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Cite as: Appl. Phys. Lett. **87**, 012904 (2005); <https://doi.org/10.1063/1.1990253>

Submitted: 03 February 2005 . Accepted: 26 May 2005 . Published Online: 30 June 2005

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Dielectric anomalies of the relaxor-based $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.1\text{PbTiO}_3$ single crystals

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(Received 3 February 2005; accepted 26 May 2005; published online 30 June 2005)

The temperature, frequency, and orientation dependence of complex electrical permittivity in $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.1\text{PbTiO}_3$ (0.9PMN-0.1PT) unpoled single crystals have been investigated in detail. The spontaneous ferroelectric-to-relaxor (FE-R) phase transition was observed in 0.9PMN-0.1PT crystals at about 280 K. Interestingly, the Vogel-Fulcher-type anomaly of the dielectric constant has been obtained, with the fitted temperature T_f being very close to this FE-R phase transition temperature. A small frequency dependence of electric permittivity magnitude appears at and below 280 K. The changes of the polar nanoregion subsystem and the peculiarities of the domain structure play an important role in the dielectric anomalies and the appearance of the FE-R crossover region. © 2005 American Institute of Physics. [DOI: 10.1063/1.1990253]

The perplexing nature of relaxor ferroelectrics (relaxors) has triggered much interest and intensive research on the fundamentals of their structures and physical properties in various areas. In these strange “relaxors,” especially for $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN), no macroscopic symmetry breakdown can be observed at all. It would undergo an ergodic-to-nonergodic transition, which shows a Vogel-Fulcher freezing process of nanodomains in a simulation work using a spin-glass model.¹⁻³ In a cooling process, an external electric field could increase the correlation length of these polar domains and ultimately induce a relaxor-to-ferroelectric (R-FE) phase transition. The neutron inelastic diffraction has shown that the structure change also appears in the development of long-range ferroelectric order from the disorder relaxor system.⁴⁻⁷

In the relaxor family, lead magnesium niobate (PMN) is such a typical example that it has been intensively investigated using various physical models with different nanostructure features.^{8,9} The prototypical PMN remains in a relaxor state down to very a low temperature of even 5 K, and no spontaneous ferroelectric phase transition is observed.⁹ However, PbTiO_3 (PT) of more than 0.05 mole % [i.e., $x > 0.05$ in $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$, that is, $(1-x)\text{PMN-}x\text{PT}$, pseudobinary system] could induce a ferroelectric phase.¹⁰ Indeed, the PT with increasing content in the $(1-x)\text{PMN-}x\text{PT}$ solid solution modified the relaxor behavior and induced the inconspicuous spontaneous R-FE phase transition, such as for $x=0.1$.^{11,12} Recent mechanical properties, including internal friction Q^{-1} peak associated with Young's modulus Y softening related to the R-FE transition, were assumed to be the ferroelectric phase transition from the paraelectric matrix in the $(1-x)\text{PMN-}x\text{PT}$ (x

$= 0, 3, 5, 7, 9, 11$) ceramics.¹³ However, none of previous dielectric spectroscopy research could disclose the spontaneous R-FE phase transition in the $(1-x)\text{PMN-}x\text{PT}$ ($0 \leq x \leq 13$) crystals.¹⁴ In this letter, however, we will present our finding that there indeed occurs a spontaneous FE-R phase transition in the 0.9PMN-0.1PT unpoled single crystal.

The 0.9PMN-0.1PT single crystals have been grown by a modified Bridgman technique.¹⁵ From as-grown single crystal, several wafers with different orientations ($\langle 111 \rangle$, $\langle 011 \rangle$, and $\langle 001 \rangle$) were prepared with dimensions of $8 \times 8 \times 0.7 \text{ mm}^3$. The wafers were coated with silver electrode. Their complex electrical permittivity at temperatures from -50 to $120 \text{ }^\circ\text{C}$ (controlled by VT 7004 chamber of Vötsch, Industrietechnik) was measured with a HP4192A impedance analyzer at frequencies of 0.05 to 1.0 kHz. The (P - E) hysteresis loops were tested using a Sawyer-Tower circuit at 10 Hz and at $20 \text{ }^\circ\text{C}$.

Figure 1 shows the temperature and frequency dependence of dielectric constant and dielectric loss in the $\langle 001 \rangle$ -, $\langle 110 \rangle$ -, and $\langle 111 \rangle$ -oriented 0.9PMN-0.1PT crystals at a heating rate of 1 K/min. The relative permittivity of $\langle 001 \rangle$ and $\langle 110 \rangle$ samples exhibit obvious frequency dispersion and show a maximum at a T_m of about 310 K. The dielectric loss curves also have peaks but at lower temperatures (about 285 K). It is very interesting, however, that we could find anomalous jumps at a lower temperature of about 280 K in addition to the peaks at T_m of about 310 K in the dielectric curves of the $\langle 111 \rangle$ -oriented crystals. At the same time, the dielectric loss curves also show two peaks, the lower temperature one being very sharp. The dielectric response anomaly at the lower temperature could be induced by a ferroelectric-to-relaxor transition in the heating process. In addition, the transition temperature $T_{\text{FE-R}}$ is independent of the test frequencies. Similar dielectric anomalies related to this phase transition were also observed in 0.9PMN-0.1PT

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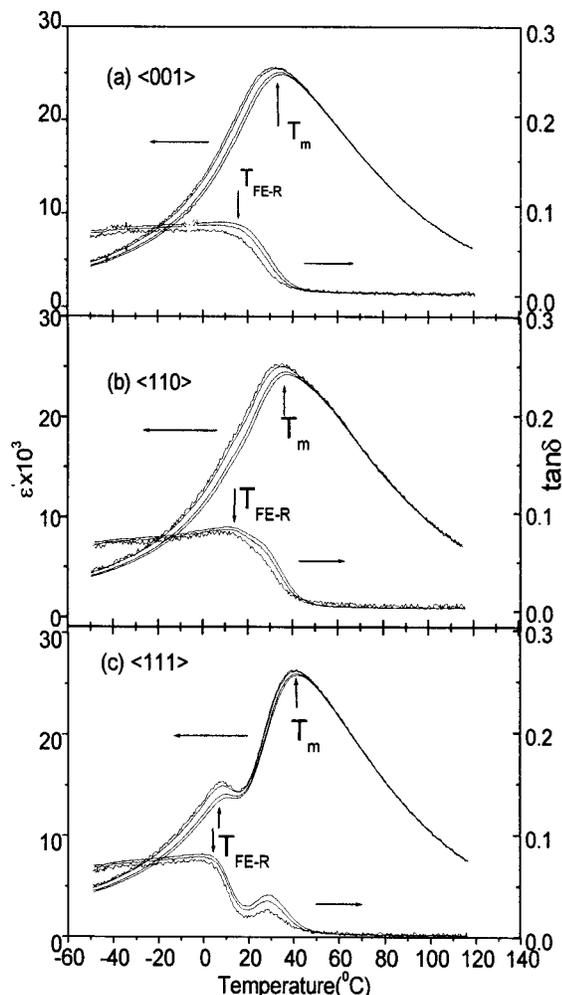


FIG. 1. The real component and dielectric loss of relative electrical permittivity properties as a function of temperature of (a) $\langle 001 \rangle$, (b) $\langle 110 \rangle$, and (c) $\langle 111 \rangle$ -oriented 0.9PMN-0.1PT crystals at frequencies from top to bottom: 0.01, 0.1, 0.5, and 1.0 kHz, respectively.

ceramics at the same temperature (280 K),^{11,12} and were hardly distinguishable shoulders on the temperature dependences of $\log \epsilon$ and $\tan \delta$ in the heating procedure.

In our 0.9PMN-0.1PT single crystals, double hysteresis loops were observed in all of the $\langle 111 \rangle$, $\langle 011 \rangle$, and $\langle 001 \rangle$ directions at a temperature above the T_{FE-R} , such as 293 K, as shown in Fig. 2. The double loops are reminiscent of the electric-field-induced ferroelectric phase at a higher temperature than the Curie temperature in a first-order ferroelectric phase transition. This behavior may imply a first-order phase transition at T_{FE-R} and the coexistence of polar and nonpolar phases at temperatures a little above the T_{FE-R} . The corresponding coercive field E_c and remnant polarizations P_r decrease in the order of $\langle 001 \rangle$, $\langle 011 \rangle$, and $\langle 111 \rangle$ directions. It seems that the long-range ferroelectric order is most easily induced along the $\langle 111 \rangle$ direction by an external electric field. From the evident orientation dependence of P - E characteristics, it is much more reasonable for us to interpret the special T_{FE-R} dielectric anomaly in $\langle 111 \rangle$ direction in Fig. 1 as a spontaneous FE-R phase transition. In the $\langle 011 \rangle$ and $\langle 001 \rangle$ directions, however, the transition although does exist but could not be revealed by the dielectric constant, which is strongly dependent on crystal orientations and domain pattern.

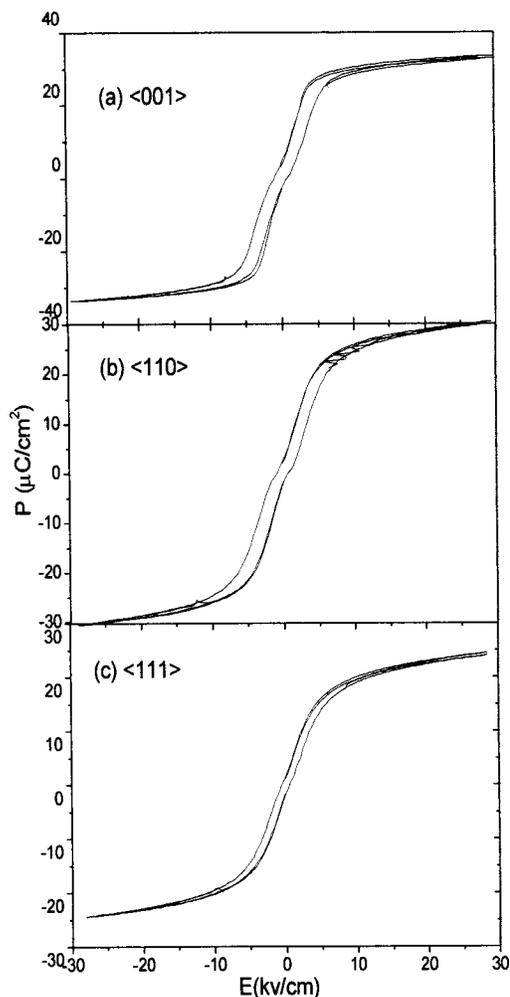


FIG. 2. The double pattern of hysteresis loops for (a) $\langle 001 \rangle$, (b) $\langle 110 \rangle$, and (c) $\langle 111 \rangle$ -oriented 0.9PMN-0.1PT crystals at 10 Hz and at 20 °C.

The high-temperature diffused and dispersive maximum at temperature $T = T_m \approx 310$ K is not directly related to any structural phase transition. Instead, it indicates a typical relaxor behavior associated with the polarization and relaxation of polar nanoregions (PNR) exhibiting the average cubic phase.¹¹ The T_m and ϵ_m of dielectric permittivity peak show frequency dependence, which was described by the derivative Smolenskii's relation based on commonly theoretical approach,¹⁶ given by

$$\epsilon_m \epsilon^{-1}(f, T) = 1 + [T - T_m(f)]^2 / 2\delta_r^2, \quad (1)$$

where ϵ_m is equal to the value of permittivity ϵ at temperature $T = T_m$. The parameter δ_r which, changes with compounds, is used as the measure of diffuseness. The dielectric permittivity ($T_m \leq T \leq T_m + 80$ K) fit the quadratic law well (shown in Fig. 3) with independent δ_r (37.65 K). Indeed, this behavior is characteristic of ferroelectric relaxors. The possible contributions are (i) the vibration of the boundaries between PNR and nonpolar matrix,¹⁷ (ii) the reorientation of the dipole moments of PNR, and (iii) the reorientation of the dipole moments of "free" unit cells inside PNR, as described by the "soft polar nanoregions" model.¹⁸

The main contribution to the dielectric anomaly at the Curie point (T_C) in normal perovskite ferroelectrics comes from the peak of the susceptibility of ionic lattice caused by phonon softening. This is not the case for relaxor ferroelec-

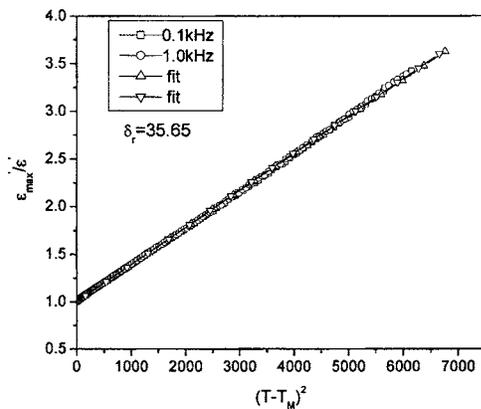


FIG. 3. The plots of $\epsilon_m \epsilon^{-1}(f, T)$ vs $[T - T_m(f)]^2$ for 0.9PMN-0.1PT crystals at different frequencies: 1.0 and 0.1 kHz.

trics, especially for PMN. Within the temperature range of the permittivity maximum, it accounts for less than 1% of the total permittivity at 1 kHz.¹⁹ Furthermore, ionic lattice susceptibility is frequency independent in our test frequency range. It could be noted that in the $\langle 111 \rangle$ -oriented crystal, the small frequency dispersion of permittivity still appears at and below T_{FE-R} . Although there is frequency dependence in the magnitude of ϵ at T_{FE-R} , there is no dispersion in its temperature position T_{FE-R} . Stated simply, the peaks of FE-R transition behave distinctly from the broad T_m peaks associated with the ergodic relaxor phase. Therefore, we think in our 0.9PMN-0.1PT crystals, the permittivity maximum at the spontaneous FE-R phase transition is caused mainly by the change in polar nanoregion subsystem. During this transition, the PNRs grow in size to form mesoscopic ferroelectric domains, just like the development of polar phase from the nonpolar matrix in the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ crystals.^{20,21} In relaxors, the transition from relaxor to ferroelectric state is diffused and the PNRs and related domain patterns change gradually but slightly with temperature¹⁸ (i.e., the size and number of PNRs at $T > T_C$ is not very different from those of domains at $T < T_C$). Thus, the dielectric anomaly at T_C may be weak in the heating procedure.

We also fit the dielectric constant and frequency of T_m peaks according to the Vogel-Fulcher $\tau = 1/2\pi f = \tau_0 \exp[U/(T - T_f)]$ law. The parameters f , U , and τ_0 are frequency, the activation energy, and a pre-exponential term, respectively. At T_f , all relaxation times are supposed to diverge and their distributions become infinitely broad to induce such a relationship in low-frequency limit.²² Interestingly, we found the obtained temperature T_f is very close to the T_{FE-R} in our unpoled 0.9PMN-0.1PT crystals. After the least-squares fitting, we obtained the fitting parameters as $U = 860$ K and $T_f = 286$ K, as shown in Fig. 4. The T_f is nearly the same as the depolarization temperature obtained in poled samples (as shown elsewhere). In the present samples, free from electric field, the correlation length at the low temperature region is not large enough to permeate the samples entirely to precipitate completely a FE state. The composition of 0.9PMN-0.1PT crystal is close to the normal-to-relaxor FE boundary. A small decrease in correlation length is sufficient to produce full relaxor behavior. Thus, the frequency dispersion below T_{FE-R} may reflect the dielectric response as a consequence of the compositional disorder and the ferroelectric multidomain nature. This spontaneous, first-order FE-R crossover region has emerged as a general fea-

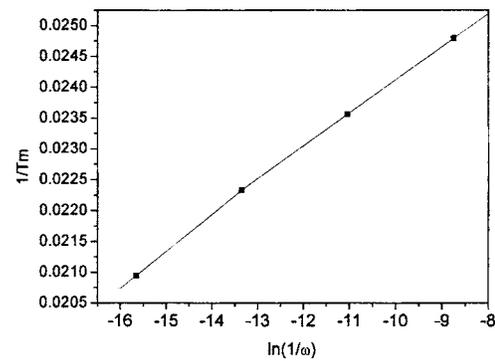


FIG. 4. The peak temperature T_m as a function of measurement frequency can be fitted with Vogel-Fulcher relation (●) experiment data and (—) fitting curve.

ture of soft-mode ferroelectrics with dipole impurities or polar nanodomains.²³

In summary, we have found the spontaneous ferroelectric-to-relaxor phase transition at temperature T_{FE-R} in 0.9PMN-0.1PT unpoled crystals from the investigation on the frequency, temperature dependence of the complex electric permittivity. The fitted Vogel-Fulcher characteristic temperature T_f is very close to this first-order phase transition temperature T_{FE-R} . The small frequency dispersion at and below T_{FE-R} , that is, the FE-R crossover region, still appears and could be attributed to the changes of PNR subsystem and the ferroelectric multidomain nature.

The research was supported by NNSF, China (Grant Nos. 50272075, 50432030, and 50331040), 863 project of China (Grant No. 2002AA325130), and Innovation Funds from Chinese Academy of Sciences (Grant Nos. SCX200411 and KJCXZ-SW-105-03).

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