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Investigating the physical meanings of diffused phase transition models

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ABSTRACT

The empirical laws, $\varepsilon = \varepsilon_m/[1+(T-T_m)^{\gamma}/2\sigma^2]$ and $\varepsilon = \varepsilon_m/\{1+[(T-T_m)/\Delta]^{\xi}\}$, proposed by Burfoot et al. and Eiras et al. are usually used to describe the dielectric diffused characteristics of relaxor ferroelectric materials. In this study, we continue our previous work to present the physical and mathematical meanings of the parameters in these laws. Based on the experimental results in the $(1-x)Pb(Fe_{2/3}W_{1/3})O_3$–$xPbTiO_3$ relaxor system and theoretical modelling analysis, it is shown that the law proposed by Eiras is more suitable to explain the behaviour of both more complete relaxor systems and incomplete relaxor systems.

1. Introduction

The diffused phase transition (DPT) model is popularly used to describe the dielectric behaviour of relaxor ferroelectric (RFE) materials [1–19]. Smolensky hypothesized that different transition temperatures exist in different micro regions due to compositional fluctuation. According to the Gauss law, the phase transition temperature (T_c) shows a normal distribution and the related equation is described as in Eq. (1) [1]. Kirilov and Isupov made use of Taylor's expansion and neglected the higher terms to obtain Eq. (2) [2]. Eqs. (1) and (2) are shown as:

$$\varepsilon = \varepsilon_m \exp\left[-\frac{(T-T_m)^2}{2\delta^2}\right] \quad (1)$$

$$\varepsilon = \varepsilon_m \frac{1}{1+((T-T_m)^2/2\delta^2)} \quad (2)$$

where the quadratic of the temperature is obtained according to the Guass law [1,2]. ε_m is the maximal dielectric constant in each micro region; T_m is the mean value of T_c distribution and the maximal distribution probability; δ is the standard deviation of T_c distribution. The δ value can be used to describe the degree of variance of T_c distribution; when δ is larger, T_c distribution is broader and the diffused characteristic is obvious. Unfortunately, Eqs. (1) and (2) cannot well describe the diffused behaviours of incomplete DPT materials [3–7].

To describe the diffused phase transition behaviours of both more complete and incomplete DPT materials, Burfoot et al. and Eiras et al. modified Eqs. (1) and (2) and proposed Eqs. (3) and (4) as [3–7]:

$$\varepsilon = \varepsilon_m \frac{1}{1+((T-T_m)^{\gamma}/2\sigma^2)} \quad (3)$$

$$\varepsilon = \varepsilon_m \frac{1}{1+((T-T_m/\Delta)^{\xi})} \quad (4)$$

where ε_m and T_m are the maximum dielectric constant and corresponding temperature. γ and σ (ξ and Δ) are the diffused parameters. The diffused phase transition property is more obvious with larger values of γ and σ (ξ and Δ). Moreover, Eqs. (3) and (4) show better fitting adaptability compared with Eqs. (1) and (2) for both more complete DPT materials and incomplete DPT materials [3–8]. Recently, Mitoseriu et al. and Chu et al. used the ξ and Δ values of Eq. (4) to investigate the effects of $PbTiO_3$ composition and synthesized method on the diffused phase transition for the $(1-x)Pb(Fe_{2/3}W_{1/3})O_3$–$xPbTiO_3$ ($(1-x)$PFW–xPT) and 0.75PFW–0.25PT ceramics, respectively [9,10]. Bera et al., Xu et al., Parkash et al. and Fan et al. investigated the effects of lanthanum cations on the diffused phase transition by using the γ value of Eq. (3) in the $BaBi_{4-x}La_xTi_4O_{15}$ (synthesized by cost-effective chemical method), $(Na_{0.5}K_{0.5})_{1-3x}La_xNb_{0.95}Ta_{0.05}O_3$,

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$(Ba_{1-x}La_x)(Ti_{0.85}Sn_{0.15})O_3$, and $BaBi_{4-x}La_xTi_4O_{15}$ (synthesized by solid state reaction) ceramics, respectively [11–14]. Liu et al., Yang et al. and Qu et al. discussed the diffused phase transition of the $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$, $Sr_{0.53}Ba_{0.47}Nb_{2-x}Ta_xO_6$ and $(1-x)BaTiO_3$–$x(Bi_{0.5}Na_{0.5})TiO_3$ ceramics by using the γ value of Eq. (3) [15–17]. Furthermore, Fang et al. and Stojanovic et al. used the γ value of Eq. (3) to examine the RFE behaviours of $Sr_4Eu_2Ti_4Ta_6O_{30}$ and $BaBi_4Ti_4O_{15}$ ceramics [18,19]. As mentioned before, researchers have frequently used both Eqs. (3) and (4) to discuss the dielectric diffused characteristics of RFE materials [9–19]. However, the fitting adaptability between Eqs. (3) and (4), and the physical and mathematical meanings of these parameters in Eqs. (3) and (4) have never been discussed. In our previous study, we have shown that the fitting curve is the same between Eqs. (3) and (4) according to the experimental results and the statistical regression theories [8]. Furthermore, when the compositions, dopants, synthesized methods, and so on different, the ε_m and T_m are changed. In our previous study, we also showed that the values of γ and σ (ξ and Δ) are not affected by the values of ε_m and T_m [20]. Therefore, Eqs. (3) and (4) can be used to describe and compare the degrees of the diffused phase transition among different samples. Furthermore, we can carefully investigate the effect of γ and σ (ξ and Δ) values on the dielectric diffused characteristics and its physical meanings based on the experimental results of different samples and the different ε_m and T_m values. Now we continue our study and try to systematically investigate the physical and mathematical meanings of the parameters used in the laws mentioned above. Based on the experimental results of the $(1-x)Pb(Fe_{2/3}W_{1/3})O_3$–$xPbTiO_3$ ($(1-x)$PFW–xPT) relaxor system, more diffused phase transition is obtained with decreasing $PbTiO_3$ content [8,9]. Through the experimental results in the PFW–PT system, the curve fitting data and theoretical modelling analysis, we successfully demonstrate that the law proposed by Eiras is more suitable to explain the behaviour of diffused phase transition in relaxor systems.

2. Physical and mathematical theory and viewpoint

Since Eqs. (3) and (4) are modified from Eq. (2), and Eq. (2) is obtained from Taylor's expansion of Eq. (1), the physical and mathematical meanings of the parameters in Eqs. (3) and (4) are supposed to be the same as those in Eqs. (1) and (2). Since $\exp[-(T-T_m)^2/2\delta^2]$ in Eq. (1) represents the probability distribution function of T_c [1,2], $1/[1+(T-T_m)^2/2\delta^2]$ in Eq. (2), $1/[1+(T-T_m)^\gamma/2\sigma^2]$ in Eq. (3), and $1/\{1+[(T-T_m)/\Delta]^\xi\}$ in Eq. (4), it should also represent the probability distribution of T_c. Since Eqs. (3) and (4) are used to describe the temperature–dielectric constant and ε_m is a constant, they can also reasonably represent the probability distribution of T_c.

In order to reasonably inspect the effects related to the temperature–dielectric constant curve and the T_c probability distribution, Figs. 1 and 2 show the effects of σ and γ for Eq. (3) and Δ and ξ for Eq. (4), respectively, on the dielectric constant and the T_c probability distribution as a function of temperature. In Figs. 1 and 2, we assume ε_m and T_m to be constant, for the sake of simplicity.

As shown in Figs. 1 and 2, no matter how γ (ξ) or σ (Δ) change, the distribution of T_c is bilateral to the temperature T_m. In other words, T_m is the mean value of T_c distribution in Figs. 1 and 2. T_m is also the maximal probability distribution of T_c, it meaning that the phase-transition temperature of numerous micro regions in the relaxor materials focuses at T_m.

Comparing Curve 1 and Curve 2 in Fig. 1, the T_c distribution becomes smoother as the σ value is increased, which means that the variance of T_c distribution is smaller and the diffused characteristic is obvious. Comparing Curve 2 and Curve 3 in Fig. 1, the T_c distribution curve becomes less steep and the diffused characteristics are more obvious when the γ value is smaller. Based on the experimental results, several researchers have found that both the σ and γ values potentially increase when the relaxor materials tend to exhibit more complete DPT behaviour [9–19]. These experimental results are contrary to our previous discussion of Eq. (3) and in Fig. 1 (Curve 2 and Curve 3).

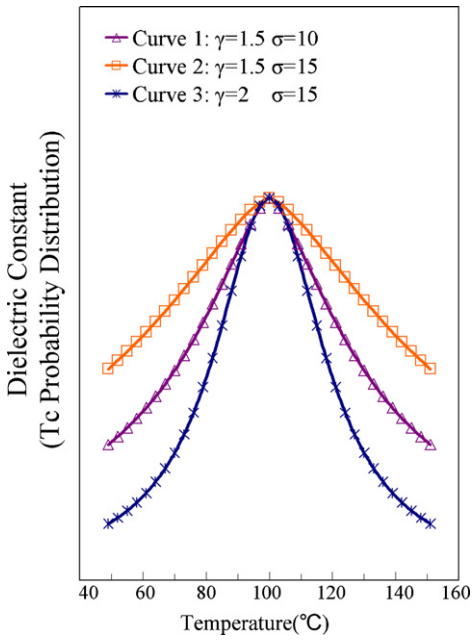

Fig. 1. The effects of the parameters γ and σ in Eq. (3) on the dielectric constant and the T_c probability distribution as a function of temperature.

Fig. 2 shows the relation between the Δ and ξ changes and the T_c probability distribution. Comparing Curve 1 and Curve 2 in Fig. 2, the T_c distribution curve becomes less steep and the dielectric diffused characteristics are obvious when the Δ value is increased. Comparing Curve 2 and Curve 3 in Fig. 2, the change of T_c distribution is very small when the ξ value is increased. When the ξ value is increased, the T_c distribution will only become less steep in the half-height half-width area (T = 60–140 °C), which represents

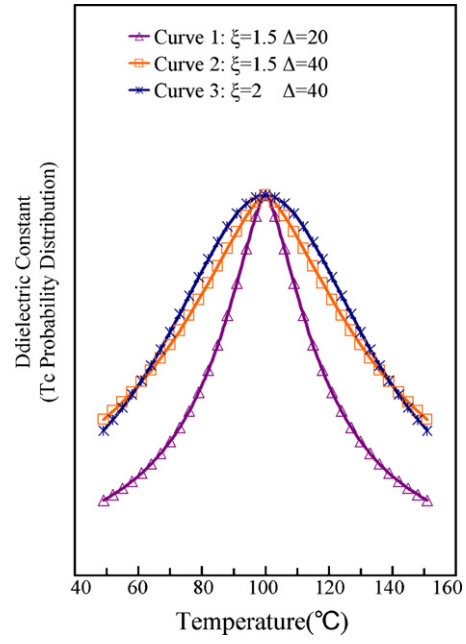

Fig. 2. The effects of the parameters ξ and Δ in Eq. (4) on the dielectric constant and the T_c probability distribution as a function of temperature.

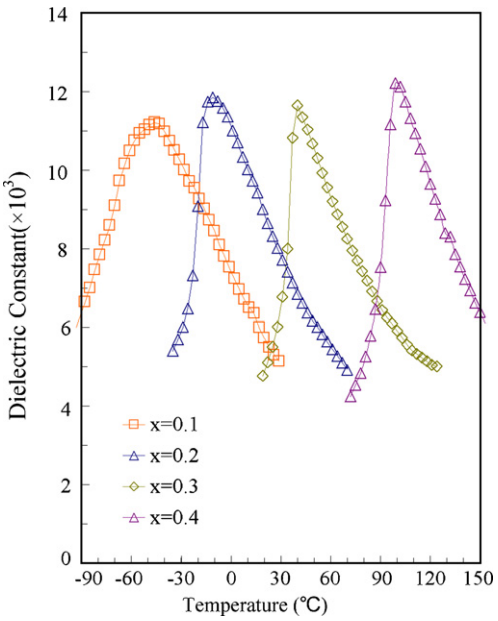

Fig. 3. The 1 MHz dielectric constant as a function of temperature for the $(1-x)$PFW–xPT system with $x = 0.1$, 0.2, 0.3 and 0.4.

that the diffused phase transitions is more obvious. Although the changes of ξ does not generally affect T_c distribution so much, a larger ξ value still represents a more diffused phase transition in the half-height half-width area. Based on other reports, more complete DPT relaxors show larger ξ and Δ values, and the value of ξ is close to 2 for total DPT material [9–19]. These experimental results are not contrary to our previous discussion of Eq. (4) and Fig. 2.

Based on the effects of the parameters on the T_c distributions in Eqs. (3) and (4), and the experimental results of the dielectric diffused characteristics in relaxor materials, it is concluded that the parameters in Eq. (4) provide a more reasonable explanation of the T_c distribution and the diffused characteristics. This conclusion is in accordance with the experimental results and Smolensky's physical hypothesis.

3. Experiment and ceramic preparation

Raw materials were mixed using pure reagent PbO, Fe_2O_3, WO_3, and TiO_2 powders (99.5% purity). The materials $(1-x)Pb(Fe_{2/3}W_{1/3})O_3$–$x$PbTiO$_3$, $x = 0.1$–0.4 were synthesized by calcining at 800 °C for 2 h followed by pulverization. The samples were pressed into a disk with a diameter of 12-mm and a thickness of 2-mm. Specimens were sintered isothermally at 900 °C for 2 h. The dielectric properties of the samples were measured using an impedance analyzer (HP4294A) in a temperature-controlled container. The phase relations for the sintered samples were identified using an X-ray diffractometer (XRD) and a second phase was not found [8].

4. Experimental results and discussion

In the $(1-x)$PFW–xPT relaxor system, the polarizations caused by electric conductivity and space charge are usually induced at higher temperatures in the paraelectric region and smear the DPT characteristics [9]. Since these polarizations can be filtered at higher frequencies, the dielectric behaviour caused by the x ratio is discussed only at 1 MHz. Fig. 3 shows the 1-MHz dielectric constant as a function of temperature for $(1-x)$PFW–xPT with $x = 0.1$, 0.2, 0.3 and 0.4. As the x ratio increases, the Curie temperature increases and the dielectric properties change to the normal ferroelectric characteristics with the sharper temperature–dielectric constant curve caused by the B-site order [9,21].

Table 1
The fitting parameters of Eqs. (3) and (4) for the $(1-x)$PFW–xPT system with $x = 0.1$, 0.2, 0.3 and 0.4.

	Eq. (3)		Eq. (4)	
	γ	σ	ξ	Δ
$x = 0.1$	1.7628	28.20	1.7628	65.49
$x = 0.2$	1.6030	19.53	1.6030	62.84
$x = 0.3$	1.3438	11.11	1.3438	60.28
$x = 0.4$	1.3037	9.50	1.3037	53.79

The T_m value, ε_m value and parameters of Eqs. (3) and (4) in the $(1-x)$PFW–xPT relaxor system are changed by changing the x ratio [8,9]. In our previous study, we have shown that the values of γ and σ (ξ and Δ) are not affected by the values of ε_m and T_m [20]. Furthermore, the purpose of the present work is to determine whether the diffused characteristics of the RFE dielectric materials can be explained soundly by using the parameters γ, σ, ξ, and Δ in Eqs. (3) and (4). To avoid the effects of ε_m and T_m, we normalize all measured dielectric constants (in Fig. 3) by setting the ε_m value to a constant 10,000, and shifting the T_m value to 0 °C as the reference point. These curves, the temperature–dielectric constant curves before and after normalizing and shifting, are fitted with Eqs. (3) and (4) by the least squared method. The values of the parameters are summarized in Table 1. It is shown that the parameters of Eqs. (3) and (4) are not affected by normalizing and shifting of the experimental data [20]. Furthermore, the values of γ and σ (ξ and Δ) are larger with decreasing $PbTiO_3$ content, which represents a more diffused phase transition [8,9].

Considering the region where the temperature is larger than T_m, the smaller dielectric constant variance means that there are more diffused characteristics. The dielectric constant variance can be determined as follows [8]:

$$\mathrm{var}(T) = \frac{1}{n}\sum(\varepsilon_i - \varepsilon_m)^2 \quad (5)$$

where var(T) is the dielectric constant variance in the specific temperature area deviated from T_m (between T_m and $T_m + T$); n represents the measure points in the deviated temperature area; ε_i is the dielectric constant at an individual measure point and ε_m is the maximal dielectric constant at T_m. Therefore, we can investigate the diffused characteristics of the $(1-x)$PFW–xPT relaxor system with the variation of the dielectric constant in a certain temperature area, and interpret the effects of the parameter changes in Eqs. (3) and (4) on the dielectric diffused characteristics of the relaxor as in the following discussion.

After normalizing and shifting for $x = 0.4$ and $x = 0.1$ in the $(1-x)$PFW–xPT system, the experimental data (in Fig. 3, $T > T_m$) are substituted into Eq. (5) and we can obtain the dielectric constant variance at different bias temperature ranges. The results are shown as Curve 1 ($x = 0.4$) and Curve 2 ($x = 0.1$) in Figs. 4–6. Comparing Curve 1 and Curve 2, the dielectric constant variance is smaller for $x = 0.1$, representing that the diffused characteristic is obvious. The fitting values when using Eq. (3) are $\gamma = 1.3037$, $\sigma = 9.5$ and $\gamma = 1.7628$, $\sigma = 28.2$ for $x = 0.4$ and $x = 0.1$, respectively. By using Eq. (4), the fitting values are $\xi = 1.3037$, $\Delta = 53.79$ and $\xi = 1.7628$, $\Delta = 65.49$ for $x = 0.4$ and $x = 0.1$, respectively. Substituting these fitting results into Eq. (5), we can obtain the theoretical temperature–dielectric constant variance curves as shown in Fig. 4 (Curve 3 and Curve 4). The theoretical curves (both Eqs. (3) and (4)) fit the experimental results very well and the fitting curves obtained by using Eqs. (3) and (4) are the same [8].

Since the γ value can be used to explain the dielectric diffused phenomenon, the temperature–dielectric constant variance will be

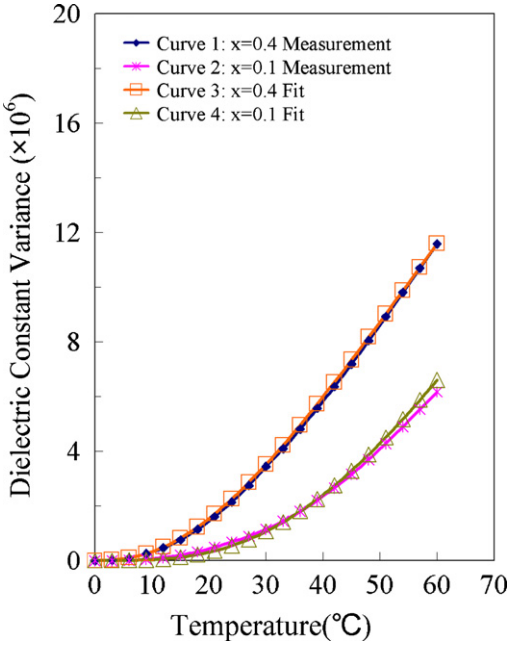

Fig. 4. The fitting results (Eqs. (3) and (4)) and the experimental data for the $(1-x)$PFW–xPT system with $x=0.4$ and $x=0.1$, respectively.

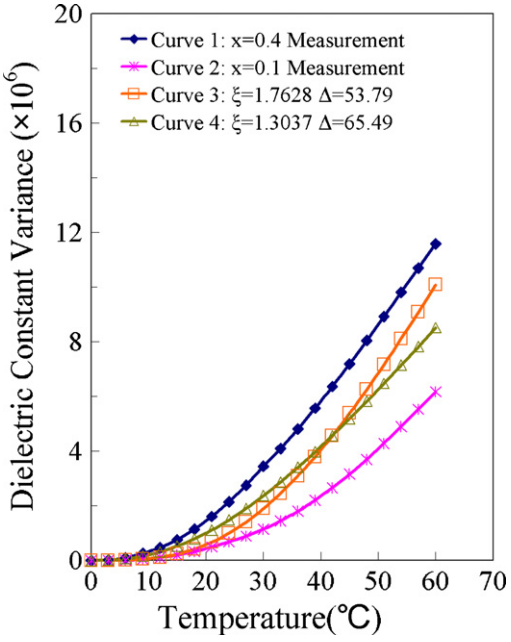

Fig. 6. The fitting results with different ξ and Δ values of Eq. (4) and the experimental data.

smoother and approach the curve for $x=0.1$ when the γ value is more large. For $x=0.4$ (see Fig. 5), this only occurs when the γ value is changed from 1.3037 ($x=0.4$) to 1.7628 ($x=0.1$). The theoretical temperature–dielectric constant variance for $\gamma=1.7628$ and $\sigma=9.5$ is shown in Fig. 5, Curve 3. Based on the same reasons, when only changing the σ value from 9.5 ($x=0.4$) to 28.2 ($x=0.1$) for $x=0.4$, the theoretical temperature–dielectric constant variance for $\gamma=1.3037$ and $\sigma=28.2$ is shown in Fig. 5, Curve 4. In Fig. 5, when the x ratio decreases from 0.4 to 0.1, the experimental results show that the diffused characteristic is enhanced and the dielectric constant variance is reduced as in Curves 1 and 2. If we increase the γ value only

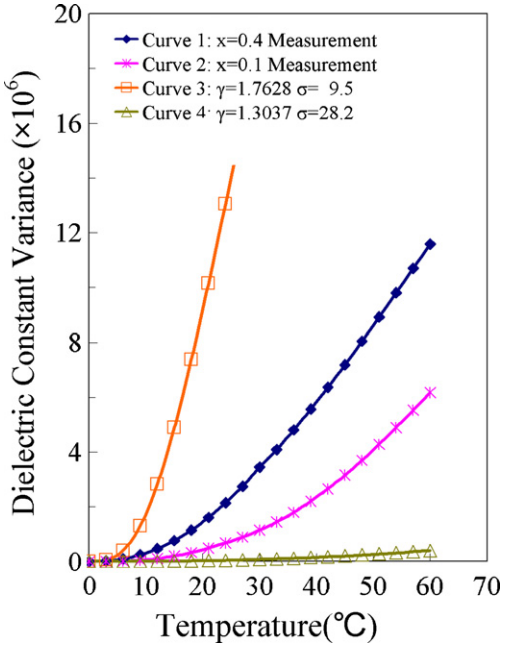

Fig. 5. The fitting results with different γ and σ values of Eq. (3) and the experimental data.

(as in Curve 3 in Fig. 5), the theoretical dielectric constant variance increases, contradicting the diffused characteristics. These results are different than the other experimental reports which show that the more diffused phase transition is obtained with increasing γ value [9–19]. If we increase the σ value only (as Curve 4 in Fig. 5), the theoretical dielectric constant variance decreases compared to $x=0.4$ (as Curve 1 in Fig. 5) and is much lower than that of $x=0.1$ (as Curve 2 in Fig. 5).

The parameters from fitting Eq. (4) are $\xi=1.3037$, $\Delta=53.79$ for $x=0.4$ and $\xi=1.7628$, $\Delta=65.49$ for $x=0.1$, respectively. Similarly, the theoretical dielectric constant variance for $\xi=1.7628$ and $\Delta=53.79$ is shown in Fig. 6, Curve 3. Curve 4 in Fig. 6 shows the theoretical dielectric constant variance for $\xi=1.3037$, $\Delta=65.49$. In Fig. 6, the theoretical dielectric constant variance will decrease with increasing ξ value (as in Curve 3), compared to $x=0.4$ (as in Curve 1), and approach $x=0.1$ (as in Curve 2). Similarly, comparing Curve 4 with Curve 1 and Curve 2, we find that the effect of the Δ value related to the dielectric constant variance is similar to the result obtained for the ξ value. Thus, larger ξ and Δ values cause the lower dielectric constant variance which can describe the dielectric diffused characteristic and coincides with the experimental results [9–19].

In the previous sections, we discussed the effects of the parameters values based on Eqs. (3) and (4) for $x=0.1$ and 0.4 only. In other respects, the effects of the parameters values for $x=0.1$, 0.2, 0.3 and 0.4 in the $(1-x)$PFW–xPT system are similar to those discussed previously. Hence, they are not discussed here.

5. Conclusions

In this study, we extend the opinions of Smolensky and Isupov to evaluate dielectric diffused characteristic by analyzing T_c distribution patterns and dielectric constant variant. According to the experimental results and the theoretical analysis, it is concluded that:

(1) In Eq. (3), when γ value is larger, the diffused characteristic is less obvious. This result contradicts the experimental

data (based on the experimental data, the relaxors with more diffused phase transition have the larger γ value) [9–19], providing an opposing explanation of the dielectric diffused characteristic.

(2) In Eq. (3), the larger the σ value is, the more diffused the characteristic becomes. Although this result is compatible with the experimental data, the change of the σ value overemphasizes the change of the diffused characteristic.

(3) The larger the ξ value of Eq. (4) is, the more obvious the diffused characteristic is. This result coincides with the experimental data. The ξ value can soundly explain diffused characteristic, especially near the T_m area.

(4) The diffused characteristic is obvious with increasing Δ value in Eq. (4). Though the Δ value cannot fully explain the behaviour of the relaxor materials, it does not distort the explanation. Combining increasing ξ value will induce the improvement of the diffused characteristic and reasonably explain the diffused behaviour of the relaxor.

In a logical physical model, all the changes of the related parameters should fully describe the change of the physical phenomenon. Though the laws of Eqs. (3) and (4) show the same fitting curve, their parameters affect the physical phenomenon in different ways. From the above discussion, it is obvious that the description of the diffused characteristic by Eq. (4) provides a more correct explanation and the ξ and Δ values can explain the dielectric diffused characteristic soundly, which coincides with the experimental results.

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