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Analysis of dipole behavior in PMN–PT single crystal from modeling of dielectric spectrum

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Abstract

Some diverse characters between relaxor ferroelectric ceramics and their single crystals remain unknown. Based on dual polarization model used in ceramics, we modeled and analyzed dielectric spectrum of PMN–PT single crystals above characteristic temperature T_m. An indistinct characteristic temperature T_2 was made clear. The results of simulation for single crystals fitted with experiments. It is shown that high temperature model in the dual polarization model is also valid for single crystals, and a characteristic temperature T_2 may signify the onset of dipolar regions freezing. The relaxor materials experience different polarization processes in different temperature ranges divided by T_2. The reasons resulted in the discrepancy between ceramics and single crystals were analyzed. We believe that the divergence between ceramics and single crystals is induced by the difference of polar region concentration, electric interaction and inner elastic stress among polar regions.

Keywords: Relaxor ferroelectrics; Dual polarization model; Polar regions freezing

1. Introduction

A typical relaxor ferroelectric displays a diffused phase transition, a strong frequency dispersion of the dielectric properties, and an absence of macroscopic polarization at zero electric field. Although the origin of these dielectric features is still controversial, it has been suggested that the presence of polar microregions in nano scale is crucial to the relaxor behaviors. Various models have been presented to account for the unusual physical properties of relaxor ferroelectrics. Based on these models, several methods were proposed to describe the temperature dependence of the dielectric permittivity. But there is no universal formula describing the temperature dependence of the dielectric permittivity in a wide temperature range.

By studying the PMN–*x*PT single crystals, Tu et al. [1] found that the dielectric permittivity ε' above the dielectric spectrum peak T_m fitted the empirical formula:

$$\frac{\varepsilon'_m}{\varepsilon'(f, T)} = 1 + \frac{[T - T_m(f)]^\gamma}{2\delta_\gamma^2} \tag{1}$$

Compared with PMN–34%PT crystals, PMN–24%PT crystals possess larger values of δ_γ and γ, and wider regions of temperature in which the experimental data obey empirical Eq. (1). In other words, the dielectric relaxation strength of PMN–34%PT is smaller than that of PMN–24%PT. At higher temperature regions, deviations from Eq. (1) were found in both crystals. The authors believed that it could be attributed to the contribution of the ionic conductivity activated by thermal energy. However, in PMN and PMN–25%PT (ceramic samples), the dielectric permittivity obeys the relation $\varepsilon'_A/\varepsilon'(f, T) = 1 + [T - T_A(f)]^2/2\delta_\gamma^2$ in a wide temperature range above T_m [2]. But, such an empirical quadratic law could not fit better than Eq. (1) with the dielectric data of PMN–34%PT and PMN–24%PT single crystals. They could not explain this difference between ceramics and single crystals, and wished to find a formula describing the temperature dependence of ε' in a wider temperature range.

Cheng et al. [4] assumed that there are two kinds of polarization processes in relaxor ferroelectrics. One is associated with thermally activated flips of the polar regions, which dominated the dielectric behaviors at high temperatures. Above an indistinct critical temperature T_2, the temperature dependence of dielectric permittivity can be

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written as:

$$\varepsilon_{\mathrm{H}}(T) = \exp(\alpha - \beta T) \tag{2}$$

where α and β are constants. The value of β is associated with the production of the polar regions in the materials. T_2 is defined by Cheng as a characteristic temperature at which the differential of dielectric permittivity with temperature is minimum. Another feature of T_2 is that dielectric permittivity of aged sample deviates from that of their fresh state when temperature decreasing at T_2. This phenomenon was observed by Cheng [6], but he could not give it reasonable account. The dielectric behaviors at low temperatures are mainly contributed from another polarization process originating from a breathing model. The simulation formula derived from Cheng's dual polarization model fitted the measure results with high precision in a very wide temperature range. Furthermore, Cheng believed that there is no substantial contribution from the grains and grain boundaries to dielectric permittivity of relaxor ceramics. And dielelctric behaviors of ceramics didn't show any difference with a single crystal. Using concise formula, Cheng described the temperature dependence of ε' at high temperatures and low temperatures. In the vicinity of T_m, complex formula is used to model experimental data. That results depiction of the process complication.

In this paper, the behavior of polar regions was analyzed based on modeling the dielectric temperature spectrum. The relation of some above-cited models was compared. The meaning of a characteristic temperature, T_2, was made clear. The temperature dependency of ε' of PMNT single crystals was also compared with PMNT ceramics. We also discussed the influence of frequency on the dynamic behavior of the polar regions.

2. Experimental procedure

We take a typical relaxor, single crystal PMN–32%PT, as a sample in our experiment. The crystal was grown by a modified Bridgman method [5]. Plate-like specimens were cut into dimensions of 0.5 cm × 0.5 cm × 0.1 cm and electroded with silver paste. Dielectric measurements were operated on an automated system, which was composed of a precision LCR meter (Model HP 4284A), an automated temperature-controlling chamber and computer automated control programme. The frequencies used were 1, 10, 100, and 1000 kHz, respectively. The dielectric spectra of sample at 1 and 100 kHz were chosen in our discussion. Measurements under weak field were made in the temperature range of 20–350 °C at heating rate of 2 °C/min.

3. Results and discussion

An illustration of temperature dependence of the dielectric constants at different frequencies, 1 and 100 kHz, is shown in Fig. 1. The fitting results using Eq. (2) are shown alongside the experimental data.

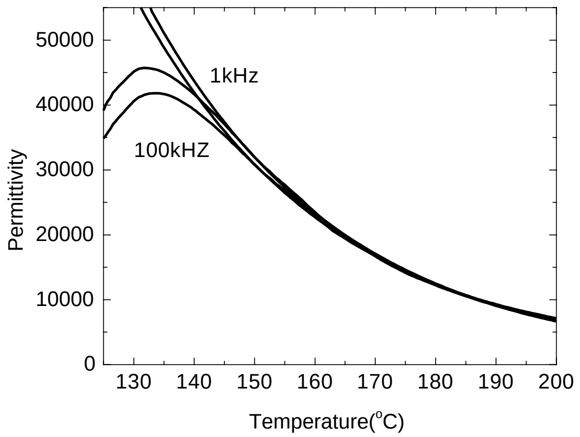

Fig. 1. Temperature dependence of dielectric permittivity at 1 and 100 kHz.

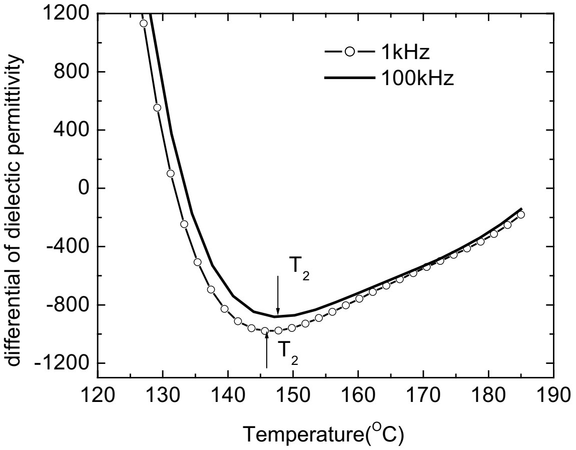

Fig. 2. Differential of dielectric permittivity with respect to temperature.

The β constants from the fitting using Eq. (2) are 0.0313 and 0.0306 for frequencies 1 and 100 kHz, respectively. We note that the fitting results are very close to the experimental data at temperatures more than 15 °C (ΔT) higher than T_m. For 100 kHz, this temperature interval ΔT is larger than that of 1 kHz. Fig. 2 shows the differential of ε' with respect to temperature above T_m. As we expected, the extremum of differential is near T_2. For 100 kHz, this characteristic temperature is larger than 1 kHz.

Fitting the measured results with empirical Eq. (1), the values of the parameters γ, δ_γ, and T' at 1 and 100 kHz are obtained. They are given in Table 1. T' is a critical

Table 1
Parameters from the fits of Eq. (1) to the dielectric permittivity, ε' (above T_m)

	γ	δ_γ	$T'-T_m(\Delta T)$
1 kHz	1.967	18.5	15.9
100 kHz	1.782	13.9	17.3

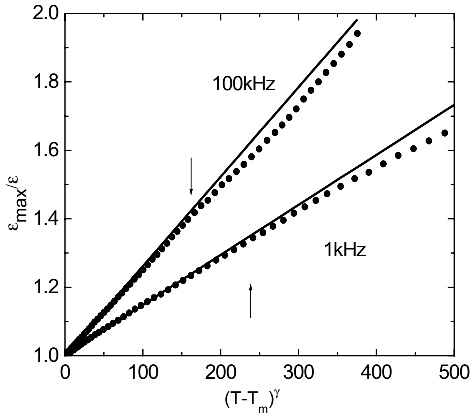

Fig. 3. $\varepsilon_{\mathrm{max}}/\varepsilon$ vs. $(T-T_{\mathrm{m}})^{\gamma}$ for PMN–32%PT at 1 and 100 kHz.

temperature which reflects the onset of deviation from Eq. (1).

The relationship between $\varepsilon_{\mathrm{max}}/\varepsilon$ and $(T-T_{\mathrm{m}})^{\gamma}$ at 1 kHz and 100 kHz is shown in Fig. 3. Because the fitting procedure is rather sensitive to the choice of temperature range, we first determined the modeling temperature range. As can be noticed from literature [6], the relationship between log $(\varepsilon_{\mathrm{max}}/\varepsilon-1)$ and log $(T-T_{\mathrm{m}})$ has two linear ranges when modeling is made in a wide temperature region. In the high temperature region, slope γ was larger than that of the low temperature range. We chose experimental data in the temperature range near T_{m} for analyzing.

From experiment and our modeling results, it can be seen that the high temperature model in the dual polarization model proposed by Cheng was also valid for single crystal above T_2. The results implied that T' equals the characteristic temperature T_2. In the temperature range above T_2, dipolar regions begin to increase in number and grow in size with decreasing temperature. Compared with the results taken from ref. [6], the modeling parameter β in PMNT single crystals is larger than that in PMNT ceramics. This implies that there are more polar regions in single crystals near T_{m}. That is consistent with the result of Skulski [7]. In temperature range above T_2, temperature dependence of dielectric permittivity obeys Eq. (2).

With decreasing temperature, the dielectric permittivity ε' deviates from temperature T_2 according to Eq. (2). This reflects the onset of polar regions freezing and the phase transition of ergodic space shrinking in succession [8]. Between T_{m} and T_2, temperature dependence of ε'obeys Eq. (1). Liu [9] calculated the proportion of frozen polarization in PMNT on the basis of a Landau-type phenomenological theory. In his works, the upper limit temperature of frozen polarizations occurrence is about 20 °C above T_{m}. That is consistent with our characteristic T_2. The supposition that the deviation from Eq. (1) may be attributed to the contribution of the ionic conductivity by thermal energy is untenable. Since the dielectric loss is small at temperature a bit higher than T_{m}. The deviation from Eq. (1) is due to onset of another process. A rational explanation for T_2 on aging is also elicited. The dipolar regions whose T_{c} are higher than aging temperature turned from meta-stable states to stable states. The bond energy that constrains those dipoles is to be enhanced. Therefore, aged samples are deficient in unfrozen dipoles with respect to fresh samples at temperatures below aging temperature. So their dielectric permittivity is less than that of fresh samples with increasing temperature until T_2. Above T_2, there are no frozen dipoles and no influence resulting from aging. Thus, T_2 is also a crucial temperature that dielectric permittivity of aged sample deviates from that of their fresh.

In PMNT ceramics, there are numerous grain boundaries. Besides, there are more defects and larger internal field than in single crystal. So, the coupling between the dipoles is relative weak. The factors which influence the dipole frozen temperature are random [10]. Generally, a random variable influenced by many uncertain factors will have a Gaussian-like distribution. That means the distribution of the numbers of dipoles according their T_{c} with temperature is Gaussian-like. It corresponds to the distribution deduced from composition fluctuations [3]. Therefore, the dielectric permittivity in ceramics obeys quadratic law: $\varepsilon'_A/\varepsilon'(f,T) = 1 + [T - T_{\mathrm{A}}(f)]^2/2\delta_\gamma^2$. On the other hand, in PMNT single crystal, there are large numbers of dipolar regions. Since high polar region concentration and almost no affection coming from boundaries and defects, the electric interactions and elastic stress between the dipoles are relative strong. The strong coupling between dipolar regions results in intense phase transition. In the temperature range between T_2 and T_{m}, being accompanied by merging each other and growing in size, the polar regions transform into microdomains rapidly. The temperature range of the transformation is relatively narrow. That would result in a more distinct change in dielectric permittivity. Consequently, exponent γ becomes small for PMN single crystal. The exponent γ is known as the expression of the degree of dielectric relaxation in a RFE. And we believe it also shows the speed and intense degree of dipoles transition near T_{m}. In our modeling results, some differences between various measurement frequencies are observable. Fig. 1 shows results at two different measuring frequency. When the frequency increases, β gets small. This implies that with increasing frequency the dipolar regions concentration decreases. Because the timescale of polarization flipping is shortened when frequency increases, so some large dipolar regions cannot reach their equilibrium state within the observation time, i.e. these large dipolar regions are frozen under high frequencies. For the same reason, modeling parameters T_2 and ΔT would increase with increasing frequency. The parameters ΔT and δ_γ have been used as a measure of degree of diffuseness for the diffuse phase transition in relaxor-based ferroelectrics [6]. For various materials, δ_γ and ΔT of high relaxation degree materials are usually larger than that of low relaxation degree materials under same frequency. In our modeling result, δ_γ decreases with increasing frequency, whereas ΔT increases with increasing frequency. That indicates the degree of dielectric relaxation at 1 kHz is higher than that at 100 kHz. The narrow temperature interval implies that the transition of polar regions is abrupt near T_m.

4. Conclusions

In summary, the dielectric temperature spectrum has two processes above T_m. They can be divided by a characteristic temperature T_2. T_2 signifies onset of dipolar regions freezing. In ceramics, the strength of interaction between dipolar regions is weaker than that in single crystal. The dipolar regions in ceramics is apt to behave as composition fluctuations [3]. However, strong coupling between dipolar regions within single crystal results in abrupt phase transition and formation of an ordered configuration among dipoles. This results in narrower temperature intervals ΔT of single crystals than that of ceramics.

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