Relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$: A Ferroelectric with Multiple Inhomogeneities

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Despite intensive studies on $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) relaxor, understanding the exact nature of its giant dielectric response and of its physical ground state is a fundamental issue that has remained unresolved for decades. Here, we report a comprehensive study of PMN relaxor crystal, and show that (i) its anomalous dielectric behavior in a broad temperature range results from the reorientation of polarization in the crystal, and (ii) the PMN relaxor is essentially a nanosized ferroelectric material with multiscale inhomogeneities of domain structure in addition to the well-known inhomogeneities of chemical composition and local symmetry. Such inhomogeneities are believed to play a crucial role in producing the huge and enigmatic physical effects in relaxor system, and may be used to design other new systems with giant effects such as a relaxor system.

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Intrinsic inhomogeneities play a crucial role in inducing colossal effects in complex oxides. These effects are known as giant dielectric and electromechanical responses in relaxors [1] or as colossal magnetoresistance in manganites [2]. Such complex physical phenomena open new avenues for various technical applications and challenge our understanding of solid-state physics. In relaxors such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [3], both chemical and structural inhomogeneities coexist due to the chemical and valence mixing in the same site of the structure. The effort to elucidate the role played by these inhomogeneities in relaxors is a prime example of such a challenge.

One of the most intriguing properties exhibited by a relaxor is the huge dielectric response with strong frequency dispersion within a large temperature range as shown in Fig. 1 for a prototypical relaxor PMN crystal. However, in contrast with a normal ferroelectric such as $BaTiO_3$, the PMN crystal shows no sharp phase transition in the crystal, despite continuous increases in the dielectric constant around room temperature. Such anomalous dielectric behavior has puzzled solid-state physicists over the past 50 years [4–8]. Despite intensive investigations, a precise interpretation of the behavior has not been established. It was initially believed that this is a diffuse phase transition due to the distribution of the phase transition temperature T_c in crystals. However, it is now recognized that such a broad peak is not due to the distribution of the T_c, but is closely related to the response of polar nanoregions (PNR) that begin forming around the so-called Burns temperature T_{Burns} (600 K for PMN) [9]. After Burns's proposal, many measurements including neutron diffractions [10–13] and NMR [14] have been performed, and the occurrence of PNR in relaxor has been confirmed. However, in a length scale of x-ray diffraction, the PMN relaxor seems to remain an average centrosymmetric cubic structure [15] in which ferroelectricity should be prohibited. Apparently, this structural inhomogeneity is closely related to the coexistence of two B-site cations with different chemical-bonding characteristics in the ABO_3 structure, which also gives rise to nanoscale chemical ordering regions (COR) in the crystal [16–18]. Such CORs carry negative charges and are therefore a source of quenched

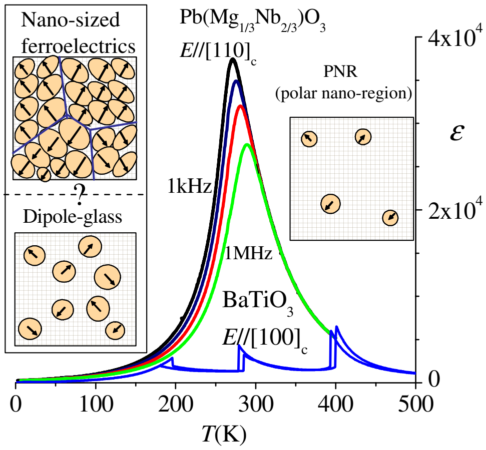

FIG. 1 (color online). Two different pictures of the evolution of PNR in the PMN crystal. The dipole-glass scenario suggests a freezing of PNRs at $T_f \sim 220$ K, below which a glass state occurs [6]. In contrast, the system may have ferroelectric ordering at the ground state, but the transition is smeared due to the strong random field [5]. For comparison, the dielectric behavior of $BaTiO_3$ crystal are also given.

random electric fields. These complex inhomogeneities have complicated our exact understanding of their anomalous behavior, and there remain two long-standing questions in PMN relaxor: (i) what is the origin of the giant dielectric constant over a broad temperature range [4,7]; and (ii) is the relaxor state (a) a ferroelectric state broken up into nanodomains under the constraint of quenched random electric fields [5] or (b) a dipolar-glass state with randomly interacting polar nanoregions in the presence of random fields [6] (Fig. 1).

Obviously, we can discriminate the ferroelectric state from the dipolar-glass state if we are able to probe all histories of the evolution of electric polarization in the crystal. If the PMN relaxor is ferroelectric, then we may see domain-switching behavior and phase transition as with the normal ferroelectrics. In contrast, there should be no structural phase transition in the dipolar glass, in which only randomly interacting PNRs will be frozen and, consequently, the polarization will remain unchanged below freezing temperature T_f. In order to give an answer to this question, we therefore performed measurements on probing all histories of polarization evolution of the PMN crystal at various temperatures by a Sawyer-Tower circuit. In the measurements, E was applied along the $[110]_c$ direction. Before each polarization measurement at a temperature, the crystal was heated to 360 K to recover a history-independent state, and was then cooled to the desired temperature for measurement. We generated 5 circles of sine wave (100 Hz in frequency) to measure its polarization evolution under the electric field. In fact, we observed all essential features of normal ferroelectric behavior in the PMN relaxor, but not that expected from dipole-glass freezing. Figure 2(a) summarizes some typical results on the evolution of electric displacement (D) and dielectric response $\partial D/\partial E_{T,E}$. It can be seen that the PMN crystal shows normal polarization switching behavior at low temperature (see D–E loop at 190 K) like those observed in $BaTiO_3$ crystals [19,20]. We may divide the polarization evolution into three categories. (i) For $T < \sim 220$ K, the static polarization (here, the static state is used in the experimental time scale of $\sim\tau = 10$ ms to get one cycle of the D–E loop.) is identical to the saturation polarization even after removing the electric field (E), and the ferroelectric state is firmly established. (ii) For ~ 220 K $< T < \sim 300$ K, there is a large static polarization at $E = 0$, but its value is significantly lower than the saturation polarization at high field, indicating that there is a strong relaxation of polarization in the crystal. (iii) For $T > \sim 300$ K, the static polarization nearly vanishes after removing the electric field, but nonlinear polarization is detectable at high electric field.

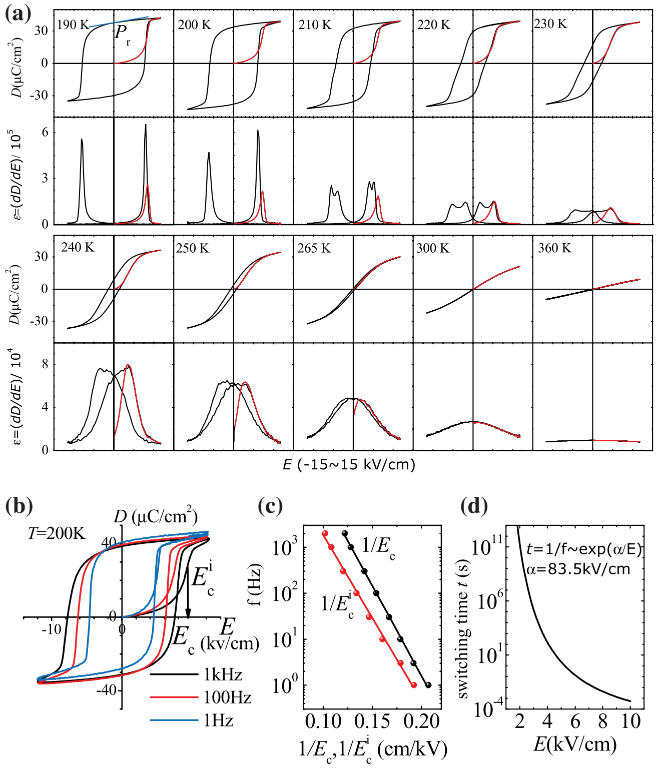

FIG. 2 (color). Polarization evolution in PMN relaxor. (a) All histories of the polarization state and the derived dielectric constant $(\partial D/\partial E_{E,T})$ at various temperatures. A red color indicates the initial state. (b) The $D - E$ loop for several frequencies at 200 K. (c) shows that the coercive field (determined from the peak of the displacement current, E_c^i for the first-quarter loop and E_c for the following cycles) for the polarization switching exactly follows the Merz's switching law [19,20]. (d) An estimation of the time required to activate the domain growth for various electric fields at $T = 200$ K.

To understand the broad dielectric peak in PMN, we mapped out the $\epsilon(T, E) = \partial D/\partial E_{T,E}$ diagram (Fig. 3) of the initial state using the first quarter of the initial D–E loop. Immediately, we see a broad peak of the dielectric constant at various electric fields in this diagram. Such behavior shares the same feature of dielectric response observed with the LCR technique. The agreement between $\epsilon(T, E = 0)$ and those obtained by the LCR technique is very good. Subsequently, we concluded that the broad peak observed in PMN resulted from reorientation of the polarization in the crystal, as clearly shown in the inset of Fig. 3. This experimental finding thus gives us a clear physical basis for understanding the broad dielectric peak in PMN, which has puzzled many researchers for a half century. In the $\epsilon(T, E)$ diagram, we also see that the peak position shifts to lower temperature with increases in the electric field. This result suggests that a higher activation field is required to reorient the polarization at a lower temperature.

It has long been thought that an electric field triggers a phase transition of the glass state into the ferroelectric state at low temperature when $E > E_{\text{critical}}$ ($E_{\text{critical}} = 1.7$ kV/cm for $T = 200$ K) [6]. However, this phase transition has not occurred in Fig. 2(b). In the initial state, we merely see a continuous increase in polarization with electric field but not a sudden change in the polarization at $E = E_{\text{critical}}$ as expected from an electric-field-induced

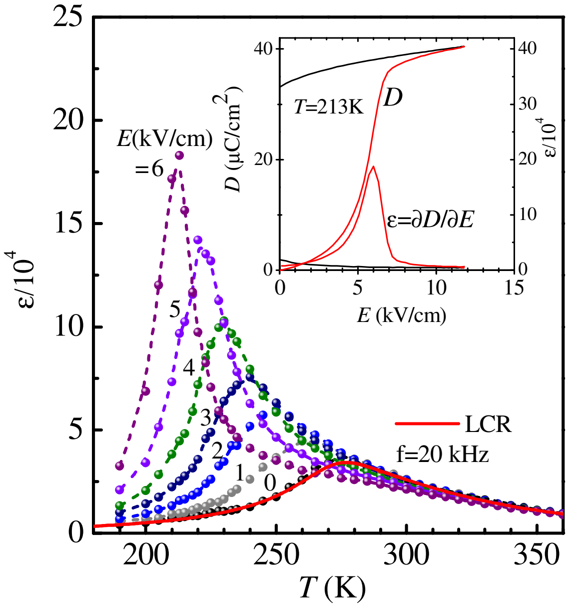

FIG. 3 (color online). $\epsilon(T, E)$ diagram of the PMN relaxor for the initial state. For comparison, the results obtained by the LCR meter with a weak ac field of 0.01 kv/cm are also given. The used frequency just corresponds to the sampling rate of $t_s = 0.05$ ms in the polarization measurements. The inset shows the polarization and the derived dielectric constant at 213 K for the initial state.

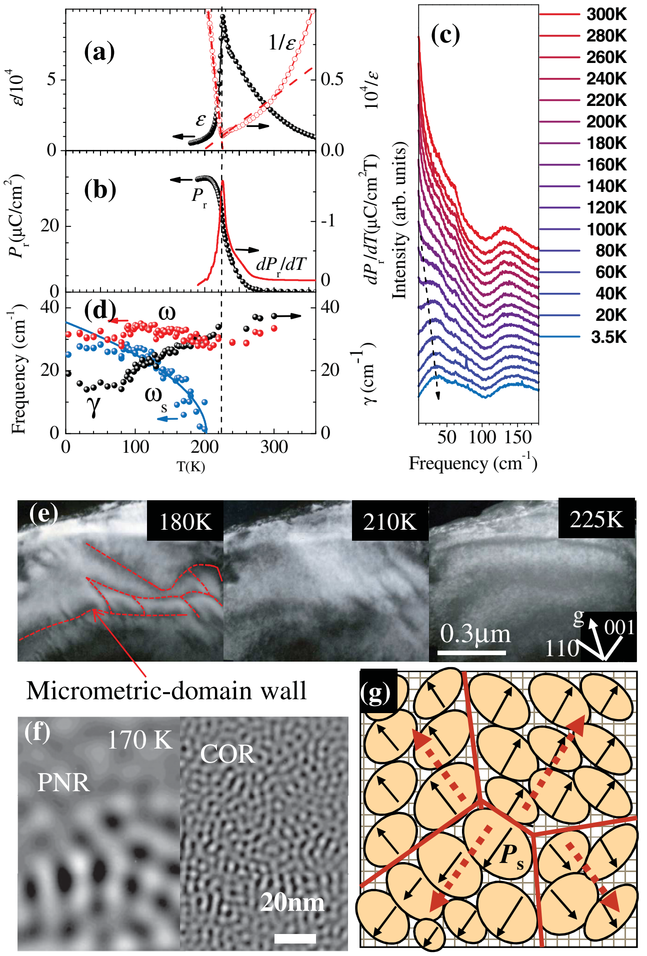

FIG. 4 (color). Soft mode-driven phase transition in PMN ferroelectrics. (a) $\epsilon = \partial D/\partial E_{E=0}$ vs T. (b) $\partial P_r/\partial T$ vs T. (c) Raman scatterings at zero field. (d) The soft mode ($\omega_s = (\omega^2 - \gamma^2)^{1/2}$, where ω, γ represent the observed frequency and damping factor, respectively.) softens toward the phase transition at T_c. (e) Micrometric deformation of lattice along the $[111]_c$ direction (see nervelike curves. Some domain walls are indicated by the red curves for 180 K.) was observed for $T < T_c$ from the 111-reflection dark field image of TEM. (f) shows the structures of PNR and COR in the same region within a micrometric domain at 170 K, which was obtained from an inverse Fourier transform of the TEM image. (g) A schematic structure of PMN relaxor at low temperature [24,25].

phase transition. This polarization evolution is similar to the case of the domain switching observed in BaTiO$_3$ crystal [19,20]. The coercive field E_c follows precisely the Merz's switching law: $\tau \propto 1/f \propto \exp(\alpha/E)$, where τ is switching time, f is frequency, and α is the activation field required for generation and growth of antiparallel nuclei [19,20] [Figs. 2(b) and 2(c)]. A remarkable feature of PMN crystal is that its activation field is nearly 10 times larger than that of BaTiO$_3$ crystal. Such a high activation field due to the existence of a large quenched random field leads to great difficulties in switching the domain at low temperature. It can be seen that an impractical amount of time is necessary to form a large domain at low temperature at weak field [see Fig. 2(d)].

Indeed, we detected a displacive-type phase transition in PMN crystal around $T_c \sim 225$ K. We summarize the results in Fig. 4. This phase transition is clearly visible after the polarization domain is aligned by the electric field. The dielectric constant at zero field [Fig. 4(a)], which was derived from the D–E loop after the first quarter, exactly follows the Curie-Weise law around T_c. Because of the existence of local polarization in the temperature range where large dielectric relaxation occurs, the remnant polarization P_r does not disappear for $T > T_c$, but the polarization current ($\partial P_r/\partial T$) exhibits a sharp peak at $T = T_c$, which also characterizes the transition nature of the polarization ordering in the system. The value of the Curie-constant ($C \sim 2.05 \times 10^5$ K) for PMN crystal is characteristic of that of the displacive-type phase transition, suggesting a soft mode-driven phase transition in the system, which should be detectable by the Raman scattering technique. We then carried out zero-field Raman scattering measurements to probe such local symmetry breaking in structure [21]. Using a special polarizing configuration along the $[110]_c$ direction of the perovskite structure, we greatly suppressed the extremely strong first-order Raman scattering from the F_{2g} mode of $Fm\bar{3}m$ symmetry of COR [22], and successfully observed the lowest soft mode in PMN [Figs. 4(c) and 4(d)]. Such a soft mode ($\omega_s = (\omega^2 - \gamma^2)^{1/2} \approx 26$ cm^{-1} $= 3.3$ meV) is underdamped at low temperature and is therefore easily detected by the

Raman scattering. However, it becomes overdamped near T_c, creating a relatively large error when determining its frequency. Despite such mode overdamping, we see a softening of such a mode in a conventional way [indicated by the blue solid curve in Fig. 4(d)] toward the phase transition. This result is in good agreement with the Curie-Weise law of the dielectric constant in Fig. 4(a). Our new experimental findings thus robustly establish a physical picture of the ferroelectric phase transition in the prototypical relaxor PMN.

Surprisingly, the cooperative phenomenon is exhibited not only in the local symmetry breaking of the lattice, but also in the formation of a micrometric domain consisting of PNRs. Such a cooperative phenomenon was discovered in our temperature-variable TEM measurements using a JEOL JEM200CX equipped with an EM-SCTH10N low-temperature holder (for 300 K–120 K) and an EM-SHH4 high-temperature holder (for temperatures higher than room temperature). This can be clearly seen in the evolution of a streaky structure after the phase transition in the images given in Fig. 4(e). The formation of these micrometric domains is essentially due to deformation of the lattice along the $[111]_c$ direction, which corresponds to the direction of Pb shifting to produce a spontaneous polarization in PNR [11,14]. The domain wall may extend to several hundred nanometers. Surprisingly, such a microdomain consists of an inhomogeneous substructure, in which elliptically shaped PNRs $15 \sim 25$ nm in size coexist with spherically shaped CORs less than 5 nm in size [see Fig. 4(f)]. We can reasonably say that such a micrometric deformation is due to the collective alignment of all PNRs within a micrometric domain [see a schematic image in Fig. 4(g)] because CORs should not be responsible for the ferroelectricity in PMN. Basically, CORs remain stable within our observed temperature range of 130–675 K, which does not overlap with that of the PNRs, but tend to block the growth of neighbor PNRs.

In addition, TEM measurements also show sudden changes in PNRs around T_c: (i) For $T < T_c$, PNRs show anisotropy and have an elliptical shape rather than a spherical shape at higher temperatures; (ii) the observed strain contrast from the PNRs increase suddenly around T_c, indicating a sudden increase of local polarization; (iii) the PNR's size increase suddenly from 10 to 20 nm around $T \sim T_c$. (iv) A number of PNR show a peak around $T \sim T_c$. Apparently, new polarization regions occur and connect the existing smaller PNRs to form larger PNRs, leading to the increase in size and decrease in the number of PNRs after the phase transition. Therefore, either dielectric macroscopic measurements or Raman/TEM microscopic measurements clearly show a ferroelectric phase transition at T_c in PMN. The local polarization occurring above T_c may be understood as precursor phenomenon in ferroelectric phase transitions, which lasts for a very large temperature range due to the strong quenched random field when comparing with a conventional ferroelectric such as $BaTiO_3$ [23].

In summary, we have obtained clear answers to two long-standing questions regarding the PMN relaxor: (i) its anomalous dielectric relaxation in a broad temperature range results from the reorientation of polarization in the crystal, and (ii) the PMN relaxor is essentially a nanosized ferroelectric material with a soft mode-driven phase transition and has multiscale inhomogeneities. Such multiscale inhomogeneities are believed to play a crucial role in producing the huge and enigmatic physical effects in this system. We also hope that our findings will stimulate novel theoretical or experimental investigations in this and related systems with giant effects.

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