

Revisit of the Vögel–Fulcher freezing in lead magnesium niobate relaxors

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The Vögel–Fulcher (VF) equation $\omega = \omega_0 \exp[-E_a/k_B(T_m - T_f)]$ was frequently used to describe the dielectric relaxation of relaxor ferroelectrics where ω is the probe frequency at the peak temperature T_m of either the real or imaginary parts of the dielectric constant. We revisited this relation in a typical relaxor lead magnesium niobate and found that the parameters obtained were not physically meaningful. Meaningful results can only be obtained by fitting the VF relation on the characteristic relaxation time τ_c , whose temperature dependence can be obtained from the Cole–Cole model. The freezing temperature we obtained is 230 K, below which τ_c becomes temperature independent.

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Although relaxor ferroelectrics (RFEs) have been found for more than 50 years and have been intensively investigated, a precise interpretation of their dielectric properties has not been established.^{1,2} Lead magnesium niobate $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) can be regarded as an archetypal RFE. It is characterized by a broad and rather strongly frequency-dependent dielectric peak at radio frequencies, whose temperature for maximum permittivity T_m shifts to higher values with increasing frequencies. This frequency dispersion is observed in a frequency range from millihertz to gigahertz, and is commonly attributed to the temperature evolution of the broad distribution of relaxation times $f(\tau)$.^{1–4} Infinite (or very large) relaxation time τ usually means a glasslike “freezing” of the spectrum. The similarities between RFE and glass in macroscopic properties have been studied for a long time.^{5–7} It has been found that in many RFEs the relationship between the probe frequency ω and the temperature T_m can be described by the Vögel–Fulcher (VF) equation, similar to those observed in canonical glasses as follows:^{5,6}

$$\omega = \omega_0 \exp\left[\frac{-E_a}{k_B(T_m - T_f)}\right], \quad (1)$$

where T_f is the static freezing temperature, ω_0 the attempt frequency, and E_a the activation energy. Consequently, a dipolar glass model for relaxors was proposed.⁵

However, TagansteV⁸ argued that a similar situation may take place in dielectrics if the static permittivity $\epsilon_s(T)$ has a maximum at T_f . In this respect, the relaxation spectrum may broaden upon cooling without an infinite increase in τ at T_f , that is, Eq. (1) does not necessarily imply the freezing of the spectrum. Later, the relaxor state of PMN was proposed to be a ferroelectric one broken up into nanodomains (not the dipolar glass state) under the constraint of quenched random electric fields,^{9–11} which was originated from charged compositional fluctuations. In this letter, we investigate the dielectric relaxation behavior of PMN ceramics by careful

Cole–Cole analysis. It seems that T_f derived from the fitting of Eq. (1) does not give a true value of freezing temperature.

PMN ceramics with a perovskite structure were prepared from high purity raw materials and sintered for 2 h at 1150 °C by a two-step procedure.¹² For dielectric measurement, disk samples with a thickness about 1 mm and a diameter about 10 mm were used. Gold electrodes were dc sputtered on both surfaces of the disk samples. The dielectric properties were measured as a function of temperature between 600 and 110 K (at a cooling rate of 0.8 K/min) using an LCR meter (Hewlett Packard 4274A) over a frequency range of 100 Hz to 100 kHz. Before measurements, the samples were thermally treated at a temperature much higher than T_m to remove any effects of aging or electric history.

Figure 1 shows the temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the relative dielectric permittivity at various frequencies. For ϵ' , it can be observed that its maximum value decreases with increasing frequencies and T_m shifts to higher temperatures, displaying a frequency dispersion. The value of T_m is 258.5 and 273.6 K at 100 Hz and 100 KHz, respectively, showing a shift in temperature ΔT of approximately 15 K, which is in good agreement with previous reports.^{1–4} For ϵ'' , its temperature at maximum T'_m also shifts to higher values with increasing frequencies. The inset of Fig. 1 shows plots of $\ln(\omega)$ versus T_m and T'_m .

Applying Eq. (1) to the experimental data, we can get the fitting results of ω_0 , E_a , and T_f which are summarized in Table I. It can be seen that T_f is consistently about 205 K from fitting by $T_m - \omega$ and $T'_m - \omega$ relations. However, the value of ω_0 ($\sim 10^{15}$ Hz) is higher than the attempt frequency of ions in solid state materials which is only on the order of 10^{12} Hz. Similar results have also been observed by Cheng *et al.*,¹³ where a much higher value of ω_0 ($\sim 10^{20}$ Hz) was reported in 0.9PMN-0.1PbTiO₃. It can also be found that the activation energy E_a derived from $T'_m - \omega$ relation is 0.103 eV, much lower than that derived from $T_m - \omega$ relation (0.145 eV). Therefore, the results obtained by fitting the dielectric response according to the VF law on probe frequency are not physically reasonable.

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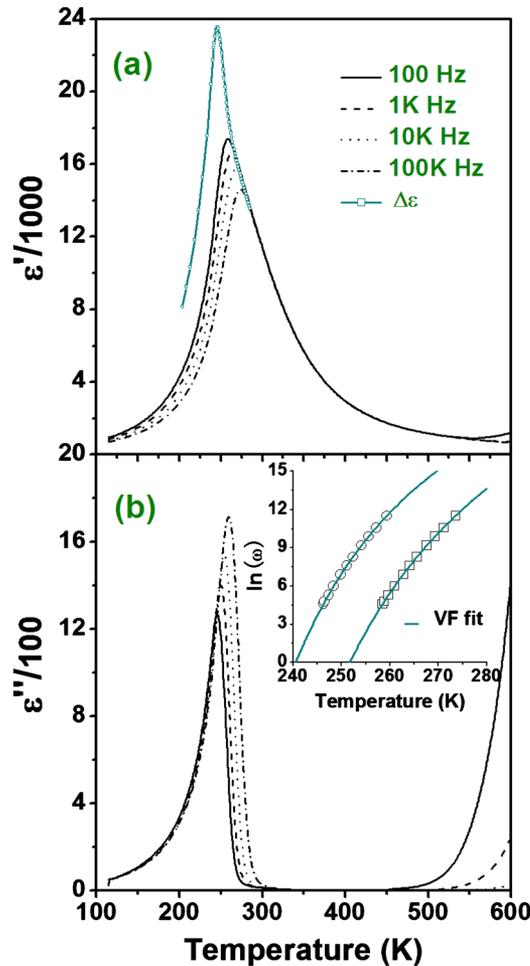


FIG. 1. (Color online) Temperature dependence of the (a) real and (b) imaginary parts of the relative dielectric permittivity at 100 Hz, 1 kHz, 10 kHz, and 100 kHz. $\Delta\epsilon$ in (a) was obtained by fitting Eqs. (3) and (4). The inset in (b) shows the plots of $\ln(\omega)$ vs T_m and T'_m . The solid curves in the inset were fitted according to the VF relation.

Knowing that the VF relation is also valid for the characteristic relaxation time τ_c (mean or maximum cutoff),^{8,14}

$$\tau_c = \tau_0 \exp\left[\frac{E_a}{k_B(T - T_f)}\right], \quad (2)$$

we use a Cole–Cole approach to study the relaxation process in PMN. The temperature dependence of τ_c can be obtained by fitting the Cole–Cole model as follows:¹⁵

$$\epsilon'(\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{2} \left[1 - \frac{\sinh(\beta\psi)}{\cosh(\beta\psi) + \cos(\beta\pi/2)} \right], \quad (3)$$

TABLE I. Fitting results according to the VF relation.

	ω_0 (Hz)	τ_0 (s)	E_a (eV)	T_f (K)
$T_m - \omega$ [Eq. (1)]	4.53×10^{15}	2.21×10^{-16}	0.145	205.11
$T'_m - \omega$ [Eq. (1)]	3.33×10^{14}	3.00×10^{-15}	0.103	204.73
τ_c [Eq. (2)]	5.92×10^9	1.69×10^{-10}	0.018	230.53

$$\epsilon''(\omega) = \left(\frac{\Delta\epsilon}{2} \right) \frac{\sin(\beta\pi/2)}{\cosh(\beta\psi) + \cos(\beta\pi/2)}, \quad (4)$$

where $\psi = \ln(\omega\tau_c)$, $\Delta\epsilon = \epsilon_s - \epsilon_\infty$, ϵ_s the static permittivity, ϵ_∞ the permittivity at high frequency, and $\beta = 1 - \alpha$, where α reflecting the distribution width of the relaxation time. For PMN, the frequency dependence of ϵ' and ϵ'' can be described by using Eqs. (3) and (4), respectively. Figure 2 shows the experimental data (diamond points) and the corresponding fitting results (solid lines) at various temperatures, where a good agreement between experimental data and theoretical values were obtained.

Figure 3 shows the temperature dependence of the parameter α and τ_c . There exist two characteristic temperatures, T_1 (~ 275 K) and T_f (~ 230 K), for α and τ_c . Above T_1 , α decreases with decreasing temperatures. Below T_1 , the trend is reversed and α tends to an almost temperature independent constant value for temperatures below T_f . For τ_c , it displays a strong dispersion at a temperature above T_1 and becomes temperature independent at below T_f , with a constant value around 4×10^{-4} s.

Further analysis reveals that, between T_1 and the maximum temperature $T_{m,\Delta\epsilon}$ [~ 244 K, the temperature for maximum $\Delta\epsilon$, as shown in Fig. 1(a)], τ_c can be well-described by Eq. (2). The obtained parameters $\omega_0 = 5.92 \times 10^9$, $E_a = 0.018$ eV, and $T_f = 230.5$ K (see Table I) are physically reasonable. The ω_0 and E_a derived from $\tau_c(T)$ are much lower than that obtained from the $T_m - \omega$ and $T'_m - \omega$ relations. Meanwhile, the freezing temperature T_f derived from $\tau_c(T)$ does not coincide with the one obtained from the fitting of $T_m - \omega$ and $T'_m - \omega$ relations. This again suggests that the $T_m - \omega$ and $T'_m - \omega$ relations are not suitable for the determination of T_f , at least for Pb-based RFEs.

It is worth noting that Colla *et al.*¹⁶ also reported that the most probable relaxation frequency tends to a constant value for temperatures below 230 K, which was consistent with the T_f derive from $\tau_c(T)$ in our case. Vakhruhev *et al.*¹⁷ investigated the temperature dependence of the inverse correlation radius R_0 of the ferroelectric fluctuation in PMN by neutron scattering and found that R_0 also became temperature independent at $T < 230$ K.¹⁷ This led us to conclude that the $T_f = 230.5$ K is the freezing temperature for PMN samples. It seems dangerous to use the probe frequency as the characteristic frequency for relaxation at the peak temperature T_m [Eq. (1)] to derive the freezing temperature. Recent studies¹⁸ on PMN reveal that the polar nanoregions (PNRs) show a suddenly increase from 10 to 20 nm at around 225 K, which is close to the T_f in our study. Raman scattering results also confirm a soft mode-driven ferroelectric phase transition at around 225 K.¹⁸ These results clearly show that PMN undergoes a ferroelectric phase transition at T_f , below which PMN is in a nanodomain ground state, not the dipole glass state. The VF freezing in PMN implies that the relaxor behavior is a collective phenomenon where short range interactions between PNRs control the kinetics of the polarization fluctuations and the freezing process.⁵ Above T_1 , the short range interactions can be neglected and the characteristic relaxation time τ_c would not follow the VF relationship. With decreasing temperatures, the kinetics of the polarization fluctuations may be controlled by the change in size of PNRs, and not by the interactions between them. Therefore the deviation of τ_c from VF relationship starting at $T_{m,\Delta\epsilon}$ may be attributed to

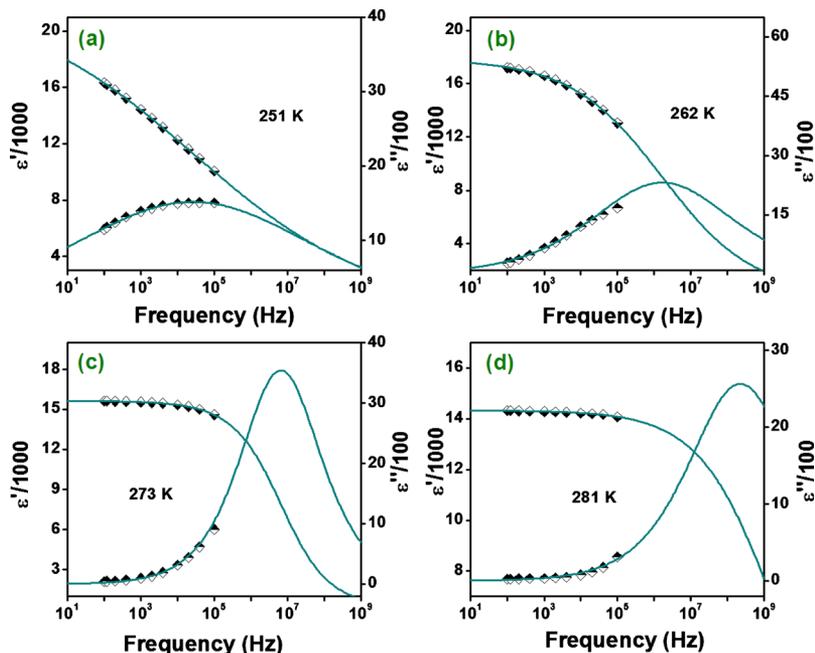


FIG. 2. (Color online) Frequency dependence of the dielectric permittivity (real and imaginary parts) at various temperatures: (a) 251, (b) 262, (c) 273, and (d) 281 K. Diamond dots were the experimental data and the solid curves were simulated according to Eqs. (3) and (4).

the progressive coarsening of PNRs, which act as precursors of ferroelectric domains. An almost constant value of τ_c below the freezing temperature implies that the nanodomains in PMN would not evolve further into much larger ones.

To summarize, the dielectric relaxation of PMN ceramics was investigated. A critical temperature T_1 was con-

firmed, below which a VF freezing process started. Below a “freezing” temperature around 230 K, the relaxation time became temperature independent, which implied that the PNRs cannot grow in size any more.

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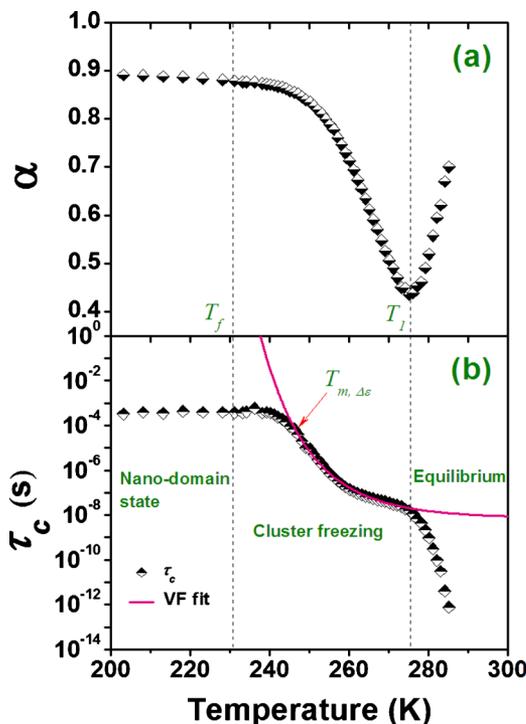


FIG. 3. (Color online) Temperature dependence of (a) α and (b) τ_c , which were obtained from the fitting of data shown in Fig. 2. The solid curve in (b) was fitted according to the VF relation.

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