

Lorentz-type relationship of the temperature dependent dielectric permittivity in ferroelectrics with diffuse phase transition

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The temperature dependence of the dielectric permittivity of perovskite Ba(Zr_xTi_{1-x})O₃ solid solutions, PbMg_{1/3}Nb_{2/3}O₃ relaxor, and BaTiO₃ ferroelectric ceramics was measured. It is found that a Lorentz-type law can be used to describe the dielectric permittivity of either the normal ferroelectrics with or without diffuse phase transitions (DPT) or the typical ferroelectric relaxors. The ferroelectric DPT can be well described by just one fitting process using the Lorentz-type law, while the relaxor ferroelectric transition needs two independent fitting processes. The Lorentz-type law fails at the low temperature side of the dielectric maximum of a first-order ferroelectric phase transition. Above the transition temperature, the dielectric curves of all the studied materials can be well described by a Lorentz-type law. © 2008 American Institute of Physics.

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A broad peak in the temperature dependence of dielectric permittivity ε is the main feature of ferroelectrics with a diffuse phase transition (DPT), especially for ferroelectric relaxors.¹⁻⁴ Actually, systems showing a broad dielectric peak at the frequency-independent peak temperature T_m are different from the relaxor-type DPTs.^{1,4} In typical relaxors, strong frequency dispersion in dielectric permittivity is observed at the low temperature side of the dielectric peak, while the high temperature permittivity is almost frequency independent. The temperature for maximum permittivity T_m shifts to higher values with increasing frequencies following the Vogel-Fulcher law.³

For a ferroelectric phase transition, the Curie-Weiss law $1/\varepsilon=(T-T_C)/C$ is known to describe the high temperature side of the sharp permittivity peak in normal ferroelectrics. However, in ferroelectrics with DPT this law is observed only at temperatures significantly higher than T_m [over 300 K for PbMg_{1/3}Nb_{2/3}O₃ (PMN)].^{1,2} When the temperature is decreased below the Burns' temperature T_B , polar nanoregions (PNRs) appear and the displacive-type soft mode is overdamped.⁵ The Curie-Weiss law becomes invalid within the temperature range of T_m - T_B .

Since Smolenskii's⁶ work, the temperature dependence of the dielectric permittivity above T_m has been widely studied in order to find out the characteristic dielectric behavior of ferroelectrics with DFT. There are several models to quantitatively describe the temperature dependent dielectric permittivity of DPT. A brief review of these models has been given by Bokov and Ye.⁷ Among these models, the following power law^{8,9} is the most popular one:

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

where the parameters γ and δ reflect the diffuseness of dielectric relaxation. Normally, $\gamma=1$ describes a Curie-Weiss

behavior of normal ferroelectrics, while $\gamma=2$ is valid for a classical ferroelectric relaxor.⁸ It should be mentioned that the maximum permittivity ε_m and the temperature at maximum permittivity T_m are frequency-dependent quantities for relaxors. So the parameters δ and γ also depend on frequency, and therefore Eq. (1) is not appropriate to describe the frequency-independent dielectric behavior at high temperatures ($T > T_m$). Moreover, the parameters γ and δ appear to be different in different temperature ranges of the same material.^{10,11}

Recently, several relations have been attempted to describe the dielectric permittivity $\varepsilon(T)$ of relaxors at $T > T_m$, one of which is the Lorentz-type empirical relation^{7,12}

$$\frac{\varepsilon_A}{\varepsilon} = 1 + \frac{(T - T_A)^2}{2\delta_A^2}, \quad (2)$$

where T_A ($T_A \neq T_m$) and ε_A are the parameters defining the temperature of the dielectric peak and the extrapolated value of ε at $T=T_A$, respectively. The parameter δ_A is frequency independent at high enough frequencies and it reflects the diffuseness of the dielectric peak. The above equation describes the high temperature ($T > T_m$) dielectric permittivity quite well in a number of relaxor ferroelectrics.^{7,12} Lei *et al.*¹³ also found that both high temperature and low temperature sides of the dielectric maximum of Ba(Ti_{0.8}Sn_{0.2})O₃ ceramics can be described by the above Lorentz-type relation. In this letter, we propose that this Lorentz-type behavior is not only observed in relaxors but also universally observed in ferroelectrics with or without DFT. Furthermore, Eq. (2) is found to describe well the low temperature slope of the broad dielectric peak too in ferroelectrics with DPT.

Ba(Zr_xTi_{1-x})O₃ ($x=0.25-0.45$, abbreviated as BZT100x) solid solutions, PMN relaxor, and ferroelectric BaTiO₃ (BT) have been selected. Pure perovskite ceramic samples were prepared by solid state reaction method starting from the mixing of appropriate quantities of high purity raw powders. Top and bottom electrodes were made by coating silver paste

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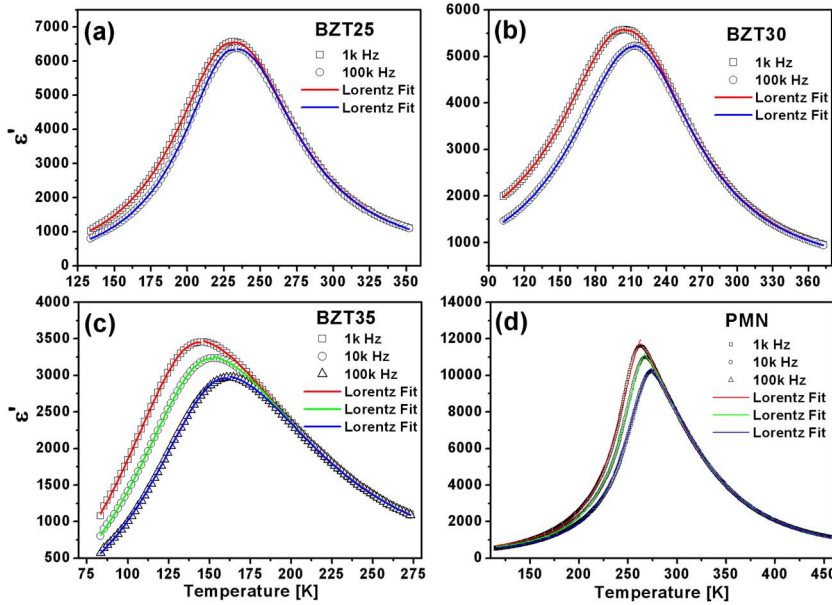


FIG. 1. (Color online) Temperature dependence of the dielectric permittivity ϵ' of (a) BZT25, (b) BZT30, (c) BZT35, and (d) PMN ceramics. The solid lines are the fitting curves using Eq. (2).

on both sides of the sintered disks and followed by firing at 650 °C for 20 min. The dielectric permittivity was measured under a multifrequency LCR meter (SR720, Stanford Research System).

The temperature dependence of the real part of dielectric permittivity $\epsilon'(T)$ at various frequencies for the BZT25, BZT30, BZT35, and PMN samples is shown in Fig. 1. Only one broad dielectric peak is observed for all the compositions. A slight frequency dispersion in $\epsilon'(T)$ starts to appear in BZT25. Stronger frequency dispersions are observed in BZT30, BZT35, and PMN. Among those samples, BZT25 can be regarded as a ferroelectric with DPT (not a relaxor) since the ferroelectric-relaxor crossover composition for BZT solid solution is BZT27.¹⁴ At $T > T_m$, $\epsilon'(T)$ can well be fitted by Eq. (1) for all the studied compositions in Fig. 1. However, the parameter γ seems to be different in different temperature intervals of the same material. For instance, under a measuring frequency of 10 kHz, γ is 2.21 in the temperature range of $T_m - T_m + 24$ K and 1.83 at a much larger temperature range for BZT25. The fitting results show that within the same temperature range, the parameter γ decreases monotonically with composition from 1.83 (BZT25) to 1.53 (BZT45). However, the dielectric spectra [Figs. 1(a)–1(c)] show more and more clearly a relaxor behavior from BZT25 to BZT35. This leads to a conclusion that γ is not a good parameter to describe the degree of dielectric relaxation and γ close to 2 is not always valid for relaxors. Therefore, it can be concluded that Eq. (1) is not a good fit for materials with a broad dielectric peak.

The fitting results of Eq. (2) are shown as solid lines in Fig. 1 and the best-fit parameters are listed in Table I. It is interesting to find that $\epsilon'(T)$ can be fitted quite well by Eq. (2) at $T < T_m$ and $T > T_m$, respectively. For BZT25 and BZT30, the fitting parameters are very close in two temperature ranges, $T < T_m$ and $T > T_m$, indicating that there should be only one polarization process in BZT25 and BZT30. The very different fitting parameters in two different temperature ranges for BZT35 and PMN suggest that there should be two polarization processes in these materials, one dominating in the high temperature range and the other dominating in the low temperature region. Recently, Cheng and co-workers^{10,15} observed that the measured dielectric constant of PMN and PMN-PT-BT relaxors could only be strictly fitted if two kinds of polarization processes are considered. The polarization process, which dominates in the high temperature range, may be associated with the thermally activated flips of the PNRs^{1,10} or with the boundaries of these PNRs.¹⁶

In the high temperature range ($T > T_m$), the parameter δ increases from 72 to 114.4 for BZT25 and BZT35, which reflects the increase in the degree of diffuseness. Bokov and Ye⁷ discussed that deviations from the Lorentz-type law [Eq. (2)] will appear at both the low and high temperature sides of the fitting for temperature $T > T_m$. For most dielectrics, the low-frequency dispersion at high temperatures¹⁷ and the contribution of ϵ_∞ (from electronic and ionic polarizations) will lead to deviations from Eq. (2). For relaxors (BZT35 and PMN here), the existence of the two polarization processes leads to deviations from Eq. (2) at the low temperature side

TABLE I. Curve fitting results for BZT, PMN, and BT.

Sample	f (kHz)	T_m (K)	ϵ_m	T_A (K)		ϵ_A		δ_A (K)	
				$T < T_m$	$T > T_m$	$T < T_m$	$T > T_m$	$T < T_m$	$T > T_m$
BZT25	10	232.5	6474.4	230	233.3	6751	6364	69	72
BZT30	10	208.8	5434.5	207.5	208.6	5111	5221	91.9	93.8
BZT35	10	152.6	3237.3	150.4	147.6	4232	3081	82.6	114.4
PMN	10	267.7	10986	271.1	250.6	11225	11954	48.9	103.6
BT	10	393	23371	393	358	18235	61670	7.3	37

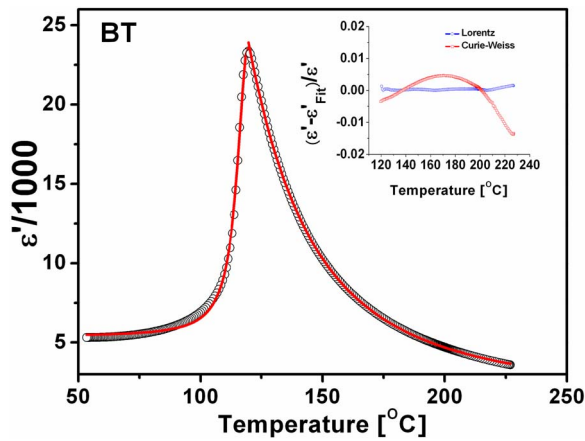


FIG. 2. (Color online) Temperature dependence of the dielectric permittivity ϵ' of BT ceramics. The solid lines are the fitting curves using Eq. (2). The inset shows the percentage difference $[(\epsilon' - \epsilon'_{\text{fit}})/\epsilon']$, where ϵ' is the experimental value and ϵ'_{fit} is the fitted result between the fitted results and the experimental dielectric permittivities above the Curie temperature. Two fitting results are compared: one by the Curie–Weiss law and the other by Eq. (2).

for fitting at $T > T_m$, as well as the high temperature side for fitting at $T < T_m$. The slight frequency dependence of the parameters (T_A , δ , and ϵ_A) of the current fitting process is mainly attributed to the relaxor dispersion.

From the above results, it is noted that Eq. (2) is valid for describing the temperature dependence of ϵ' for relaxors and ferroelectrics with DFT. Because the structure and properties change gradually in the BZT solid solution system, it is reasonable to assume that the size and response of the PNRs also change gradually with decreasing Zr substitution. Since Eq. (2) provides a good fit for BZT20 (ferroelectric with DFT) as well as for BZT45 (relaxor), it is quite natural to ask whether the same equation is valid for normal ferroelectrics. Figure 2 displays the dielectric constant $\epsilon'(T)$ of BT and the fitting curves by using Eq. (2). It can be seen that in the case of $T > T_C$, $\epsilon'(T)$ can be precisely described by Eq. (2), while in the case of $T < T_C$, significant deviation occurs at low temperatures. However, the fitting process in the vicinity of T_C gives some meaningful parameters ($T_A = T_C = 393$ K and $\delta = 7.3$ describing a sharp peak), suggesting the validity of the Lorentz-type phenomenological description in the ferroelectric phase transition. The deviation from Eq. (2) at the low temperatures may be attributed to disturbance by a ferroelectric-to-ferroelectric phase transition of BT at about 300 K. It is interesting to note that the Curie–Weiss law was traditionally used to describe the dielectric behavior above the Curie temperature of normal ferroelectrics like BT. However, as indicated in the inset of Fig. 2, the Lorentz-type relation gives better fitting results than the Curie–Weiss law does.

Equation (2) has also been used to describe a pure Debye relaxation behavior. Figure 3 shows the simulated data by using the time-honored Debye relaxation equations with Arrhenius-type temperature dependent relaxation times.¹⁸ It can be found that for a Debye relaxation process, Eq. (2) is only valid at temperatures above T_m .

In summary, a Lorentz-type relation can be used to describe well the temperature dependent dielectric permittivity

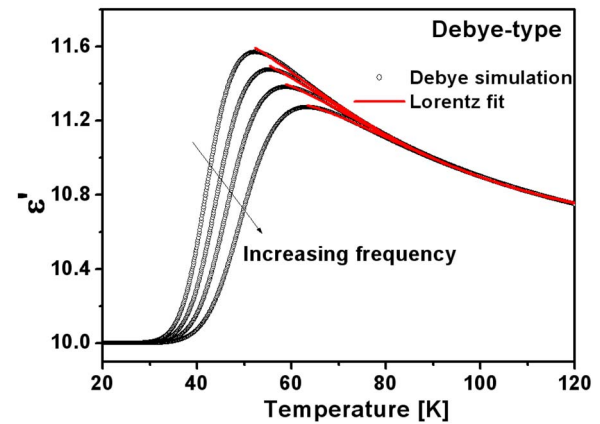


FIG. 3. (Color online) The simulated data using the time-honored Debye relaxation equations with Arrhenius-type temperature dependent relaxation times. The solid lines are the fitting curves using Eq. (2).

of ferroelectrics with DPT, classical relaxors, and normal ferroelectrics. Although the structures of these materials are significantly different, the applicability of the Lorentz-type law suggests an astonishing universality extending from normal to relaxor ferroelectrics. This universality may be helpful to the understanding of the origin of the ferroelectric DPT and relaxors. Further investigations are needed to understand the fundamental physical mechanism underlying this phenomenon.

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¹⁸Debye relaxation $\epsilon'' = \epsilon_\infty + (\epsilon_S - \epsilon_\infty)/(1 + \omega^2\tau^2)$, where the relaxation time follows the Arrhenius-type temperature dependence $\tau = \tau_0 \exp(T_0/T)$.