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Determining the gaussian distribution width of Curie-Weiss temperatures and relaxation times

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Some new possibilities of determining the gaussian distribution of Curie-Weiss temperatures and relaxation times in relaxors and in ferroelectrics with a diffused phase transition are presented in this paper. The method of determining the width of gaussian distribution of Curie-Weiss temperatures with the use of the reciprocal of dielectric permittivity on normalized plots is applied to solid solution $Ba(Ti_{1-x}Sn_x)O_3$. The method of estimating the gauss-logarithmic distribution of relaxation times based on normalized plots is proposed for relaxors. It is shown that the Vogel-Fulcher behaviour of real and imaginary parts of the dielectric permittivity in PMN is caused by gauss-logarithmic distribution of relaxation times and by its temperature dependence.

Key words: *ferroelectrics, relaxors, diffused phase transition, relaxation time*

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1. Introduction

Ferroelectrics with a diffused phase transition (DPT) were discovered in nineteen fifties [1–3]. There is a big practical importance of such materials because their properties weakly depend on temperature. The main properties of relaxor ferroelectrics are as follows:

- diffused and dispersive phase transition,
- Curie-Weiss law is not fulfilled above T_c,
- mean square of polarization is not equal to zero up to 200–300 K above T_c,
- temperatures of transition estimated by various methods are different.

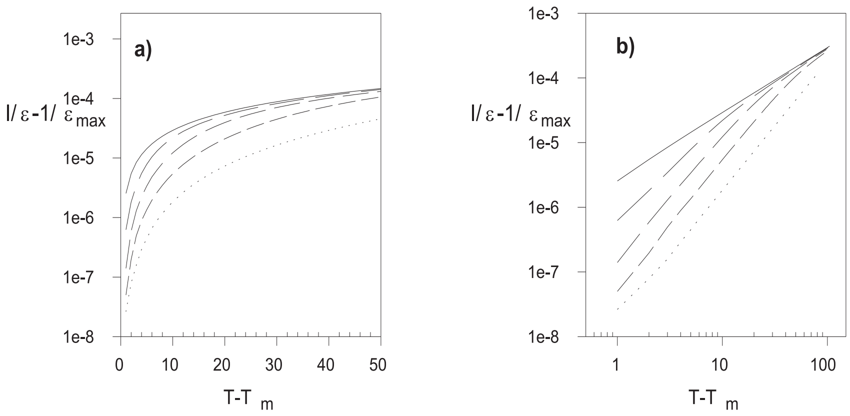

Figure 1. Normalized plots $\log(1/\epsilon - 1/\epsilon_{\max}) = f(T - T_{\mathrm{m}})$ for $BaTiO_3$ obtained as a result of numerical integrating of local dielectric permittivity with Gauss function: a) linear scale of temperatures; b) logarithmic scale.

Diffused phase transitions are observed, for example, in the fine grained ceramics (even if a sharp phase transition is always observed in single crystals). For example, Moreira and Lobo [4] investigated diffused phase transitions in the fine grained $BaTiO_3$ ceramics obtained by sol-gel method and estimated the width of gaussian distribution of local Curie temperatures using the normalized plots.

The main aim of this paper is to present some new possibilities and the results of determining the width of gaussian distribution of Curie-Weiss temperatures and relaxation times in relaxors and in ferroelectrics with a diffused phase transition.

2. The width of gaussian distribution of Curie-Weiss temperatures

Assuming that:

$$\varepsilon(T) = \int_0^\infty \varepsilon_a(T,\theta) g(\theta) \mathrm{d}\theta, \tag{1}$$

where $\varepsilon_a(T,\theta)$ – local dielectric permittivity, $g(\theta)$ – Gauss distribution of local Curie-Weiss (C-W) temperatures (θ). In practice, we want to determine the width of the Gauss curve having experimental ε(T) data. Recently Moreira [4] has presented the method of determining the width of the Gauss curve using a special graphical presentation. Earlier, Clarke [5] generalized the so called quadratic Curie-Weiss law for the case $1 < \gamma < 2$:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_{\max}} + A(T - T_{\mathrm{m}})^{\gamma}, \tag{2}$$

where $\varepsilon_{\max}$ – maximum value of dielectric permittivity, T_{m} – temperature in which the maximum of dielectric permittivity is observed, A – constant (for $\gamma = 1$ – C-W constant), γ – exponent (from range 1-2). For different values of σ, the transition from $\gamma = 2$ to $\gamma = 1$ takes place at various temperatures – T_{L}. Moreira stated that in $BaTiO_3$ $T_L = T_m + 4\sigma$. The results of calculations for $BaTiO_3$ are presented in figure 1.

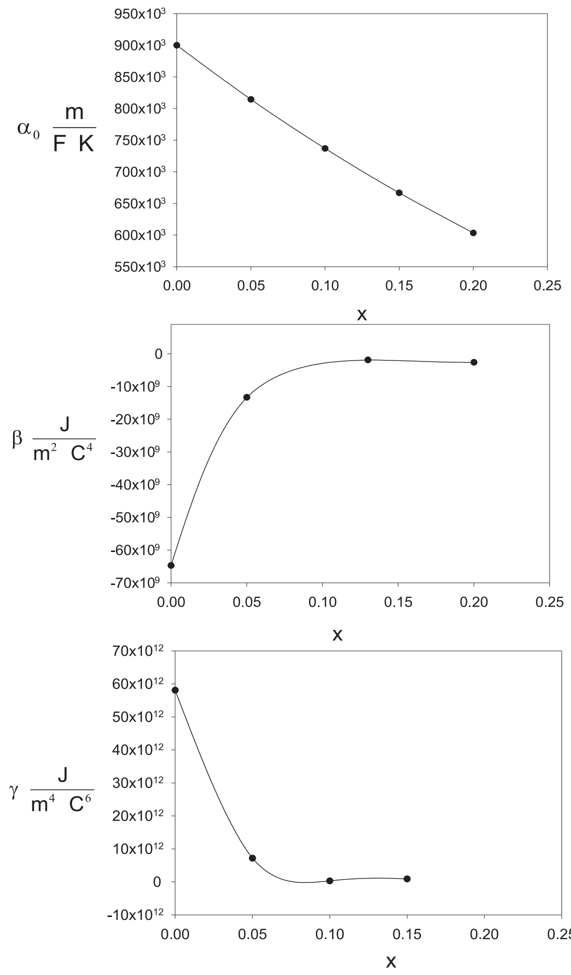

Figure 2. Dependencies $\alpha\,(x)$, $\beta\,(x)$ and $\gamma\,(x)$ used in calculations.

Similar calculations made by the author for $PbTiO_3$ have shown that in this case the dependency $T_L = T_m + 4\sigma$ is also valid. So it is possible to calculate the dependency $\sigma(x)$ for various compounds, for example, for $Ba(Ti_{1-x}Sn_x)O_3$ solid solutions. The dielectric properties of this solid solution are well known (for example [6,7]).

Rolov and Yurkevich [8,9] developed the Landau-Ginsburg-Devonshire (LGD) theory concerning the case of solid solution (but without taking into account the diffusion of the phase transition).

The author made many trials which showed that to obtain a relatively good agreement with the experimental data for various compositions we must assume that all parameters i.e. α, β and γ depend on x. All three dependences have been obtained by fitting to the literature experimental data ([15]) for various compositions. Dependency $\alpha_o(x)$ can be described by the function:

$$\alpha_o(x) = \alpha_o(0)\exp(-Bx), \qquad (3)$$

where $\alpha_o(0) = 0.9 \cdot 10^6$ [m/FK] (value for $BaTiO_3$ ceramics), $B = 2$.

The values of β^2/γ have been calculated for every composition from (well known from LGD theory) the relation:

$$T_c = T_0 + \frac{3\beta^2}{16\alpha_0\gamma}, \qquad (4)$$

β parameter has been calculated from $P(T)$. $\alpha_0(x)$, $\beta(x)$ and $\gamma\,(x)$ dependencies which give a good fitting to experimental data, and are presented in figure 2.

Calculations have shown that for the increasing x, the difference between T_c and T_o streams to zero and as a result the phase transition gradually streams to the second order. Curie-Weiss temperatures for every composition have been calculated from the relation:

$$T_0(x) = T_0(0) - ax, \qquad (5)$$

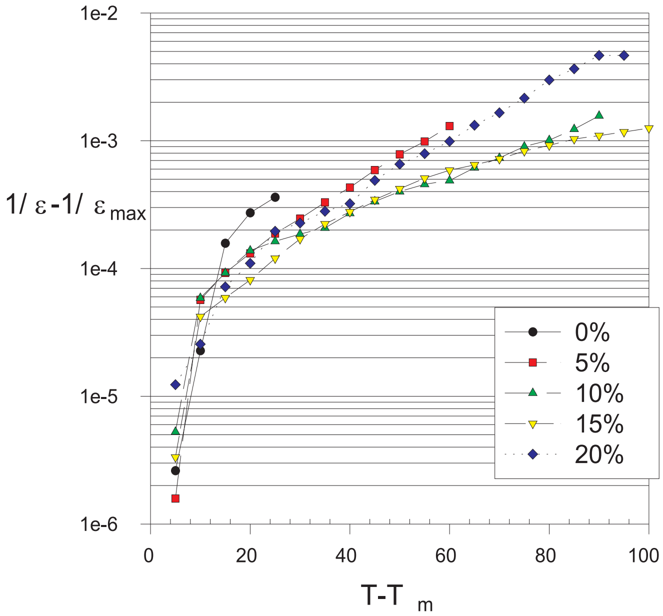

Figure 3. Normalized plots of $(1/\varepsilon - 1/\varepsilon_{\mathrm{max}}) = f(T - T_{\mathrm{m}})$ for $\mathrm{Ba(Ti_{1-\mathit{x}}Sn_{\mathit{x}})O_3}$ solid solutions (experimental data from [7]).

where $T_0(0)$=381.8 K (value for $BaTiO_3$ ceramics), a=745 K.

Next, we can calculate $P_{\mathrm{s}}(T)$ for various x:

$$P_{\mathrm{o}}(T,x) = \begin{cases} \sqrt{\frac{(\beta(x)^2 - 4\alpha(T,x)\gamma(x))}{2\gamma(x)}}, & T < T_{\mathrm{c}}(x), \\ 0 & T > T_{\mathrm{c}}(x). \end{cases} \tag{6}$$

Substituting the obtained $P_0(T,x)$ into the formula $\varepsilon^{-1} = \alpha + 3\beta P^2 + 5\gamma P^4$ it is possible to obtain dependencies $\varepsilon(T,x)$ but without taking into account the diffusion of a phase transition. To introduce the diffusion we must know the width of gaussian distribution of C-W temperatures for every composition. It can be obtained using the method described above. Normalized plots of $(1/\varepsilon - 1/\varepsilon_{\mathrm{max}})$ vs. $(T - T_{\mathrm{m}})$ for $\mathrm{Ba(Ti_{1-\mathit{x}}Sn_{\mathit{x}})O_3}$ (BTS) are presented in figure 3.

The obtained σ(x) dependency is presented in figure 4.

The results presented in figure 4 can be fitted to a function:

$$\sigma(x) = 5.58\exp(6.27x). \tag{7}$$

Dependence (7) can be introduced into the Gauss function for every x and as a result it is possible to obtain $P_{\mathrm{s}}(T,x) = \int P(T,x,\theta)\mathrm{d}\theta$ (presented in figure 5).

In the next step we can calculate $\varepsilon(T,x)$ by numerical integrating with Gauss function for every x. Results are presented in figure 6.

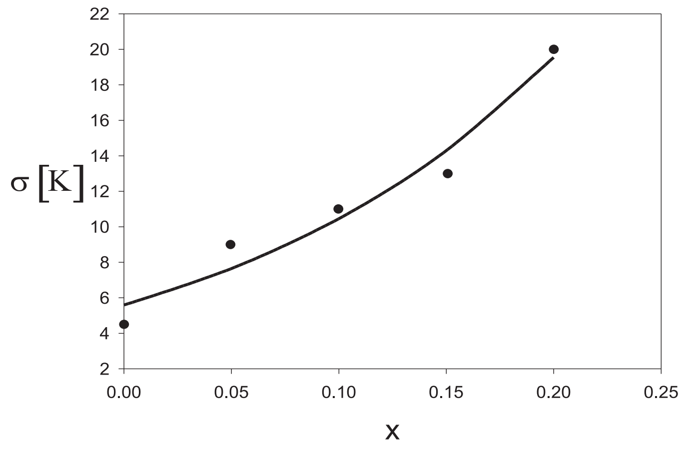

Figure 4. Dependency $\sigma(x)$ obtained as a result of calculations described in the text (symbols) and the plot of equation (7) – solid line.

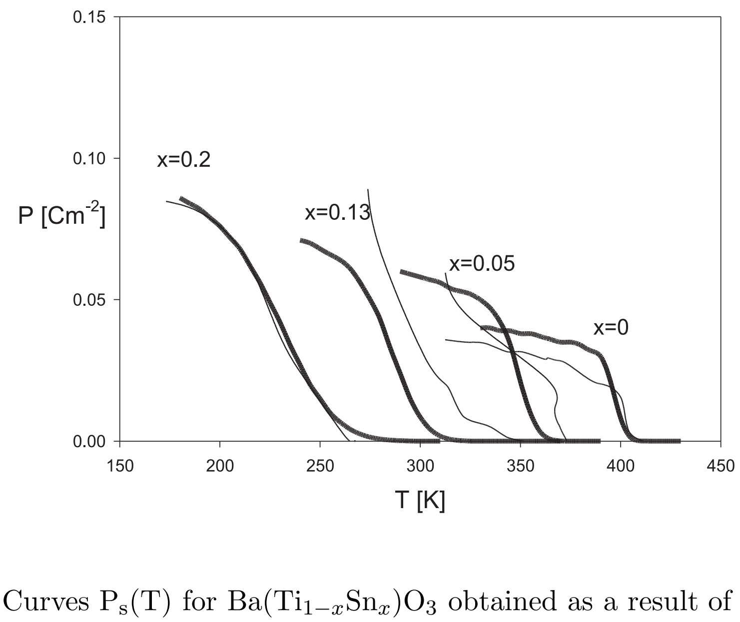

Figure 5. Curves $P_s(T)$ for $Ba(Ti_{1-x}Sn_x)O_3$ obtained as a result of calculations based on the formulas (4–7) (thick lines) compared with the literature experimental data from [16] (thin lines).

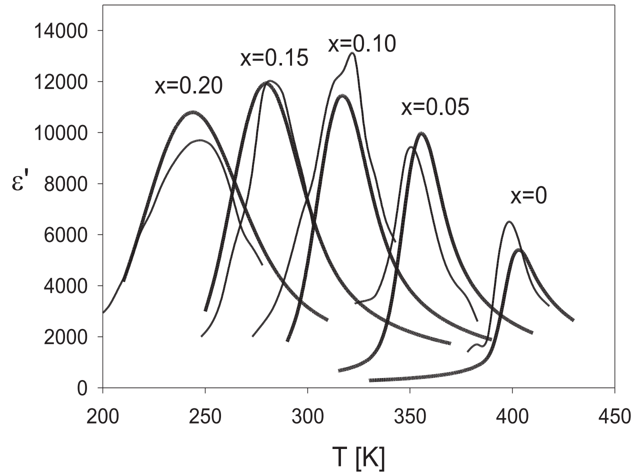

Figure 6. Dependencies ε(T) for $Ba(Ti_{1-x}Sn_x)O_3$ obtained as a result of calculations based on the formulas (4)–(7) (thick lines) and experimental data from [7] (thin lines).

3. The method of estimating the width of gaussian-logarithmic distribution of relaxation times

Obviously, in the relaxors, the shift of the range of dielectric dispersion into low frequencies is observed. It is related with the dependence of relaxation time on temperature. For the majority of the materials this dependency is of Arrhenius type (equation (8)):

$$\frac{1}{\tau} = \frac{1}{\tau_0} \mathrm{e}^{\frac{-E_0}{kT}} \qquad \text{or} \qquad \ln\left(\frac{1}{\tau}\right) = \ln\left(\frac{1}{\tau_o}\right) - \frac{E_o}{kT}. \tag{8}$$

But in some cases this dependency is of Vogel-Fulcher (V-F) type (equation (9)):

$$\frac{1}{\tau} = \frac{1}{\tau_o} \mathrm{e}^{\frac{-E_0}{k\left(T-T_f\right)}} \qquad \text{or} \qquad \ln\left(\frac{1}{\tau}\right) = \ln\left(\frac{1}{\tau_0}\right) - \frac{E_0}{k\left(T-T_f\right)}, \tag{9}$$

where τ – relaxation time at a given temperature T, τ_o – relaxation time at $T \to \infty$, E_0 – activation energy, T_f – freezing temperature at which $\tau \to \infty$. Some authors conclude that V-F relation for relaxation times leads to V-F dependence of T_m on frequency ω [10,11]. However V-F type relation between T_m temperature and frequency ω should not be a consequence of V-F relation between relaxation time and temperature.It may be a result of the widening of distribution of the relaxation times with the decreasing temperature. Such a suggestion has been presented in the work of Tagantsev [12] and supported by analytical relations, but the numerical calculations for real materials have not been done. Numerical calculations for PMN and SBN presented below confirm the suggestion that V-F relation between T_{m} and ω is caused by the widening of gaussian-logarithmic distribution of relaxation times. Details of numerical calculations are published in [17] and here only the main results are presented.

Assuming that distribution (in logarithmic scale) of relaxation times takes place, we must calculate the integral:

$$\varepsilon^*(T) = \int_{-\infty}^{\infty} \varepsilon^*(T,\tau) y(\tau(T)) \mathrm{d}\tau, \tag{10}$$

where $\varepsilon^*(T,\tau)$ is the temperature dependent complex dielectric permittivity, $y(\tau(T))$ is the temperature dependent distribution function of relaxation times. $\varepsilon^*(T,\tau)$ is given by Debay's relation with a single relaxation time depending on temperature

$$\varepsilon^*(T,\tau) = \frac{\varepsilon_{\mathrm{s}}(T) + \varepsilon_{\infty}(T)\mathrm{i}\omega\tau_{\mathrm{o}}(T)}{1 + \mathrm{i}\omega\tau_{\mathrm{o}}(T)}. \tag{11}$$

Gaussian (in logarithmic scale) distribution of relaxation times is given by a function:

$$y(\tau(T)) = \frac{1}{\sqrt{2\pi}\sigma(T)} \mathrm{e}^{\frac{-[\ln(\tau)-\ln(\tau_{\mathrm{o}})]^2}{[2\sigma(T)]^2}}, \tag{12}$$

where τ_0 is the value around which the distribution takes place, $\sigma(T)$ is the temperature dependent half-width of the Gauss distribution. So, it is necessary to estimate this half-width from the experimental data. The method of estimating the width of gaussian-logarithmic distribution of relaxation times was based on the diagrams $\frac{\varepsilon'-\varepsilon_\infty}{\varepsilon_{\mathrm{s}}-\varepsilon_\infty}$ vs. $\log(\omega\tau_{\mathrm{o}})$. The τ_{o} value has been taken from the frequency at which the expression $\frac{\varepsilon\prime-\varepsilon_\infty}{\varepsilon_{\mathrm{s}}-\varepsilon_\infty}$ is equal to 0.5. It is well known (it is the general conclusion from Debay's theory) that such a diagram would be identical for all materials. But, in real cases, as a rule, the deviation from such a theoretical curve is observed which can be related with the distribution of relaxation times. So, the magnitude of this deviation may be used as a measure of the width of the distribution. In the first step, trial calculations have been made by the author for various τ_{o}, $\varepsilon_\infty, \varepsilon_{\mathrm{s}}$ which showed that the shapes of the curves depend only on σ. To estimate the width of distribution, the procedure based on comparing the experimental curves of $\frac{\varepsilon\prime-\varepsilon_\infty}{\varepsilon_{\mathrm{s}}-\varepsilon_\infty}$ vs. $\log(\omega\tau_{\mathrm{o}})$ with the theoretical ones, can be used. For every σ, the value of $\log(\omega\tau)$ was estimated at which $\frac{\varepsilon\prime-\varepsilon_\infty}{\varepsilon_{\mathrm{s}}-\varepsilon_\infty}$=0.3 (this value was chosen arbitrarily). The obtained dependency between $\log(\omega\tau)$ and σ was linear which permits us to determine the dependency $\sigma(T)$ for real materials as well. It has been done for PMN and SBN.

In the case of PMN using $\varepsilon_{\mathrm{s}}(T)$ dependency (introducing data from [13] to C-W law) and constant value $\varepsilon_\infty = 0$, the value of expression $\frac{\varepsilon\prime-\varepsilon_\infty}{\varepsilon_{\mathrm{s}}-\varepsilon_\infty}$ has been calculated at various temperatures. As a result, it was possible to obtain the values of the frequency at which the expression $\frac{\varepsilon\prime-\varepsilon_\infty}{\varepsilon_{\mathrm{s}}-\varepsilon_\infty}$ was equal to 0.5. Next, we can obtain the dependency of the logarithm of the mean relaxation time at the temperature. It was stated that the dependency $\ln(\tau) = f(1/T)$ can be described by the equation (8)

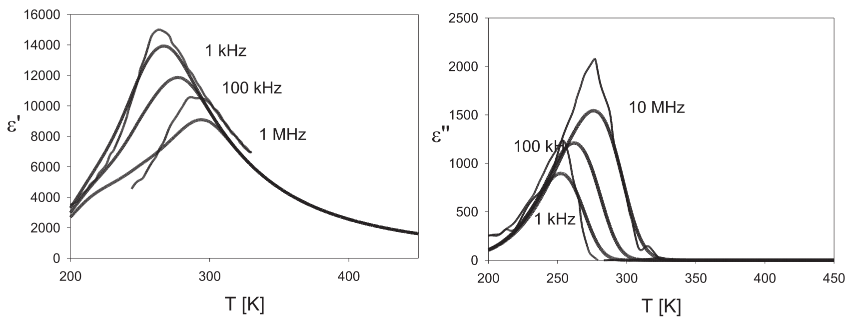

Figure 7. Dependences $\varepsilon'(\omega,T)$ and $\varepsilon''(\omega,T)$ obtained as a result of numerical calculations (thick lines) compared with the experimental data from [13].

(i.e. Arrhenius type) with $\ln\left(\frac{1}{\tau_o}\right) = 27.44$ and $\frac{E_o}{k} = 5500$ ($\tau_o = 1.21 \cdot 10^{-12}$s and $E_o = 7.59 \cdot 10^{-20}$J).

As a result, the construction of the diagram $\frac{\varepsilon\prime-\varepsilon_\infty}{\varepsilon_s-\varepsilon_\infty} = f(\log(\omega\tau_o))$ for PMN became possible. Next, we can find $\sigma(T)$ dependency using the procedure described above. The obtained relation can be expressed as:

$$\sigma(T) = \frac{\sigma_o}{(T-T_\infty)^n} \tag{13}$$

with $\sigma_o = 2.69 \cdot 10^3$, $T_\infty = 194\ K$, $n = 1.61$. It means that at temperature 194 K, the width of Gauss curve streams to infinity (not relaxation time). Next, we can calculate $\varepsilon'(T)$ and $\varepsilon''(T)$ for PMN at various frequencies (presented in figure 7).

From figure 7 we can find the dependency $T_m(\omega)$ and fit it to equation (8) or (9). As a result, it was stated that the obtained $T_m(\omega)$ dependency can be fitted to V-F equation in spite of the fact that the dependency $\tau(T)$ is of Arrhenius type.

Similar calculations for $Ba_{1.25}Sr_{3.75}Nb_{10}O_{30}$ – SBN – 75 showed that $\sigma(T)$ dependency in this case can be fitted to the equation:

$$\sigma(T) = a + bT + cT^2 \tag{14}$$

with $a = 16.76$, $b = -0.087$ K^{-1}, $c = 1.15 \cdot 10^{-4}$ K^{-2}. Experimental data for SBN-75 were taken from [14]. Equation (14) is different in its nature from the dependency obtained for PMN (equation (13)). In the case of SBN, σ(T) does not stream to infinity at any finite temperature. Finally, taking ε_s(T), ε_∞(T) from Cole-Cole plots in [14] and having σ(T), we can calculate $\varepsilon'(T)$) and $\varepsilon''(T)$ (as earlier for PMN). Results are presented in figure 8.

Also, in this case, the dependency $T_m(\omega)$ obtained from $\varepsilon'(\omega,T)$ is of V-F type (T_f= 118.4 K, E_a= 6.4·10^{-20} J, ω_o= 39.6·10^{14} Hz) in spite of the fact that $\tau(T)$ dependency is of Arrhenius type and $\sigma(T)$ does not stream to infinity at any finite temperature.

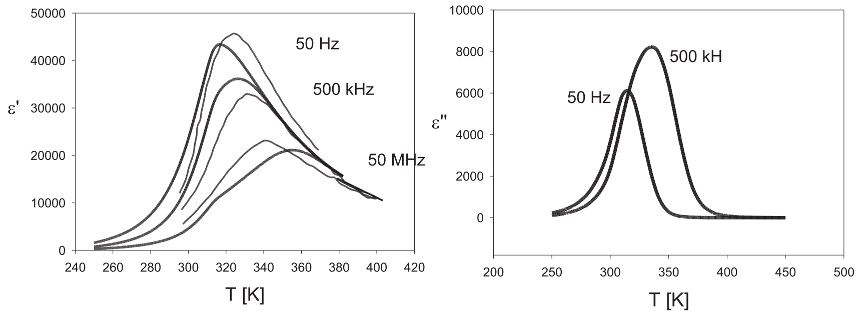

Figure 8. a) Dependencies $\varepsilon(T)$ obtained as a result of numerical calculations for SBN-75.

4. Conclusions

Some new possibilities of determining the gaussian distribution of Curie-Weiss temperatures and relaxation times are presented for relaxors and ferroelectrics with a diffused phase transition:

- the method of determining the width of gaussian distribution of Curie-Weiss temperatures using the normalized plots of the reciprocal of dielectric permittivity has been applied to BTS solid solutions with DPT. The results of calculations for BTS have shown that it is possible to describe the dependences observed in the experiment;

- the method of estimating the gauss-logarithmic distribution of relaxation times in relaxors based on normalized plots (applied for relaxors PMN and SBN) was suggested;

- the Vogel-Fulcher behaviour of real and imaginary parts of the dielectric permittivity in PMN and SBN can be caused by the Arrhenius type dependency of relaxation times on the temperature and widening the gauss-logarithmic distribution of relaxation times.

All the results have been obtained using numerical methods and experimental data from literature.

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Визначення ширини гаусового розподілу температур Кюрі-Вейса і часів релаксації

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У цій роботі представлено деякі нові можливості щодо визначення гаусового розподілу температур Кюрі-Вейса і часів релаксації у релаксорах і сегнетоелектриках з розмитим фазовим переходом. До твердого розчину $Ba(Ti_{1-x}Sn_x)O_3$ застосовано метод визначення ширини гаусового розподілу температур Кюрі-Вейса з використанням графіків оберненої діелектричної проникності. Запропонований графічний метод оцінки гаус-логарифмічного розподілу часів релаксації для релаксорів. Показано, що фогель-фульчерівська поведінка дійсної та уявної частин діелектричної проникності PMN є наслідком гаус-логарифмічного розподілу часів релаксації і його температурної залежності.

Ключові слова: *сегнетоелектрики, релаксори, розмитий фазовий перехід, час релаксації*

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