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Are the parameters of the empirical law dependent on the dielectric properties of the ferroelectric relaxors?

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Abstract

The empirical law, $\varepsilon = \varepsilon_m/[1 + (T - T_m)^\gamma/2\sigma^2]$ or $\varepsilon = \varepsilon_m/\{1+[(T - T_m)/\Delta]^\xi\}$, are usually used to estimate the degree of the diffused phase transition of the ferroelectric relaxors. As the values of γ or σ (ξ or Δ) are larger, the diffused phase transition is more obvious. However, values of T_m and ε_m are different upon different compositions, dopants, synthesized methods, and others. Are the values of γ and σ (ξ and Δ) affected by T_m or ε_m which represents the characteristics of the relaxors? In this paper, we utilize the experimental data of the $(1 - x)Pb(Fe_{2/3}W_{1/3})O_3$–$xPbTiO_3$ ceramic system and the mathematical derivation to conclude that the values of γ and σ (ξ and Δ) are not affected by ε_m and T_m. Therefore, they can be used to properly describe and compare the degree of the diffused phase transition between the different samples with different compositions, dopants and synthesized methods since the noises (T_m and ε_m) are filtered in these empirical laws. Furthermore, we can clearly clarify the physical meaning of theses parameters, γ and σ (ξ and Δ), as well as their effect on the composition for the further study.
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Keywords: Diffused phase transition; Relaxor; Ferroelectric; Model

1. Introduction

Complex perovskite type ferroelectric relaxors (FREs) are commonly represented by $(A_1A_2)(B_1B_2)O_3$ in which A and B sites can be occupied by different cathode ions at the same time. Furthermore, relaxors show good dielectric characteristic, electrostriction, piezoelectric and pyroelectric properties, they are well applied in multilayer capacitors, piezoelectric actuators, pyroelectric detectors and non-volatile memories [1]. Since the relaxors have specific dielectric physical characteristics [2–8], many researchers propose a couple of physical models to explain them [2,5,6,9–30]. Regarding to the explanation for the diffused phase transition (DPT), Smolensky firstly hypothesizes that there exists different composition and transition temperature in different micro region according to the composition fluctuation. The phase transition temperature (T_c) shows normal distribution according to the Gauss's theory, and the related equation is described as Eq. (1) [9]. Kirilov and Isupov take use of Taylar's expansion and neglects higher terms to get Eq. (2) [10]. Eqs. (1) and (2) are described as follows:

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

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

Since Eqs. (1) and (2) are based on the hypothesis that T_c is normal distribution, the quadratic of temperature is obtained according to the Guass law. ε_m represents the same maximal dielectric constant in each micro region; T_m represents the average of T_c distribution and the maximal distribution probability; δ represents the standard deviation of T_c distribution. δ can be used to describe the variance degree of T_c distribution; when δ is larger, T_c distribution is broader, and the diffused characteristic is more obvious. Therefore, in

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Eqs. (1) and (2), δ is the only parameter to describe the degree of the diffused phase transition phenomenon of relaxor materials.

Although Eqs. (1) and (2) can well describe the characteristics of more complete DPT, larger error may exist if they are applied in incomplete DPT. To describe both total DPT and incomplete DPT materials, Burfoot et al. and Eiras et al. modifies Eqs. (1) and (2) and get Eqs. (3) and (4) as follows [11–15]:

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

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

Eqs. (3) and (4) have better fitting adaptability compared with Eqs. (1) and (2) no matter in total DPT FRE materials or incomplete DPT FRE materials. In Eqs. (3) and (4), ε_m and T_m are the same as those in Eqs. (1) and (2). Furthermore, the values of γ and σ (ξ and Δ) are larger as the diffused phase transition is more obvious [11–15,31–44]. Recently, researchers frequently use both Eqs. (3) and (4) to discuss the dielectric diffused characteristics for FRE materials [3,11–15,31–44]. However, the fitting degree between Eqs. (3) and (4) and the physical and mathematical meaning for these parameters in Eqs. (3) and (4) have never been discussed. In our previous study, we have shown the fitting curve is the same between Eqs. (3) and (4) from the experimental results and the statistical theories [45]. According to the previous discussions reported by many papers [3,11–15,31–44], the values of γ and σ (ξ and Δ) depend on the microscopic disorder to describe the degree of the diffused phase transition. Furthermore, the values of ε_m and T_m are always changed as the disorder degree is changed in many experimental results [3,11–15,31–44]. However, the value of ε_m is due to the scale, density and relaxation time of the micropolarization and T_m is the mean value of the different phase transition temperature T_c of different microregions. Therefore, ε_m and T_m are not used to determine the degree of the diffused phase transition in these empirical laws. Especially, the ε_m and T_m are not only the characteristics of the FREs but also the parameters in Eqs. (3) and (4). Furthermore, the ε_m and T_m are changed as the compositions, dopants, synthesized methods, etc., are different [31–44]. If the values of ε_m and T_m can affect the values of γ and σ (ξ and Δ) due to different compositions, dopants, synthesized methods and others, then the values of γ and σ (ξ and Δ) cannot be used to compare the degree of the diffused phase transition between different samples. Furthermore, the changes of the γ and σ (ξ and Δ) values represent not only the diffused phase characteristics also another physical meanings if the γ and σ (ξ and Δ) values were affected by different values of ε_m and T_m. Therefore, we cannot exactly tell the physical meanings of Eqs. (3) and (4) and the effect of different compositions, dopants and synthesized methods on the γ and σ (ξ and Δ) values. However, no research group has investigated if the parameters, i.e., γ and σ (ξ and Δ), of the diffused phase transition in Eqs. (3) and (4) will be affected by different ε_m and T_m which is the motivation in this work. Through the experimental data of the $(1 - x)\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$–$x\text{PbTiO}_3$ ($(1 - x)$PFW–xPT) ceramic system, the curve fitting, and the mathematical derivation, we successfully demonstrate that the values of γ and σ (ξ and Δ) are not affected by the values of ε_m and T_m.

2. Experimental procedures

Raw materials were mixed using pure reagent PbO, Fe_2O_3, WO_3, and TiO_2 powders (99.5% purity). The materials $(1 - x)\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$–$x\text{PbTiO}_3$, $x = 0.1$–0.4 were synthesized by calcining at 800 °C for 2 h followed by pulverization. After that, the powders were dried and milled with 8 wt.% of a 5% PVA solution. The samples were pressed into a disk of 12 mm diameter and 2 mm thickness at a pressure of 25 kg/cm^2. Specimens were sintered isothermally at a heating rate of 5 °C/min at 900 °C for 2 h. A PbO-rich atmosphere was maintained to minimize the lead loss during sintering. In order to measure the electrical properties, silver paste was coated to form electrodes on both sides of the sample, followed by a firing at 750 °C for 25 min. The dielectric properties of the samples were measured using an impedance analyzer (HP4294A) in the temperature controlled container [45,46].

3. Experimental data and discussion

Fig. 1 shows the dielectric constant as a function of temperature at different frequency for the 0.9PFW-0.1PT ceramics. In the paraelectric region (above the Curie-temperature T_m), the dielectric constant increases as increasing the temperature at lower frequency, i.e., the second peak dielectric. This phenomenon is caused by the space charge polarization and is filtered at higher frequency. In this work, the dielectric constant as a function of temperature is discussed

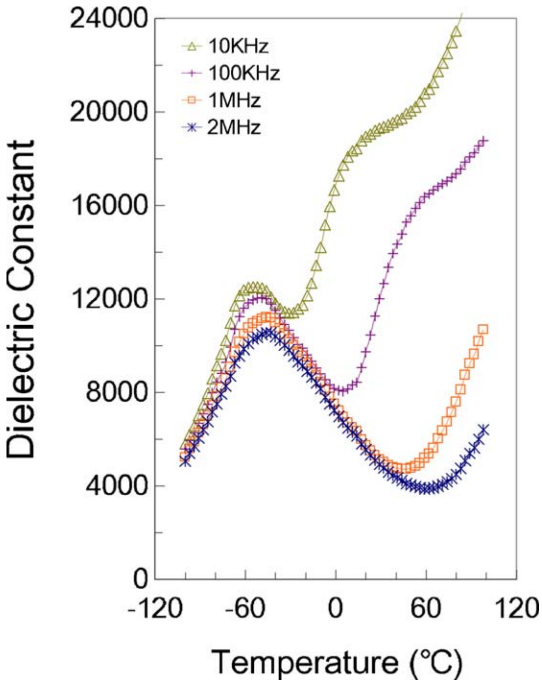

Fig. 1. The dielectric constant as a function of temperature at different frequency for $0.9\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$–$0.1\text{PbTiO}_3$ ceramics.

only at 1 MHz to avoid the effect of the space charge polarization [3,46,47].

Fig. 2 shows the 1-MHz temperature-dependent dielectric constant for the $(1-x)$PFW–xPT ceramics with $x = 0.1$, 0.2, 0.3, and 0.4 and their fitting curves by using Eqs. (3) and (4). In Fig. 2, the Curie-temperature is increased and the shape of the temperature-dependent dielectric constant is shaper as increasing $PbTiO_3$ compositions. This result is similar with Mitoseriu et al.'s report [3]. In our previous work, we have shown that the fitting curves of Eqs. (3) and (4) are the same [45]. Therefore, it has only one fitting curve in Fig. 2 for the $(1-x)$PFW–xPT ceramics with $x = 0.1$, 0.2, 0.3, and 0.4 separately. As inspecting Fig. 2, it is well fitted at the temperature region $T > T_m$. This phenomenon is similar with Mitoseriu et al.'s report [3]. In Fig. 2, the fitting curve properly describes the experimental data in the paraelectric region and the ε_m and T_m are 11,212, 11,846, 11,672, and 12,278 and −46, −11, 39, and 100 °C for the $(1-x)$PFW–xPT ceramics with $x = 0.1$, 0.2, 0.3, and 0.4 separately [45,47].

The dielectric constant is determined by the dipole moment, amount, and their relaxation time at specific temperature and frequency. T_m is the mean value of the different phase transition temperature T_c of the different microregions. To investigate if the values of γ and σ (ξ and Δ) are affected by ε_m and T_m, we suppose that the dipole moment, amount, relaxation time or phase transition temperature are different from those derived by the experimental results but the distribution of phase transition is not changed. Then, we normalize and shift all the curves in Fig. 2 and the results are shown in Fig. 3. Then, we can tell if these two figures have the same values of γ and σ (ξ and Δ) and determine if the values of γ and σ (ξ and Δ) are affected by ε_m and T_m.

Eqs. (3) and (4) can be rewritten into a new form as below:

$$\ln\left(\frac{\varepsilon_m}{\varepsilon}-1\right)=\gamma\ln(T-T_m)+\ln 2\sigma^2 \qquad (5)$$

$$ln\left(\frac{\varepsilon_m}{\varepsilon}-1\right)=\xi\ln(T-T_m)+\xi\ln\Delta \qquad (6)$$

Therefore, many researchers utilize the plot of $\ln(\varepsilon_m/\varepsilon-1)$ as a function of $\ln(T-T_m)$ to estimate the values of γ and σ (ξ and Δ), i.e., the slope is the γ (ξ) value and the σ (Δ) value can be derived from the intercept [31–33]. Fig. 4 shows the plots of $\ln(\varepsilon_m/\varepsilon-1)$ as a function of $\ln(T-T_m)$ for the original experimental data (Fig. 2) and the new data (Fig. 3) of $(1-x)$PFW–xPT with $x = 0.1$, 0.2, 0.3, and 0.4 separately.

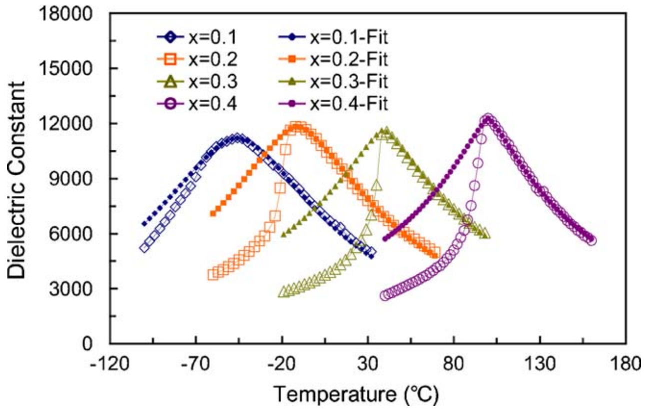

Fig. 2. The dielectric constant as a function of temperature at 1 MHz and its fitting curve by using Eqs. (3) and (4) for $(1-x)Pb(Fe_{2/3}W_{1/3})O_3$–$xPbTiO_3$ with $x = 0.1$, 0.2, 0.3, and 0.4.

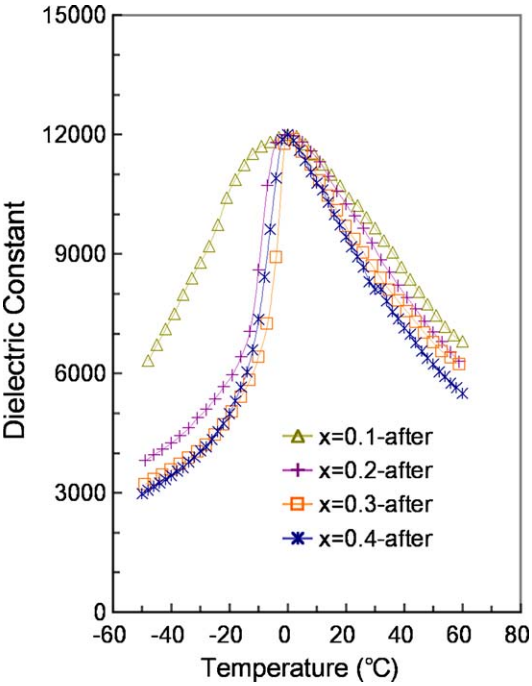

Fig. 3. The dielectric constant as a function of temperature after normalizing the dielectric constant and shifting the temperature for Fig. 2 data.

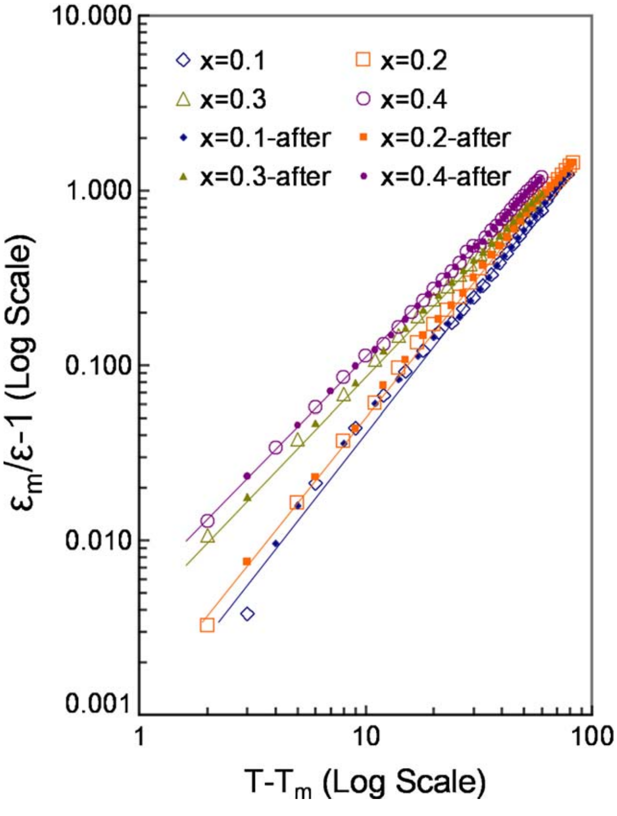

Fig. 4. The plot of $\log(\varepsilon_m/\varepsilon-1)$ as a function of $\log(T-T_m)$ at 1 MHz for the temperature-dependent dielectric constant of Figs. 2 and 3 [symbols: experimental data; the solid line: fitting curve].

As inspecting Fig. 4, the slope, i.e., γ or ξ values, is larger as decreasing $PbTiO_3$ compositions and the diffused phase transition is more obvious. Furthermore, the original experiment data and the new data have the same plots of $\ln(\varepsilon_m/\varepsilon - 1)$ as a function of $\ln(T - T_m)$. Theses results represent the diffused coefficients of γ and σ (ξ and Δ) cannot be affected by the ε_m and T_m.

4. Mathematical derivation

In the previous work, we have shown that Eqs. (3) and (4) have the same fitting curve and the same fitting data of γ and σ (ξ and Δ) by using the statistic regression technique [45]. The formulas of γ and σ (ξ and Δ) are showed below:

$$\gamma = \xi = \frac{n\sum \ln((\varepsilon_m/\varepsilon_i) - 1)\ln(T_i - T_m) - \sum \ln((\varepsilon_m/\varepsilon_i) - 1)\sum \ln(T_i - T_m)}{n\sum[\ln(T_i - T_m)]^2 - [\sum \ln(T_i - T_m)]^2} \tag{7}$$

and

$$\ln 2\sigma^2 = \ln \Delta^{\xi} = \frac{\sum \ln((\varepsilon_m/\varepsilon_i) - 1)\ln(T_i - T_m)\sum \ln(T_i - T_m) - \sum \ln((\varepsilon_m/\varepsilon_i) - 1)\sum[\ln(T_i - T_m)]^2}{n\sum[\ln(T_i - T_m)]^2 - [\sum \ln(T_i - T_m)]^2} \tag{8}$$

where ε_m represents the maximum dielectric constant, T_m represents the temperature of which the maximum dielectric constant occurs, T_i and ε_i represent the measured temperature and the related dielectric constant. ε_m, T_m, ε_i, and T_i represent one experimental data which are measured from a certain relaxor (as shown in Fig. 2) and can be used to calculate γ and σ (ξ and Δ) by using Eqs. (7) and (8). If the dipole moment, amount and relaxation time are changed due to different samples where the temperature distribution (the degree of the diffused phase transition) is not changed, the values of ε_m and ε_i will be changed with the geometric proportion. N, the normalized factor, is a constant and represents the geometric proportion. If the phase transition temperatures T_c of the micropolarization are changed and the distribution of is not changed, the value of T_m will be shifted a temperature ΔT. To verify if the values of γ and σ (ξ and Δ) are not affected by changing ε_m and T_m, we can get a new data from the following equations (as shown in Fig. 3):

$$\varepsilon'_m = N\varepsilon_m \tag{9}$$

$$\varepsilon'_i = N\varepsilon_i \tag{10}$$

$$T'_m = T_m + \Delta T \tag{11}$$

$$T'_i = T_i + \Delta T \tag{12}$$

where ε'_i represent the dielectric constants measured at different temperature and ε'_m represents the maximum dielectric constant. N is the normalized factor and is the constant. T'_m and T'_i represent the temperature at which the maximum dielectric constant occurs and the related measured temperature after shifting. ΔT is the shifting temperature and is the constant. Since ε'_m, T'_m, ε'_i, and T'_i are the new data which represent the properties of another samples, we can derive the new parameters, γ_{new} and σ_{new} (ξ_{new} and Δ_{new}), of the diffused phase transition by using the following formulas:

$$\gamma_{new} = \xi_{new} = \frac{n\sum \ln((\varepsilon'_m/\varepsilon'_i) - 1)\ln(T'_i - T'_m) - \sum \ln((\varepsilon'_m/\varepsilon'_i) - 1)\sum \ln(T'_i - T'_m)}{n\sum[\ln(T'_i - T'_m)]^2 - [\sum \ln(T'_i - T'_m)]^2} \tag{13}$$

and

$$\ln 2\sigma^2_{new} = \ln \Delta^{\xi_{new}}_{new} = \frac{\sum \ln((\varepsilon'_m/\varepsilon'_i) - 1)\ln(T'_i - T'_m)\sum \ln(T'_i - T'_m) - \sum \ln((\varepsilon'_m/\varepsilon'_i) - 1)\sum[\ln(T'_i - T'_m)]^2}{n\sum[\ln(T'_i - T'_m)]^2 - [\sum \ln(T'_i - T'_m)]^2} \tag{14}$$

Since Eqs. (9)–(12) show the relationship of the new data (ε'_m, ε'_i, T'_m and T'_i) and the original data (ε_m, T_m, ε_i, and T_i), we substitute Eqs. (9)–(12) into Eqs. (13) and (14) and get:

$$\gamma_{new} = \xi_{new} = \frac{n\sum \ln((N\varepsilon_m/N\varepsilon_i) - 1)\ln[(T_i + \Delta T) - (T_m + \Delta T)] - \sum \ln((N\varepsilon_m/N\varepsilon_i) - 1)\sum \ln[(T_i + \Delta T) - (T_m + \Delta T)]}{n\sum\{\ln[(T_i + \Delta T) - (T_m + \Delta T)]\}^2 - \{\sum \ln[(T_i + \Delta T) - (T_m + \Delta T)]\}^2} \tag{15}$$

and

$$\ln 2\sigma^2_{new} = \ln \Delta^{\xi_{new}}_{new} = \frac{\sum \ln((N\varepsilon_m/N\varepsilon_i) - 1)\ln[(T_i + \Delta T) - (T_m + \Delta T)]\sum \ln[(T_i + \Delta T) - (T_m + \Delta T)]}{n\sum\{\ln[(T_i + \Delta T) - (T_m + \Delta T)]\}^2 - \{\sum \ln[(T_i + \Delta T) - (T_m + \Delta T)]\}^2} - \frac{\sum \ln((N\varepsilon_m/N\varepsilon_i) - 1)\sum\{\ln[(T_i + \Delta T) - (T_m + \Delta T)]\}^2}{n\sum\{\ln[(T_i + \Delta T) - (T_m + \Delta T)]\}^2 - \{\sum \ln[(T_i + \Delta T) - (T_m + \Delta T)]\}^2} \tag{16}$$

As inspecting Eqs. (15) and (16), we can find that N and ΔT can be eliminated and get $\gamma_{new} = \gamma$ and $\sigma_{new} = \sigma$ ($\xi_{new} = \xi$ and $\Delta_{new} = \Delta$). Therefore, we can conclude that the degree of the diffused phase transition cannot be affected by changing the ε_m and T_m values.

5. Conclusions

γ and σ (ξ and Δ) are the diffused parameters which represent the distribution of the Curie-temperature T_c [9–15]. ε_m and T_m are another characteristics of the relaxor and are changed upon the different compositions, dopants, synthesized methods, and others [31–44]. According to Smolensky, Kirillov, and Isupov's reports [9,10], ε_m is dependent upon the dipole moment, amount, and relaxation time and T_m is the average temperature of the numerous phase transition temperature for the polar microregion. Therefore, γ and σ

(ξ and Δ) ought not to be affected by ε_m and T_m in a better physical model. In previous work, we have shown Eqs. (3) and (4) have the same fitting curve [45]. In this paper, we additionally show the values of γ and σ (ξ and Δ) cannot be affected by the ε_m and T_m. The physical meaning of the model represents that these noises ε_m and T_m can be filtered in these empirical laws. Therefore, they can be used to describe and compare the degree of the diffused phase transition between the different samples. Furthermore, the variation of the ε_m and T_m values will not affect the diffused phase degree. Therefore, we can carefully investigate the effect of the 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.

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