	0.2184
40 000	4.3400	0.2132	9.4775	0.1942
100 000	5.7633	0.1541	10.8678	0.1642

(4) The standard deviation of both m and n for the studied materials is less than 5% of its average value.

These four results confirm the validity of Eqs. (6) and the definition of the relation between the parameters (m, n, D_1, and D_2) in Eqs. (6) and the parameters (frequency and temperature) in the measurements. That is, both m and n are independent of the frequency.

When Eq. (8) is used to determine the relation between D_1 and D_2, the measured dielectric constant at T_e is overemphasized. To overcome it, we use the same value of both m and n for all the frequencies in the fitting process with independent fitting parameters of both D_1 and D_2. Using the least-squares method, we get the values of all the parameters for PMN-PT and PZN-PT-BT, respectively. The values of both m and n for the two materials and those of both D_1 and D_2 at different frequencies for both materials are shown in Tables I and II, respectively.

In Fig. 2, fitted plots of the relations between the dielectric constant and temperature are compared with the measured results. It is clear from Fig. 2 that the fitted results are of very high quality over the whole temperature range for both materials and (1) the discrepancy of the fitted results at each frequency in the most temperature range for both materials is quite smaller, on the order of 0.1%; (2) the maximum total discrepancy is about 1% for both materials at all measured frequencies and temperature.

Compared to the fitted results by using the other methods,[14–18,20] one can notice that the results of the present method are of the highest fitting quality. As PMN-PT and PZN-PT-BT relaxors belong to two different crystallographic systems, the high fitting quality for both materials at all the measured frequencies and temperatures strongly indicates the validity of Eqs. (6). First, it confirms that the RFE indeed has two polarization processes, and second, an entirely different approach is needed to understand the dielectric behavior of the RFE.

In Eqs. (6), although the parameters m and n are constant, the parameters D_1 and D_2 are strongly frequency dependent (Table II). Thus, the relations between the frequency and both D_1 and D_2, which are shown in Fig. 3 and Fig. 4 for PMN-PT and PZN-PT-BT, respectively, are very interesting

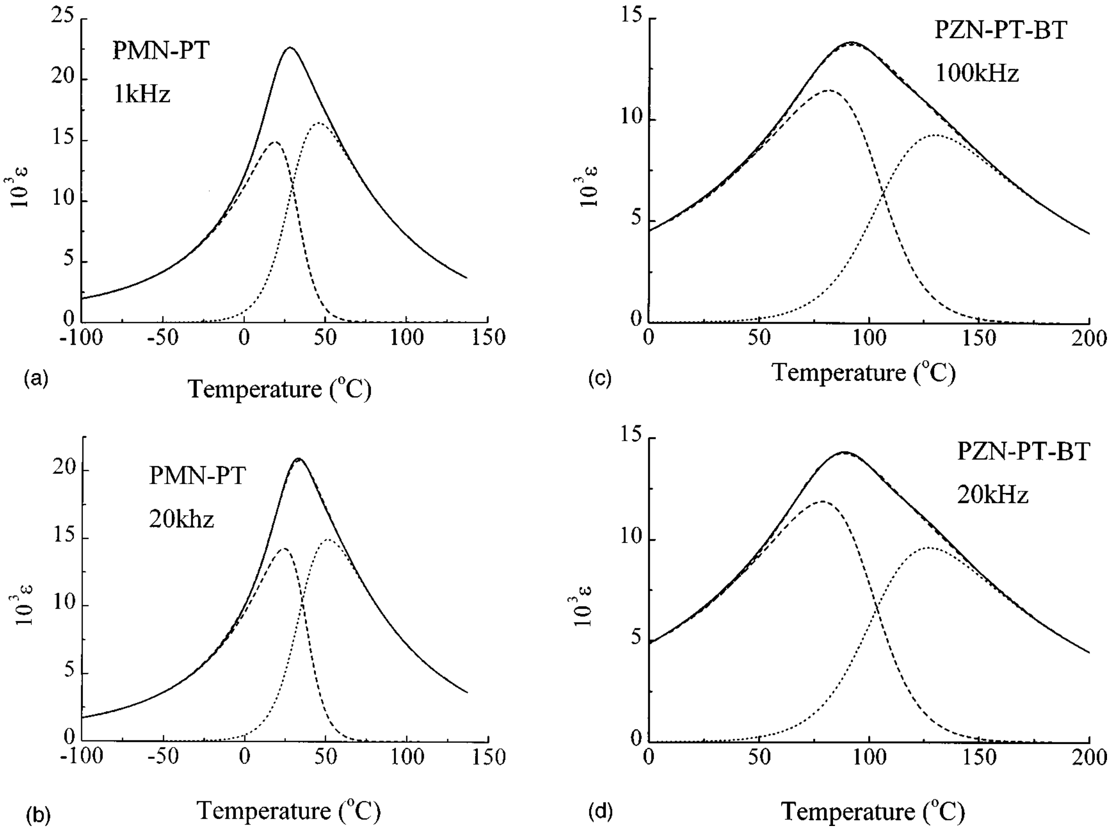

FIG. 2. Measured (dashed line) and fitted relation (solid line) between the dielectric constant and temperature for both materials at some frequencies with Eqs. (5) and (6). The results of both ε_1 (dotted line) and ε_2 (break line) are also shown.

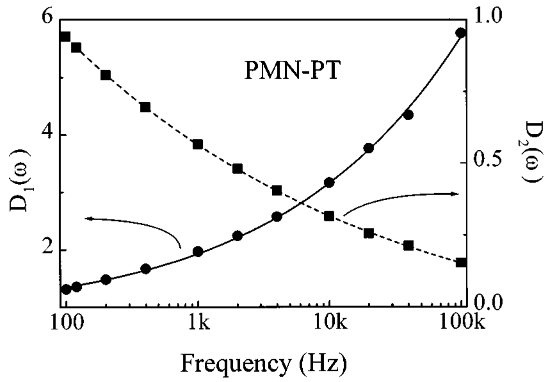

FIG. 3. Relation between frequency and fitted values of both D_1 and D_2 for PMN-PT. The solid line is the fitted results of D_1 with Eq. (9), and the dashed line is the fitted results of D_2 with Eq. (10).

to study the polarization behavior of RFE. For both materials, it is found that the frequency dependence of D_1 obeys the relation

$$D_1(\omega)=D_{10}+(\omega/\omega_1)^{\gamma}, \tag{9}$$

where $D_{10}(>0)$ and $\gamma(>0)$ are constants, $\omega_1(>0)$ is a constant in Hertz, and ω is the frequency in Hertz. The fitted points are shown in Figs. 3 and 4 as a solid line. It can be seen that Eq. (9) can indeed fit well the relation between the frequency and D_1. The fitted values of three parameters for both materials are listed in Table III.

It is also found that the frequency dependence of D_2 can be described by the relation

$$D_2(\omega)=D_{20}+(\omega/\omega_2)^{-\chi}, \tag{10}$$

where $D_{20}(<0)$ and $\chi(>0)$ are constants, and $\omega_2(>0)$ is a constant in Hertz. The fitted results are shown in Figs. 3 and 4 as a dashed line. It can be seen that Eq. (10) also fits well the relation between ω and D_2. The fitted parameters in Eq. (10) for both materials are listed in Table III.

C. Basic features of both polarization processes

It is very interesting to compare the fitted temperature dependence of both ε_1 and ε_2 under different frequencies in order to study the basic features of both polarization processes. The fitted temperature dependence of ε_1 at different frequencies is shown in Fig. 5 for both materials. The following features can be noticed from Fig. 5:

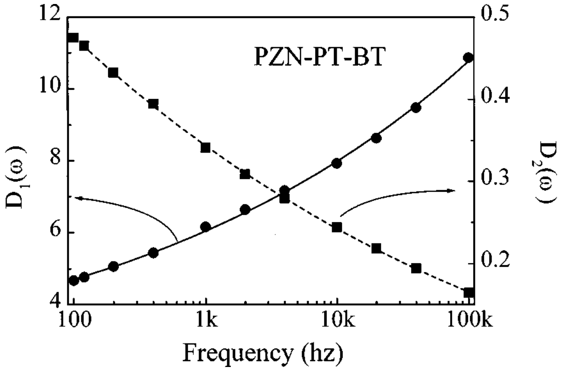

FIG. 4. Relation between frequency and fitted values of both D_1 and D_2 for PZN-PT-BT. The solid line is the fitted results of D_1 with Eq. (9), and the dashed line is the fitted results of D_2 with Eq. (10).

TABLE III. The fitted parameters of Eqs. (9) and (10) for PMN-PT and PZN-PT-BT, respectively.

Parameters		PMN-PT	PZN-PT-BT
	D_{10}	0.80769	1.7165
D_1	ω_1 (Hz)	694.04	0.1069
	$1/\gamma$	3.1283	6.237
	D_{20}	−0.16532	−0.07973
D_2	ω_2 (Hz)	174.102	0.69621
	$1/\chi$	5.55684	8.4499

(1) The value of ε_1 rapidly decreases with decreasing temperature at the temperatures lower than the temperature of ε_1 maximum (T_{m1});

(2) The value of ε_1 at T_{m1} decreases with increasing frequency;

(3) The value of T_{m1} increases with increasing frequency;

(4) At high temperature there is no dielectric dispersion, while at temperatures around and lower than T_{m1} there is a strong dielectric dispersion as the dielectric constant always decreases with increasing frequency.

All these indicate that ε_1 originates from a relaxation polarization process. This is in agreement with the definition of it, discussed in Sec. III A. That is, the micro-origin of ε_1 is the thermally activated flips of the polar regions in RFE.

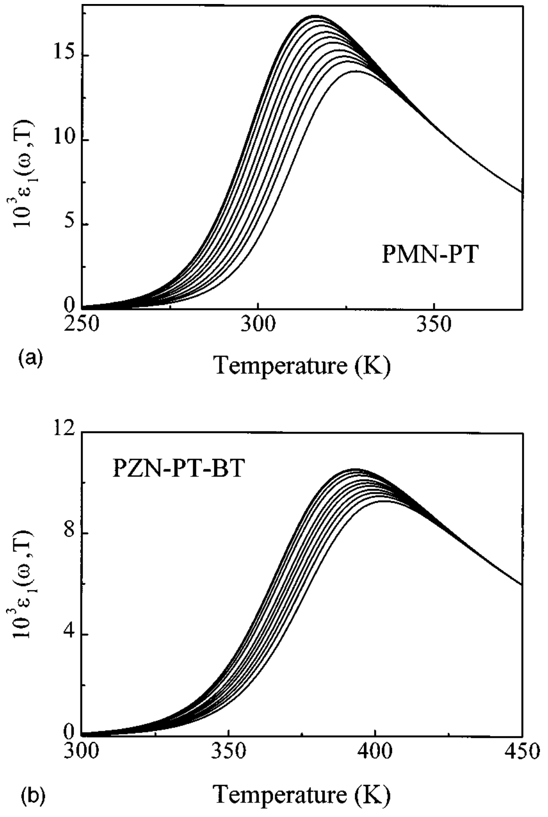

FIG. 5. Temperature dependence of ε_1 at different frequencies for PMN-PT (a) and PZN-PT-BT (b). The largest dielectric constant is for the 100 Hz, the smallest for the 100 kHz, and the other curves in between are in the order of increasing frequency.

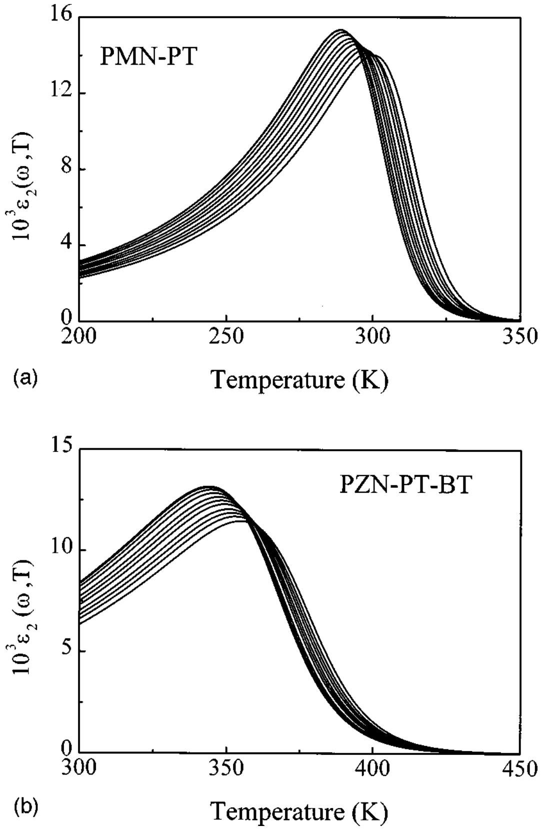

FIG. 6. Temperature dependence of ε_2 at different frequencies for PMN-PT (a) and PZN-PT-BT (b). At low temperatures, the largest dielectric constant is for the 100 Hz, the smallest for the 100 kHz, and the other curves in between are in the order of increasing frequency.

The fitted temperature dependence of ε_2 at different frequencies is shown in Fig. 6 for both materials. The following conclusions can be obtained from Fig. 6:

(1) ε_2 is of a strong dielectric dispersion in the whole temperature range at the studied frequencies.

(2) With increasing frequency, ε_2 increases at high temperatures while it decreases at low temperatures.

(3) The dielectric constant maximum temperature (T_{m2}) of ε_2 increases with increasing frequency.

(4) The value of ε_2 at T_{m2} decreases with increasing frequency.

(5) When the temperature is higher than T_{m2}, ε_2 decreases rapidly with increasing temperature.

It is impossible to explain all these features of ε_2 with a relaxation polarization process, as the dielectric constant contribution from the relaxation process always decreases with increasing frequency. It seems that ε_2 originates from a resonance polarization. For this resonance polarization process, the following characteristics can be derived from the above results. The polarization process does not exist in the materials at high temperature. With decreasing temperature from the higher temperature side, the polarization process appears rapidly in the material when the temperature approaches T_m. For the contribution to the dielectric constant of the materials, the lower the temperature the higher is the weight of the resonance process.

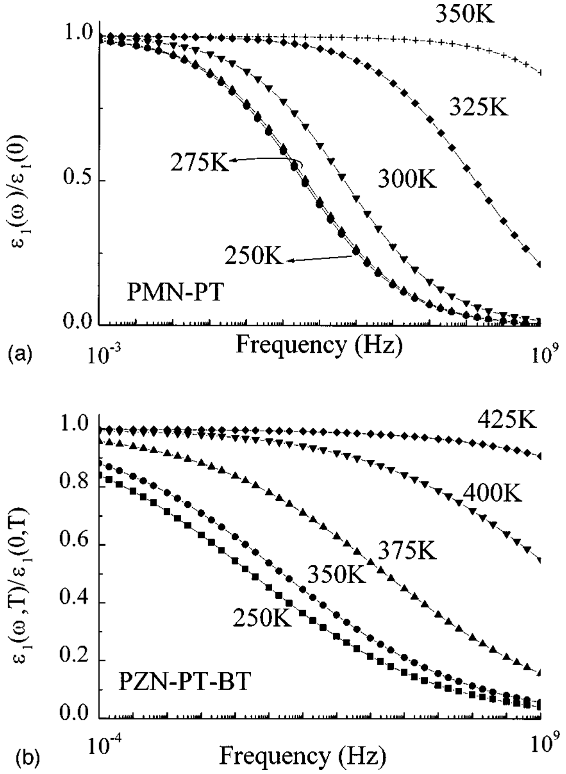

FIG. 7. Frequency dependence of ε_1 at different temperatures for PMN-PT (a) and PZN-PT-BT (b).

D. Frequency dependence of dielectric constant

To study the frequency dependence of ε_1, Eq. (6a) can simply be rewritten as

$$\varepsilon_1(\omega,T)=\frac{\varepsilon_1(0,T)}{1+\eta(T)\omega^{\gamma}}, \tag{11}$$

where $\varepsilon_1(0,T)$ is the value of ε_1 at static electric field, $\eta(T)(>0)$ increases with decreasing temperature.

Using Eq. (11) and the parameters in Tables I and III, the calculated frequency dependence of ε_1 at selected temperatures is shown in Fig. 7. Considering Debye dielectric theory,[27] the results in Fig. 7 clearly indicate that the relaxation process has a broad distribution of the relaxation times and the distribution is flat in the limited range, which is in agreement with the assumption taken for it in the method described by Cheng *et al.*[18] As $\eta(T)$ in Eq. (11) increases with decreasing temperature, Eq. (11) and Fig. 7 indicate that the distribution width of the relaxation times for the relaxation polarization increases with decreasing temperature, which is in agreement with the interpretation of the dielectric properties of relaxors based on the superparaelectric model.[7,17,18]

For the value of $\varepsilon_1(0,T)$ in Eq. (11), it is found that it increases with decreasing temperature at high temperatures, and it decreases with decreasing temperature at low temperatures. Based on the general dielectric theory, this behavior indicates that with decreasing temperature the amount of polar regions contributing to the relaxation process increases at high temperatures, while it decreases at low temperatures. That is, the amount of the polar regions associated with the relaxation process changes with temperature. This behavior

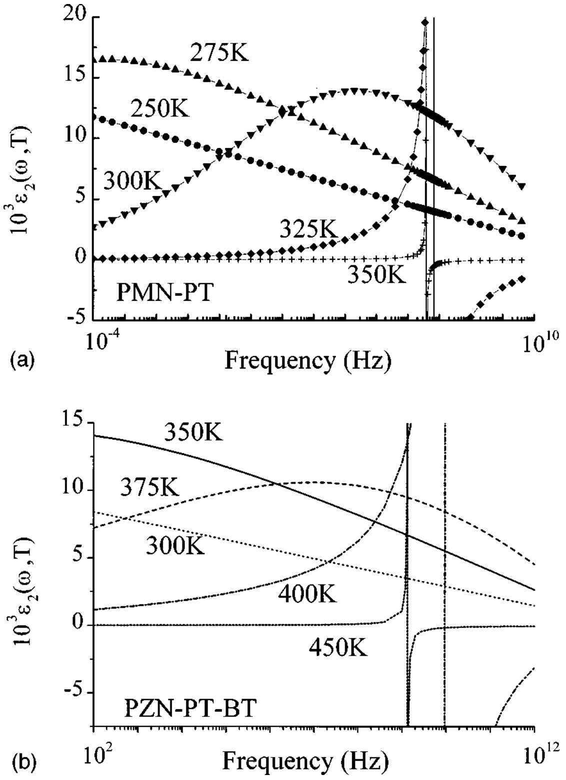

FIG. 8. Frequency dependence of ε_2 at different temperatures for PMN-PT (a) and PZN-PT-BT (b).

is different compared to that of the general dipole process, whereas the amount of the dipoles do not change with the temperature.

With regard to the frequency dependence of ε_2, Eq. (6b) can be rewritten as

$$\varepsilon_2(\omega,T)=\frac{[\varepsilon_\infty+A(T)\ln\,\omega_0]-A(T)\ln\,\omega}{\Lambda(T)+\mu(T)\omega^{-\chi}}, \tag{12}$$

where $\mu(T)=\omega_2^{\chi}(A(T)\ln\omega_0/\varepsilon_H(T))^n(>0)$ increases with increasing temperature, while $\Lambda(T)=1+D_{20}(A(T)\ln\omega_0/\varepsilon_H(T))^n$ decreases with increasing temperature. At some special temperature (T_S), $\Lambda(T)$ is equal to zero as the value of D_{20} in Eq. (10) is smaller than zero. The value of T_S is 66.8 °C and 170.9 °C for PMN-PT and PZN-PT-BT, respectively. Thus, when the temperature is higher than the special temperature (T_S), $\Lambda(T)$ is smaller than zero. In this case, ε_2 has a singularity at a frequency (ω_{SO}), which is equal to $|\mu(T)/\Lambda(T)|^{1/\chi}$.

Using Eq. (12) and the parameters in Tables I and III, the calculated frequency dependence of ε_2 at selected temperatures is shown in Fig. 8 for both materials. Comparing the results in Fig. 8 with the dielectric response of a resonance polarization process,[27] the frequency dependence of ε_2 at different temperature is indeed very similar to the frequency dependence of the dielectric constant contributions from a resonance polarization with different resonance frequencies and different damping coefficients. Using the dielectric response of the resonance polarization to analyze the results in Fig. 8, one can conclude the following features for ε_2:

(1) The damping coefficient of the resonance polarization increases with decreasing temperature.

(2) When the temperature is higher than T_s, the resonance frequency (ω_{so}), which is the singularity of ε_2, decreases with increasing temperature. In this case, ε_2 always increases with increasing frequency.

(3) When the temperature is lower than T_s, ε_2 has a maximum at a frequency (ω_m). The value of ω_m decreases with decreasing temperature. In this case, with increasing frequency, ε_2 increase at the frequencies lower than ω_m, while ε_2 decreases at the frequencies higher than ω_m.

(4) When the temperature is much lower than T_s, the maximum of ε_2 appears at the static field. Thus, ε_2 decreases with increasing frequency. In this case, the dielectric behavior of ε_2 is similar to the dielectric behavior of a relaxation process. In view of the resonance polarization mechanism,[20,27] it indicates that the damping coefficient of the process is very large (further details are given in Sec. IV). That is why the measured relation between the dielectric constant and frequency for RFE is somewhat like the response of a relaxation process.

In principle, the frequency dependence of the dielectric absorption for both polarization processes can be obtained with the Kramers-Kronig equation.[27] However, in order to obtain the frequency dependence of the dielectric absorption using the Kramers-Kronig equation, the exact frequency dependence of the dielectric constant in a very broad frequency range is needed. The present frequency dependence of the dielectric constant for both processes is obtained in a limited frequency range. Although the results extrapolated for both low and high frequencies express well the basic characteristics of each process, it is difficult to ensure that the extrapolated results are quantitatively of very high precision. In addition, most of the investigations about the dielectric characteristics of RFE are based on the analysis of the frequency or temperature dependence of the dielectric constant.[1,4,5,7–9,15] Thus, we do not pursue the frequency dependence of the dielectric absorption for each process.

IV. DISCUSSIONS

A. Micropicture of the resonance polarization

Although the results on only two materials are presented in this paper, we have studied six RFE in ceramics form. The fitted results for all of them exhibit similar characteristics. Although the result is not an occasional phenomenon, one may question the possibility of the contribution from grain boundaries to the dielectric behavior of RFE. In general, there are two cases in which the grain boundaries make a clear contribution to the dielectric behavior of the ceramics. One is the typical ferroelectric ceramics. In this case, the contribution of the grain boundaries can be resonant in nature. Thus, the dielectric behavior of the typical ferroelectrics on a single crystal is much different than that of ceramics. The resonance originates from the piezoelectric properties of the grains.[28] However, for RFE, although there are polar regions of nanosize in the grains, the grain is nonpolar on average. Thus, it is not possible to expect substantial contributions from the grain piezoelectric resonance in the case of RFE ceramics. In addition, the dielectric behavior on ceramics does not show any difference with that of a single crystal for RFE.[29,30] The other case is dielectric ceramics with conductive grain boundaries, which results in a relaxation process named the Maxwell-Wagner effect.[31] However, for the samples used in this study, at temperatures a bit higher than T_m, the dielectric loss is very small and also suggests a good quality ceramics. This is a general behavior of RFE. That is, it is improbable that the Maxwell-Wagner effect has any noticeable contribution to the measured dielectric behavior of RFE. Therefore, what we obtain in Sec. III is RFE's intrinsic behavior that excludes possible contributions from the grain boundaries. Thus, such fitting of a dielectric behavior on a single-crystal RFE will give very much the same results.

As discussed in the Introduction, it is widely accepted that the dielectric characteristics of RFE are mainly due to the micropolar regions in the materials. In addition, the density of polar regions in RFE always increases with decreasing temperature. The experimental results of the thermal expansion for RFE have shown that the polar regions appear in relaxors at temperatures much higher than T_m.[32–34] Meanwhile, the polar regions freeze with decreasing temperature over a wide temperature range.[19,20] The lower the temperature, the more frozen polar regions. For the unfrozen polar regions, it is reasonable to use a relaxation process expressing its dielectric response with the thermally activated flip model as the dielectric response is the result of the orientation of the polar regions under external electric field. However, the dielectric response of the frozen polar regions is very difficult to analyze with relaxation theory as the frozen polar regions do not have the orientation behavior.

At high temperatures, almost all polar regions are thermally activated. Thus, their dielectric response is mainly from the relaxation polarization. The distribution of the relaxation times depends on the distribution of both the size and polarization strength of the polar regions. Therefore, the contribution from the relaxation process to the static dielectric constant increases with decreasing temperature as the amount of polar regions increases. As a result, at high temperatures the value of $\varepsilon_1(0,T)$ in Eq. (11) increases with decreasing temperature and the dielectric constant of RFE at high temperatures is much more strongly dependent on the temperature, Eq. (1), than that of the Debye medium. For the Debye medium, the static dielectric constant is proportional to the inversion of the temperature in Kelvin.[35] The size distribution of the polar regions depends on the space distribution of microcompositions as all RFE are the solid solutions. The polarization strength of a polar region depends on the temperature and its composition. As the materials are homogeneous on micronanoscale, the change of the microcomposition in RFE with position is smooth. Thus, the size of the polar region distribution is of a broad range. Therefore, the relaxation times of the relaxation process has a broad range distribution. With decreasing temperature, besides the increase in the number of polar regions, the size of some polar regions also increases. Thus, the large dimension of the polar region increases with decreasing temperature. For RFE, the small dimension of a polar region is limited to the unit cell of the material. Thus, it does not change with the temperature. Therefore, the distribution of the relaxation times broadens with decreasing temperature.

As temperature decreases, the relaxation time of the polar regions increases and hence the interaction among polar regions increases. That makes some polar regions difficult to orient under external electric field. These polar regions are the frozen polar regions. Thus, they will not contribute to the relaxation process. Therefore, although the amount of polar regions in the material increases with decreasing temperature, the amount of polar regions contributing to the relaxation process decreases with decreasing temperature at low temperatures. That is why at low temperature the value of $\varepsilon_1(0,T)$ in Eq. (11) decreases with decreasing temperature.

For the frozen polar regions in the materials, its dielectric response or contribution is different with the thermally activated flips under the external electric field as its polarization direction does not change under the weak external electric field. However, the size of polar regions in RFE can change under external electric field. That is why the ferroelectric state can be induced in all RFE at low temperatures with strong external electric field. Also, under external electric field, the surface of polar region changes. With increasing electric fields, in some directions the dimension of the polar region increases, while in other directions it decreases, resulting in the shape change of the frozen polar regions resembling something like a breathing mode. The breathing of the frozen polar regions results in the change of total dipole moment per unit volume. Thus, it contributes to the dielectric behavior of the materials. This is another polarization process in RFE associated with the polar regions besides the relaxation polarization of the thermally activated flips of the unfrozen polar regions. This polarization process should be the origin of the dielectric response of ε_2, described in Sec. III. At low temperature, almost all polar regions are frozen, so the dielectric behavior of the material is mainly determined by the breathing behavior of the frozen polar regions. In cooling the material from high to low temperature, the fraction of frozen polar regions increases, so that the weight of ε_2 in the total dielectric constant increases. This is what has been obtained in Sec. III about the weight change of ε_1 and ε_2 with temperature. Using this breathing model, the dielectric response of frozen polar regions can be further discussed in the following text.

For the perovskite-structure (ABO_3) materials, the difference between the ferroelectric phase (polar state) and paraelectric phase (nonpolar state) is the difference of related position of ions, especially B and A ions in the structure.[36] Therefore, the difference between the polar region and the nonpolar region is the difference of related positions of both A and B ions. Thus, the breathing of the frozen polar regions is in fact the oscillation of the ions around its equilibrium position in the materials. It is known that the dielectric response of an electric particle oscillating around an equilibrium position is a resonance.[27,35] That is why the dielectric behavior of ε_2 resembles the dielectric response of a resonance polarization.

For the resonance polarization, there are two parameters that influence the frequency dependence of the dielectric constant. One is the resonance frequency (ω_s), which is dependent on the intrinsic properties of the electric particle and can be expressed by the relation

$$\omega_S = \sqrt{K/m_e}, \tag{13}$$

where m_e is the mass of the electric particle, and K is the elastic constant of the restoring force on the electric particle. Equation (13) conveys that the resonance frequency increases with increasing K if the mass does not change. The second parameter is the damping coefficient, which determines the damping force on the moving particle.

For the frozen polar regions in RFE, the higher the temperature, the smaller is the difference between the polar and nonpolar regions. In addition, with increasing temperature the interaction among the frozen polar regions decreases as the amount of frozen polar regions decreases. Thus, for the breathing of the frozen polar regions in a material, the higher the temperature, the smaller is the value of K. However, the mass of both A and B ions does not change with temperature. Therefore, the resonance frequency of the breathing decreases with increasing temperature. Meanwhile, with decreasing temperature, the increase of the interaction among the frozen polar regions makes the damping coefficient increase. Thus, the damping coefficient of the breathing of the frozen polar regions increases with decreasing temperature. All these features are in agreement with the results of ε_2, derived in the Sec. III.

For the dielectric response of a resonance polarization, it was shown that in two extreme cases the dielectric behavior prefers the dielectric response of the relaxation process. The first case is that the mass tends to zero while the ratio of the damping coefficient to the elastic constant maintains a constant value.[27] The second case is that both the damping coefficient and elastic constant tends towards infinity while the ratio of the damping coefficient to elastic constant maintains a constant value.[20] In both cases, the ratio of the damping coefficient to elastic constant is related to the relaxation time for the equal relaxation polarization. With regard to the breathing of the frozen polar regions, as discussed above, both the damping coefficient and elastic constant increases with decreasing temperature. At low temperature, both of these are very large, so that the dielectric response of the breathing of frozen polar regions is somewhat like the results of a relaxation process when considering the second case above. This result mistakenly leads to that all of the theoretical treatment and analysis of the dielectric behavior of RFE at low temperature are based on the relaxation theory so far.

As discussed above, there is a broad size distribution range of the polar regions. The composition of the polar regions differ from each other as A and B ions randomly occupy the lattice positions in ABO_3. Therefore, both the elastic constant and damping coefficient spread over a broad range. This results in the ratio of the damping coefficient to elastic constant being distributed over a broad range. Thus, the equifinal relaxation times have a broad distribution. That is why the dielectric behavior of RFE can be dealt with a relaxation process with very broad distribution of the relaxation times.[18]

RFE has a close relation to typical ferroelectrics as RFE belongs to the modified ferroelectrics. The frozen polar regions can be considered as ferroelectric regions of nanosize. So, the breathing of the frozen polar regions is a kind of domain-wall motion. Thus, the above discussion about the resonance of the frozen polar regions has some similarity with the domain-wall motion in a ferroelectric single crystal with multidomain. It is known that the dielectric response of the domain-wall vibrations in a ferroelectric single crystal is, in nature, resonant.[37,38] However, in some special cases this dielectric response is, in form, very similar to that of a relaxation polarization.[37,38] All these are consistent with our discussion about the dielectric response of the breathing of frozen polar regions in RFE. This can be thought of as indirect evidence to support the above discussion.

B. Peak of dielectric constant

Based on the above discussion and the fitted results in Fig. 2, the peak in the temperature dependence of the dielectric constant is determined by both the polarization processes in the RFE. The range of T_m corresponds to rapid change of the fraction of frozen polar regions. Thus, the frequency dependence of T_m cannot be simply explained with only one polarization process. That is why both Debye and Vogel-Fulcher relationships cannot describe well the experimental relation between the frequency and T_m for RFE. Therefore, any expression for the relation between the frequency and T_m is only a mathematical treatment. That is why it is also difficult to get the physical signification of a parameter in the superexponential relation, although the relation can well describe the experimental relation between the frequency and T_m.

Based on the present model, the peak of the dielectric constant does not correspond to any phase transition in the materials on macroscopic level, and hence the x-ray diffraction does not show any phase change of the RFE materials in the wide temperature range. Although, the frozen polar regions are anisotropic, the optical and mechanical properties of the material are isotropic, as the size of the frozen polar regions is smaller than a few nanometers and the polar direction of the frozen polar regions is randomly distributed. This is in agreement with the experimental results on RFE.

For regular ferroelectrics, the depolarization temperature is the same as T_m.[36] But, it is found that the depolarization temperature of RFE is always a few tens of degrees lower than T_m.[5,6,29,30] This is an important characteristic of RFE. The depolarization temperature is the temperature at which macrodomains disappear. Based on the present model, the electric-field-induced ferroelectric state for RFE is the result of expanding and coalescing of the frozen polar regions. Thus, the depolarization temperature should be the temperature at which most polar regions are frozen. Based on the fitted results of the dielectric behavior, in Sec. III B, this temperature is a few tens of degrees lower than T_m.

C. Amplitude dependence of dielectric constant

Recently, experimentally it was found that the dielectric constant of RFE is strongly dependent on the amplitude of the measuring signal at temperatures around and lower than T_m, although the dielectric constant at high temperature was independent of the amplitude.[39,40] The higher the amplitude, the higher was the dielectric constant and the lower the T_m was. The temperature dependence of the dielectric constant at different amplitudes is similar to that at different frequencies. The effect of increasing amplitude on the dielectric constant is very similar to the effect of decreasing frequencies on the small-signal dielectric constant. It was indicated that the behavior could not be explained with the orientation polarization of the polar regions. It was thought that the amplitude dependence of the dielectric constant is related to the surface behavior of the polar regions.[35]

In order to explain the experimental results, a model was proposed. Based on the model, the higher the external electric field, the smaller is the relaxation time of the domain-wall motion.[39] Thus, the dielectric constant increases with increasing external electric field. That is, the dielectric response of the domain-wall motion is thought as a relaxor. This is inconsistent with the dielectric response of general domain-wall vibration.[37,38] In this model, the volumes of the domains and domain walls are thought of as being constant. This is contrary to the experimental results of RFE. It is known that the ferroelectric state can be electrically induced in RFE. That is, the volume of domains in RFE can be changed with external electric field. In addition, this model directly results in that the dielectric absorption decreases with increasing external electric field. This is contrary to the experimental results that show that the dielectric absorption strongly increases with increasing external electric field.[40]

Based on above discussion, the contributing mechanism of the domain walls to the dielectric behavior of RFE is not clear. Based on the present model, the dielectric behavior of the materials are dependent on two processes. For the orientation behavior of the polar regions, the general Debye theory indicates that the parameter y is the key to discuss the nonlinear behavior of the dielectric behavior, i.e.,

$$y=\frac{\mu_0 E_e}{kT}, \tag{14}$$

where μ_0 is the dipole moment of the polar region, E_e is the electric field on the polar regions, and k is the Boltzmann constant. If the value of y is much smaller than unity, the dielectric behavior is independent of the signal amplitude.[35]

As the dipole moment of the polar region cannot be obtained directly from the experimental measurements, the spontaneous polarization of the ferroelectrics with perovskite structure can be used as a reference. The spontaneous polarization of the ferroelectrics with the perovskite structure is generally on the order of 10^{-1} to 10^{-2} C/m^2.[32] It is widely accepted that the size of the polar regions is not larger than a few nanometers. Thus, the value of μ_0 is smaller than that of 10^{-29} Cm. Assumed that E_e is on the order of 10^7 V/m ($=10^2$ kV/cm), which is much higher than the electric field used in the experiments on RFE. For this extreme case, the value of y is not higher than 10^{-2} (which is much smaller than the unity). Therefore, the static dielectric response of the relaxation process ε_1 in RFE does not show the amplitude dependence of the dielectric constant. Anyway, based on above discussion about the freezing of the polar regions, the increase of the amplitude of the external electric field results in the decrease of freezing temperature of a polar region. Therefore, the higher the amplitude of the external electric field is, the lower the temperature range, in which the fraction of ε_1 and ε_2 in ε_m changes rapidly, is. Therefore, the T_m decreases with increasing amplitude of the external electric field.

For the breathing of the frozen polar regions, the higher the electric field, the larger is the breathing amplitude. That is why the ferroelectric state can be induced in RFE with strong electric field. Thus, the higher the amplitude of external electric field, the larger is the dielectric constant. This is in agreement with the experimental results. Therefore, based on the present model, the dielectric response of the breathing of frozen polar regions shows the amplitude dependence of the dielectric constant. At high temperature, the weight factor of dielectric constant contribution from the breathing behavior is very small as the fraction of the frozen polar regions is very small. Thus, the measured results are independent of the amplitude of the measuring signal.

D. Infinite dielectric constant (ε_∞)

An important difference between Eqs. (2) and (1) is in the consideration of the contribution of ε_∞. In Eq. (1), the contribution of ε_∞ is not included. The results derived from Eq. (1) were not much different with or without the consideration of ε_∞. To understand this, it is interesting to compare it with the Curie-Weiss law for normal ferroelectrics. Curie-Weiss law indicates that the dielectric constant (ε) at temperatures higher than phase-transition temperatures can be described by the relation

$$\varepsilon=\frac{C}{T-T_c}, \tag{15}$$

where C is the Curie-Weiss constant, and T_c is the Curie-Weiss temperature. The contribution of ε_∞ is not included in it. When the contribution of ε_∞ is considered, Eq. (15) becomes

$$\varepsilon=\varepsilon_\infty+\frac{C}{T-T_c}. \tag{16}$$

It was expected that Eq. (16) should fit the experimental data much better than Eq. (15). However, the experimental results indicated that Eq. (15) is a much better than Eq. (16).[41] The similarity between Eq. (1) and the Curie-Weiss law indicates that the volume fraction of polar regions for RFE is very high. However, with regard to the breathing behavior of the frozen polar regions, only the surface has the contribution to the dielectric behavior. Therefore, although the fraction of polar regions at low temperature is higher than that at high temperature, the contribution of ε_∞ cannot be ignored as the volume fraction of the surface of frozen polar regions is much smaller than the volume fraction of frozen polar regions. That is why the contribution of ε_∞ must be considered in the dielectric behavior of the materials at low temperature, as shown in Eq. (2).[18]

V. CONCLUSION

Based on the general behavior of the RFE and the insufficiency of explaining the results derived from different models, it is assumed in this paper that there are two polarization processes in RFE. One part has its origin from the thermally activated flips of the polar regions and an expression is proposed to describe the relation between the dielectric constant and both the temperature and frequency dependence of the polarization processes. The formula is tested against the measured results on two relaxor compositions, namely, lead magnesium niobate:lead titante, and lead zinc niobate:PbTiO$_3$ solid solution ceramics. When compared with other methods, the fitted results from the present method are of the highest quality. The computed results show that the peak of the dielectric constant as a function of temperature is decided by the two polarization processes. The temperature, T_m, corresponds to the range in which the weight factor of ε_1 and ε_2 in determining ε_m changes rapidly with temperature.

The computed plots show that the other polarization process in the RFE materials is a resonance phenomena. Considering the frozen polar regions in the material and the characteristics of RFE, it is concluded that the origin of the resonance polarization is from the breathing of the frozen polar regions in the materials. Based on the breathing model or concept, it is easy to understand most of the characteristics of ε_2 obtained from the computation in the present method. The amplitude dependence of the dielectric constant for RFE can also be easy to understand with the present model.

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[1] L. E. Cross, Ferroelectrics **76**, 241 (1987); **151**, 305 (1994).

[2] Z. Chen, X. Yao, and L. E. Cross, Ferroelectrics **49**, 213 (1983).

[3] K. Uchino and S. Nomura, J. Mater. Sci. **16**, 569 (1981).

[4] G. A. Smolensky, J. Phys. Soc. Jpn. **28**, 26 (1970).

[5] X. Yao, Z. Chen, and L. E. Cross, J. Appl. Phys. **54**, 3399 (1983).

[6] Z.-Y. Cheng, L. Y. Zhang, and X. Yao, IEEE Trans. Electr. Insul. **27**, 773 (1992).

[7] D. Viehland, S. J. Jang, L. E. Cross, and M. Wutting, J. Appl. Phys. **68**, 2916 (1990).

[8] Z.-Y. Cheng, L. Y. Zhang, and X. Yao, J. Appl. Phys. **79**, 8615 (1996); **80**, 5518 (1996).

[9] N. Setter and L. E. Cross, J. Mater. Sci. **15**, 2478 (1982).

[10] C. A. Randall and A. S. Bhalla, Jpn. J. Appl. Phys., Part 1 **29**, 327 (1990).

[11] X. W. Zhang, Q. Wang, and B. L. Gu, J. Am. Ceram. Soc. **74**, 2846 (1991).

[12] W. Kleemann, Int. J. Mod. Phys. B **7**, 2469 (1993).

[13] J. Kuwata, K. Uchino, and S. Nomura, Ferroelectrics **22**, 863 (1979).

[14] H. Wang and Y. Xu, Acta Phys. Sin. **35**, 605 (1986).

[15] P. Groves, Ferroelectrics **76**, 81 (1987).

[16] A. J. Bell, J. Phys.: Condens. Matter **5**, 8773 (1993).

[17] Z. G. Lu and G. Valvarin, Phys. Rev. B **51**, 2694 (1995).

[18] Z.-Y. Cheng, R. S. Katiyar, X. Yao, and A. Guo, Phys. Rev. B **55**, 8165 (1997).

[19] Z.-Y. Cheng, R. S. Katiyar, X. Yao, and X. L. Wang, Philos. Mag. B (to be published).

[20] Cheng Zhong-Yang, Ph.D thesis, Xian Jaiotong University, 1995.

[21] Z.-Y. Cheng, R. S. Katiyar, and X. Yao, Mater. Res. Soc. Symp. Proc. **453**, 455 (1997).

[22] S. W. Choi, T. R. Shrout, S. J. Jang, and A. S. Bhalla, Ferroelectrics **100**, 29 (1989).

[23] W. Yu, Z. Gui, Y. C. Chan, L. Li, and X. Zhang, J. Mater. Sci. Mater. Electr. **7**, 133 (1996).

[24] A. Halliyal, U. Kumar, R. E. Newnham, and L. E. Cross, J. Am. Ceram. Soc. **70**, 119 (1987).

[25] X. L. Wang and X. Yao, Ferroelectrics **145**, 143 (1993).

[26] F. Chu, I. M. Reaney, and N. Setter, J. Am. Ceram. Soc. **78**, 1947 (1995).

[27] A. K. Jonscher, *Dielectric Relaxation in Solids* (Chelsea Dielectrics, London, 1983).

[28] X. Yao, H. Mckinstry, and L. E. Cross, J. Am. Ceram. Soc. **66**, 637 (1983).

[29] For example, dielectric behavior on PMN single crystals. D. Viehland, S. Jang, L. E. Cross, and M. Wuttig, Philos. Mag. B **64**, 335 (1991); Z.-G. Ye and H. Schmid, Ferroelectrics **145**, 83 (1993).

[30] For example, dielectric behavior on PMN ceramics. S. J. Butcher and M. Daglish, Ferroelectr. Lett. Sect. **10**, 117 (1989); T. Tsurumi, K. Soejima, T. Kamiya, and M. Daimon, Jpn. J. Appl. Phys., Part 1 **33**, 1959 (1994).

[31] B. K. P. Scaife, *Principles of Dielectrics* (Clarendon, Oxford, 1989).

[32] G. Burns and F. H. Dacol, Phys. Rev. B **28**, 2527 (1983); **30**, 4012 (1984).

[33] G. Burns and F. H. Dacol, Solid State Commun. **48**, 853 (1983).

[34] G. Burns and F. H. Dacol, Ferroelectrics **104**, 25 (1990).

[35] L. Y. Zhang and X. Yao, *Physics of Dielectrics* (Xian Jiaotong University Press, Xi'an, 1991).

[36] M. E. Lines and A. M. Glass, *Principle and Application of Ferroelectrics and Related Materials* (Oxford University Press, Oxford, 1977).

[37] N. A. Pertsev, G. Arlt, and A. G. Zembilgotov, Phys. Rev. Lett. **76**, 1364 (1996).

[38] A. Erbil, Y. Kim, and R. A. Gerhardt, Phys. Rev. Lett. **77**, 1628 (1996).

[39] A. E. Glazounov, A. K. Tagantsev, and A. J. Bell, Phys. Rev. B **53**, 11 281 (1996).

[40] A. E. Glazounov, A. K. Tagantsev, and A. J. Bell, Ferroelectrics **184**, 217 (1996).

[41] S. Roberts, Phys. Rev. **75**, 989 (1949).