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<th>Effects of volume evolution of static and dynamic polar nanoregions on the dielectric behavior of relaxors</th>
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The physical nature underlying colossal piezoelectric response and broad temperature (T) dielectric dispersion of relaxor ferroelectrics (relaxors) still remains debatable in view of a few controversies between the existing experimental and theoretical results. In contrast to wide acceptability of Curie-Weiss (C-W) relation for the sharp phase transition in normal ferroelectrics, apparent deviations from C-W law have been frequently observed in prototypical relaxors.\(^3\) Pier et al.\(^3\) found that the deviation that peaked near the Curie-temperature (T\(_c\)) was even more significant when a higher electric field (E) was imposed. More and more experiments suggested that unusual relaxor behaviors were closely related to the coexistence and competition between the long-range order and polar nanoregions (PNRs) that appeared below the Burns temperature (T\(_b\)). To-date, it is believed that the typical PNRs in relaxors are mutually coupled via interactions with polarizable matrix. In addition to the influence of local PNR polarization,\(^1\) the correlation strength of a “connected” network\(^4\) composed of high-density PNRs was easily modulated by random fields stemming from structural disorder in multivalent relaxors.\(^5\) Recently, Xu et al.\(^5\) have revealed that T- and E-driven redistribution of PNR polarizations played a key role in governing the vagarious dielectric responses of relaxors. Although PNR dynamics in relaxors have been widely studied, some of the observations clearly contradicted the related theories. First, adoption of different nanostructure was unavoidable to interpret the recently observed E-independent source of diffuse scattering intensity.\(^6\) Second, the latest neutron spin-echo (NSE) measurements\(^6\) exhibited distinct T-dependence of static and dynamic scattering intensity in Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\) (PMN) crystals. Furthermore, the following essential problems encountered for clarification of typical relaxor behaviors have yet to be resolved: (i) The methodology for distinguishing different dielectric features of static and dynamic evolution of PNRs and, hence, correlating them with bulk dielectric dispersion and (ii) explanation of the three length scales,\(^7\) i.e., 5-25 nm sized PNRs, chemical ordering region (COR) of <5 nm, and ferroelastic domain walls (DWs) of \(~100\) nm in length, which are required for a PMN crystal to stabilize inhomogeneities?

In this letter, these essential issues are addressed to better understand the dielectric behaviors and related properties of relaxors. The total volume of a PNR, V\(_{\text{total}}\), can be divided into two components, i.e., a T-dependent static volume (V\(_{\text{sta}}\)) and a dynamic volume (V\(_{\text{dyn}}\)) initiated by adequate correlation among PNRs. V\(_{\text{dyn}}\) is sensitive to T and E in terms of modulation for the interaction strength.

PNRs in PMN have rhombohedral symmetry and [111]-type polarization (with eight easy directions). In general, time (t)-dependent probability (p\(_n\)) for PNRs to occupy the \(n\)th ground state is governed by Pauli’s master equation:\(^8\)\(^9\)

\[
\tau \frac{d}{dt} p_n(t) = \sum_{m \neq n} \left[ p_m(t) - e^{U_m - U_n} p_n(t) \right].
\]

where integer \(n, m \in [1, 8]\) and \(\tau\) is relaxation time. To further simplify Eq. (1), we restrict it to a two-state system. A generic activation parameter \(U_\alpha\) that denotes the energy difference between two ground states is established by combining Néel’s proposal\(^8\) and our recent findings,\(^8\) i.e., \(U_\alpha = QV/kT\), where \(k\) is Boltzmann’s constant and \(V\) is either V\(_{\text{sta}}\) or V\(_{\text{dyn}}\). \(Q\) is the energy density given by \(2E|P|^m\), in which \(|P|^m\) denotes the PNR polarization maxima. Based on the proposed solution\(^5\) of Eq. (1), we obtain the bulk PMN polarization magnitude

\[
\langle P \rangle = |P|^m \left( \frac{1 - e^{-U_a}}{1 + e^{-U_a}} \right) (1 - e^{-t/\tau}).
\]

In order to distinguish the dielectric contributions from V\(_{\text{sta}}\) and V\(_{\text{dyn}}\), it is assumed that V\(_{\text{sta}}\) has a T-independent polarization maxima, whereas, that of V\(_{\text{dyn}}\) is the sum of a constant \(|P|^m\) and \(\varepsilon(T) \times E\), where \(\varepsilon(T)\) is T-dependent dielectric permittivity. In the asymptotic limit, substituting Eq. (2) into \(\varepsilon(T) = \partial \langle P \rangle / \partial E\) yields the contribution of V\(_{\text{sta}}\) and V\(_{\text{dyn}}\) to \(\varepsilon\), i.e., \(\varepsilon_{\text{sta}}\) and \(\varepsilon_{\text{dyn}}\)

\[
\varepsilon_{\text{sta}} = \frac{|P|^m}{E} \left( \frac{2U_\alpha}{2 + e^{U_a} + e^{-U_a}} \right),
\]

\[
\varepsilon_{\text{dyn}} = \frac{|P|^m}{E} \left( \frac{U_\alpha}{1 - U_a + e^{-U_a}} \right).
\]
The dissimilarity in $U_d$-dependence of $\epsilon_{sta}$ and $\epsilon_{dyn}$ shown in Fig. 1(a), represents the distinct dielectric features of $V_{sta}$ and $V_{dyn}$. $\epsilon_{sta}$ disperses over a wide $U_d$ range, whereas $\epsilon_{dyn}$ only shows a substantial change near $U_d = 1.278$, at which it diverges in a manner similar to normal ferroelectrics. Furthermore, since the inverse Curie constant ($1/C$) reflects $\partial\epsilon^{-1}/\partial T$, Eq. (3) indicates that the $QV/k$ ratio in relaxors is comparable with the $C$ value. For PMN crystal $Q \sim 2.3 \times 10^{-3}$ eV/(nm)$^3$ (Ref. 4) and $C \sim 2.05 \times 10^5$ K (Ref. 7), Eq. (3) predicts a mean volume of $\sim 10^3$ nm$^3$, which tallies with the PNR size of 5-25 nm observed by SEM.

In view of a latest finding 7 that the C-W relation validates even if $T$ is near $T_C$, it is postulated that Eq. (3) for local PNRs requires the C-W law to be satisfied. The inset of Fig. 1(a) shows that the $1/\epsilon_{sta}$ given by Eq. (3) is in excellent agreement with the C-W law over a broad $T$-range, while the minor deviation between them due to the absence of $\epsilon_{sta}$ divergence can be eliminated by an appropriate $1/\epsilon_{dyn}$.

The C-W behavior of $\epsilon_{sta}$ actually arises from the evolution of $V_{total}$ and $V_{dyn}$ pursuant to the thick and thin curve in Fig. 1(b), respectively. Fig. 1(b) exhibits an outstanding agreement of our predicted $V_{total}$ with the calculated volume fraction of PNRs. 10 Equation (3) underlines the existence of a peak in both the $V_{total}$ and $V_{dyn}$ curve. This suggests that the PNR correlation has both attractive and repulsive feature, and it finally becomes negligible compared with thermal fluctuations. Accordingly, the histogram of PNR evolution is divided into three regions, as depicted in Figs. 1(b) and 1(c). In region I, elliptical PNRs composed of spherical $V_{sta}$ and heterogeneous $V_{dyn}$ increase gradually while cooling till $T$ reduces even if Fig. 1(a), represents the distinct dielectric features of $V_{sta}$ (Ref. 7), Eq. (3) predicts a mean volume of fraction of PNRs. 10 Equation (3) underlines the existence of a peak in both the $V_{total}$ and $V_{dyn}$ curve. This suggests that tallies with the PNR size of 5-25 nm observed by SEM. 7

Another explanation is that the interfacial energies and resultant stresses drive the CORs and $V_{sta}$ self-assembly 11 and stabilize long-range order at low temperatures. This may help to explain the observation 12 that PNR/COR was present over a much wider $T$ range in a PMN crystal than in a Sr$_{1-x}$Ba$_x$Nb$_2$O$_6$ where the stress factor was insignificant. A smaller $V_{sta}$ near $T_d$ should be ineffective for self-stress-relaxation and, thus, formation of a sufficiently large $V_{dyn}$, e.g., $V_{dy}n/V_{sta} \approx 1$ (Ref. 6) appears inevitable for maintaining the overall cubic symmetry via elimination of stresses. This dynamics is able to redistribute bulk polarization from an initial direction close to [111] easy direction. 13 Similar to normal ferroelectrics where ferroelastic DWs are involved in minimization of mechanical energy, ferroelastic DWs such as 90° DWs in Fig. 1(c) could also be stabilized to relax the stresses of PNRs, which may be used to explain the measured perpendicularity 13 of PNR polarization to that of the matrix. Besides, once the dimension of remaining medium is less than a critical size, 11, 14 both high-aspect-ratio DWs and irregular stress field will appear and persist at low $T$s.

For explaining the unconventional NSE results, 6 Fig. 2(a) is plotted, which shows that the $V_{sta}$ curve tallies with the static intensity (SI) when $T$ is decreased from 500 K to 200 K. Besides, before reaching a sudden freezing at 190 K, the $V_{sta}$ curve could be divided into a nearly straight and a nonlinear portion, which agrees with the calculated curve 1 of local order parameter $q$, as shown in the inset of Fig. 2(a). As
for the unusual dynamic intensity (DI), we would attribute them to two causes: $\partial V_{\text{sta}}/\partial (T)$ and variation of $V_{\text{dyn}}$. Intuitively, a larger $\partial V_{\text{sta}}/\partial (T)$ is bound to augment the measured DI. Hence, $\partial V_{\text{sta}}/\partial (T)$ is plotted using the $V_{\text{sta}}$ data in Fig. 2(a), as shown in Fig. 2(b), in which another two fittings are also displayed. In a mean field case,$^4$ percolation theory predicts the PNR mean volume as

$$V = V_0/(1 - T/T_0). \tag{4}$$

The dashed-curve in Fig. 2(b) is a $dV/d(T)$ fitting based on Eq. (4) with $V_0 \sim 0.1075$ and $T_0 = 243.5$ K, which is close to 224 K given in Ref. 15. Although Pirc and Blinc$^6$ assumed that Eq. (4) was valid as long as $T > T_0$, Fig. 2(b) shows that Eq. (4) is only applicable for $T > 315$ K. However, a Lorentzian fitting based on

$$\partial V_{\text{sta}}/\partial (T) = \frac{v_m T}{\pi [(T - T_{\text{sta}})^2 + T^2]} \tag{5}$$

displays an excellent agreement with $\partial V_{\text{sta}}/\partial (T)$ data down to 250 K. $v_m = 0.369$ and $T = 59.12$ K and $T_{\text{sta}}$ indicate that the rate maxima is at 290 K, which is quite close to the calculated$^1$ 300 K [refer to Fig. 1(a)]. In general, the relaxor dynamic response is supposed to increase with the growth of $V_{\text{dyn}}$. Thus, the $V_{\text{dyn}}$ predicated is also plotted in Fig. 2(c), in which another two fittings are also displayed. In a mean field case,$^4$ percolation theory predicts the PNR mean volume as

$$V = V_0/(1 - T/T_0). \tag{4}$$

The symmetric form of Eq. (7) implies that the observed deviation of $1/\epsilon_{\text{PNR}}$ from the C-W law is solely originated from the thermal change of $\alpha$. Finally, based on Maxwell’s equation, the observed deviations of bulk permittivity from the C-W law are attributed to thermal effects on and polarization rotations that occur from $T_d$ to $T_p$. Our findings are in excellent agreement with the existing theoretical and experimental results.

![FIG. 3. (Color online) (a) Thermal-evolution of $z$; $z_\text{II}$ is determined from the best fitting of Eq. (6) for $z_{\text{Exp}}$ (Ref. 6). (b) Plots of $\partial (1/z_\text{II})/\partial T$ and $\partial (1/z_{\text{Exp}})/\partial T$; the dashed line in (a) and solid curve in (b) is a visual guide.](image-url)