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Light scattering study of acoustic phonon modes and central peaks in $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.45}\text{Ti}_{0.55}]\text{O}_3$ single crystals

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The dynamic polar nanoregions (PNRs) which form below the Burns temperature and determine the unique properties of relaxor ferroelectrics were predicted [Tinte *et al.*, Phys. Rev. Lett. **97**, 137601 (2006)] to be pinned to the quenched chemically ordered regions (CORs) usually observed in lead-containing relaxors. In $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.45}\text{Ti}_{0.55}]\text{O}_3$ crystal where CORs are known to be absent, we have found the phenomena typically related to the relaxation of dynamic PNRs, namely, the significant Brillouin quasielastic scattering, the softening of the longitudinal acoustic mode, and the deviation from the Curie-Weiss law above the Curie point. This implies that PNRs may appear in crystals without CORs. © 2007 American Institute of Physics. [DOI: 10.1063/1.2825416]

Recently, relaxor-based ferroelectric perovskite $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$ (PZN-*x*PT) and $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$ (PMN-*x*PT) single crystals have attracted great attention as promising materials in various electromechanical applications because of their superior piezoelectric properties.¹ These complex compounds are formed by combining relaxor ferroelectrics (RFEs) and lead titanate (PbTiO_3) (PT) ferroelectric materials. RFEs have been studied intensively during the last two decades from the viewpoints of fundamental physics as well as industrial applications.² RFEs exhibit unusual, complex properties different from those of normal ferroelectric materials. For example, $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$ (PMN), an archetypal RFE, shows a diffuse, frequency-dependent broad dielectric maximum, broad distribution of relaxation times with divergent leading edge on cooling, no macroscopic symmetry change down to the lowest temperature, and the existence of nanosized polar regions (PNRs) below a certain temperature, the so-called Burns temperature (T_B).^{3,4} Recent first-principles-based simulations of RFEs suggested that the PNRs may appear predominantly in the short-range chemically ordered regions (CORs).⁵

One of the key questions on PNRs of RFEs is about the upper limit of the PT content up to which the PNRs persist in PZN-*x*PT and PMN-*x*PT single crystals. Recent neutron study on PMN-60%PT showed negligible diffuse scattering related to PNRs, suggesting that short-ranged polar correlations do not form in PMN-60%PT.⁶ In contrast, dielectric properties of PMN-55%PT showed relaxorlike behavior, indicating the possibility of the existence of PNRs in this high-PT composition.⁷ In this previous study, it was found that the dielectric constant measured along the [100] direction follows the Curie-Weiss law (CW law) in the high-temperature range but deviates from it at about 610 K, which

will be denoted as T_B for convenience. Furthermore, the temperature dependence of the dielectric constant in the temperature range from the ferroelectric transition temperature ($T_C=521$ K) to T_B could be described by an empirical quadratic scaling relation.⁸ These results strongly indicate some relaxorlike nature in this PMN-*x*PT of high-PT content. This letter reports on detailed Brillouin light scattering study on PMN-55%PT single crystals in a wide temperature range, which shows very strong relaxational dynamics as well as significant softening of acoustic modes above T_C .

The $\text{Pb}[(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$ single crystals were grown by the Bridgman method with nominal composition $x=0.5$ and cut to obtain (100)-oriented platelets.⁷ It is known that the real composition of these solid solution crystals is usually different from the nominal composition. By comparing the Curie point T_C of the crystals with the published T - x phase diagram,⁶ we found that $x\cong 0.55$. T_C turns out to be equal to the maximum dielectric constant temperature (T_m). A diode pumped solid state laser at the wavelength of 532 nm was used as an excitation light source. A micro-Brillouin scattering system with a 3+3 pass Sandercock tandem Fabry-Pérot interferometer was used to measure the Brillouin spectra at a backward scattering geometry.

In the cubic phase of solids, only the longitudinal acoustic (LA) mode can be observed from the Brillouin spectrum at a backward scattering geometry. The appearance of the transverse acoustic (TA) mode at this geometry, thus, indicates a structural phase transition from cubic to tetragonal symmetry. The PMN-55%PT undergoes a ferroelectric phase transition at $T_C=521$ K, above which only one Brillouin doublet from LA mode could be seen in this study. At and below T_C , additional Brillouin doublet corresponding to the TA mode was clearly observed. The inset figure of Fig. 1(b) shows one example of the Brillouin spectra measured at $507\text{ K} < T_C$, which shows two acoustic modes as well as a CP. Figure 1(a) shows the fitted result for the Brillouin frequency shifts of the LA and TA modes (denoted as ν_{LA} and ν_{TA} , respectively) as a function of temperature. Figure 1(b)

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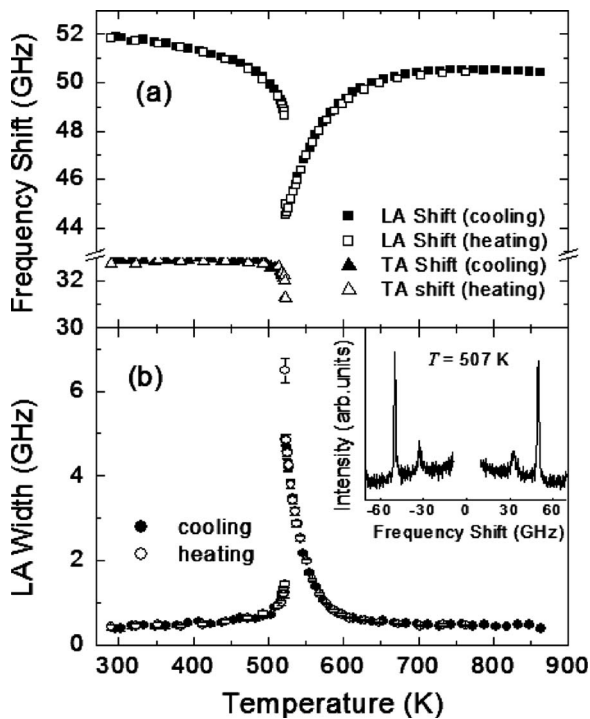


FIG. 1. (a) Temperature dependence of the Brillouin shift of LA and TA modes and (b) the FWHM of the LA mode measured at both cooling and subsequent heating processes. Inset: A Brillouin spectrum measured at 507 K.

shows the full width at half maximum (FWHM) of the LA mode, which is related to the acoustic damping of this mode. ν_{LA} shows a very mild change at above ~ 600 K, indicating that only normal anharmonic effects dominate the lattice dynamics in this high-temperature range. Below 600 K, ν_{LA} shows a substantial softening upon approaching T_C . In the same temperature range, the FWHM exhibits a sharp increase, suggesting a significant coupling between the LA waves and other degrees of freedom. When the crystal undergoes ferroelectric phase transition at 521 K upon cooling, ν_{LA} shows a discontinuous change to a higher value concomitant with the appearance of the TA mode, which indicates a structural phase transition from cubic to tetragonal symmetry.

Figure 2(a) shows the change of the Brillouin spectra as a function of temperature recorded at three selected temperatures in the range of T_C – T_B . It is readily recognizable that CP appears at ~ 570 K and grows substantially upon cooling. The intensity of the polarized component of CP was much larger than the depolarized one, suggesting that the CP is strongly polarized. The CP was nicely fitted by using a single Lorentzian function centered at zero frequency when assuming a Debye relaxation process. The temperature dependence of the integrated intensity of the CP component is plotted in Fig. 2(b). The inverse of the dielectric permittivity (ϵ) is also shown in the same figure for comparison. The solid line is a fitted result to the CW law of $1/\epsilon = (T - T_{CW})/C$. ϵ follows the CW law in the high-temperature range with $T_{CW} = 531$ K and $C = 1.7 \times 10^5$, but it shows a deviation from the high-temperature linearity at $T_B \sim 610$ K. This deviation becomes more noticeable at about 570 K, at which CP begins to appear and grow significantly on lowering the temperature. The intensity of CP reaches a maximum exactly at T_C .

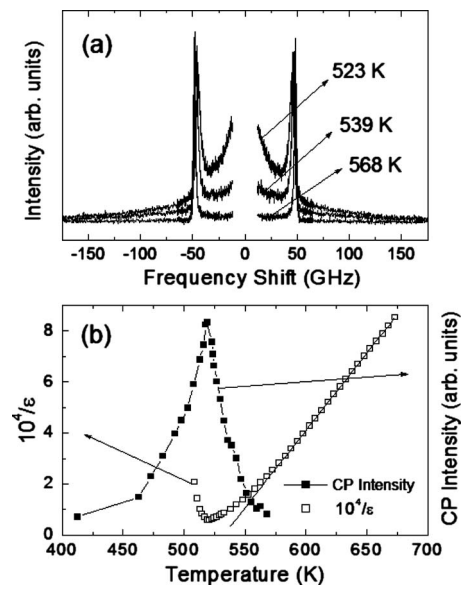


FIG. 2. (a) Brillouin spectra measured at three selected temperatures. (b) The temperature dependence of the inverse dielectric permittivity (solid squares) and the intensity of CP (open squares). The solid line is a fitted result to the CW law.

It has been found that the dielectric constant of various relaxor samples from the high-temperature slopes can be explained by using the following empirical equation:⁸

$$\frac{\epsilon_A}{\epsilon} = 1 + \frac{(T - T_A)^2}{2\delta^2}, \quad (1)$$

where T_A and ϵ_A are parameters used for defining the temperature position of the peak and the extrapolated value of the dielectric constant at $T = T_A$, and δ is a shape parameter describing the diffuseness of the dielectric properties of relaxors. Figure 3(a) gives the fitting result for the real part of the permittivity of the PMN-55%PT, which shows that the quadratic law of Eq. (1) is fulfilled in the temperature range of 521–580 K with fitting parameters of $\epsilon_A = 3.6 \times 10^4$,

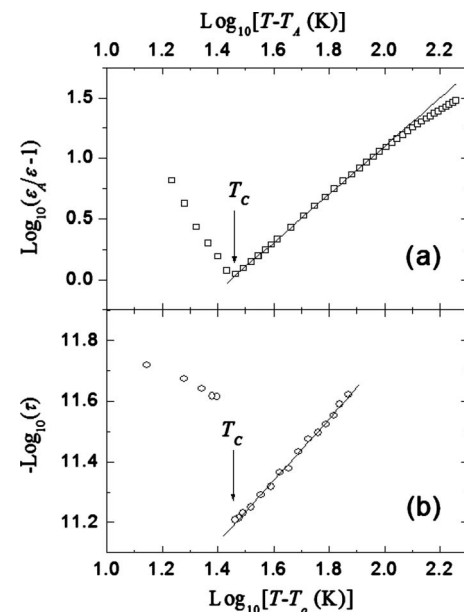


FIG. 3. (a) The temperature dependence of the dielectric permittivity fitted by Eq. (1). The solid line represents a fitted result. (b) The temperature dependence of the relaxation time estimated from the width of CP. The solid line represents a fitted result by using Eq. (2).

$T_A=492$ K, and $\delta=20$ K. These results suggest that the dielectric properties of PMN-55%PT between T_C and T_B are characterized by typical relaxor behavior rather than by the CW law commonly observed in normal ferroelectric materials, despite the fact that it undergoes a first-order ferroelectric phase transition at T_C . This unusual behavior is correlated with the strong growth of the CP component in light scattering spectrum. The half width of CP is inversely proportional to the relaxation time τ of the related polarization fluctuations.⁹ The estimated relaxation time increases substantially on cooling from 570 K towards T_C , which indicates slowing down of the relevant dynamics in the high-temperature phase ($T_C < T < T_B$) of PMN-55%PT. Therefore, we apply the following well-known relationship between τ and the temperature to fit the data:¹⁰

$$\frac{1}{\tau} = \frac{T - T_0}{\tau_0 T_0} \quad (2)$$

Figure 3(b) shows the fitting result for the relaxation times above T_C , which results in $\tau_0=0.36$ ps and $T_0=494$ K. Therefore, Eq. (2) nicely explains the temperature dependence of τ in the high-temperature phase of PMN-55%PT. This observation suggests that the CP originates from the polarization fluctuations and that an order-disorder mechanism contributes to the slowing down of the polarization fluctuations in PMN-55%PT.

However, the phase transition behavior of PMN-55%PT should be differentiated from the critical behavior observed in PT, as well as in typical order-disorder-type ferroelectrics, because the dielectric constant of PMN-55%PT does not diverge according to the CW law. Instead, a strong relaxational mode whose polarization fluctuations display a slowing down is accompanied by relaxorlike dielectric behavior in the high-temperature phase between T_C and T_B . Considering the existence of a peculiar temperature T_B below which the dielectric permittivity deviates from the CW law, the most probable origin of the strong central peak and significant softening of the LA mode observed in PMN-55%PT is the presence of PNRs and their relaxational dynamics. Note that the strong spatial correlation between PNRs and nanoscale regions of chemical ordering (or CORs) on the B sites was suggested by recent first-principles-based simulations.⁵ However, in PMN- x PT solid solutions, the size of COR decreases with increasing x and they completely disappear at x exceeding ~ 0.4 . This was found by transmission electron microscopy¹¹ and confirmed by synchrotron x-ray scattering studies.¹² Therefore, the PNRs we observed in PMN-55%PT crystal are not related to the CORs. This implies that the existence of CORs is not a necessary condition for the formation of PNRs: the latter may nucleate at $T < T_B$ in the chemically disordered matrix.

However, Stock *et al.* reported from their neutron scattering and x-ray diffraction experiments on PMN-60%PT that the diffuse scattering was found to be weak and temperature independent and, thereby, it was concluded that PNRs are not present in PMN-60%PT crystals (close to the composition of our crystal).⁶ To explain this apparent discrepancy with our results, we note that, according to the high energy resolution neutron spin-echo spectroscopy study, the diffuse scattering (in PMN) is purely elastic (within an experimental accuracy of 1 μ eV) and, therefore, can be associated with static (or quasistatic) PNRs [whose relaxation rate is less than 250 MHz (1 μ eV)].¹³ It was further sug-

gested that the static PNRs are formed inside the CORs, while the dynamic relaxing PNRs appear in the chemically disordered matrix.¹⁴ The dynamic PNRs presumably can be observed only at very small scattering vectors inaccessible in the neutron and x-ray experiments.¹³ In accordance with these ideas, neutron and x-ray diffuse scattering should not be observed in PMN- x PT crystals with $x \sim 0.5$, where CORs (and thereby static PNRs) are absent. On the other hand, by means of quasielastic light scattering (i.e., working with small wave vectors), we have found in PMN-55%PT crystal a significant central peak which, thereby, can be related to the dynamic PNRs. The relaxation of these dynamic PNRs give rise to the dielectric peak described by relation (1), which is typical of relaxor behavior.

To summarize, it was found that the phase transition of PMN-55%PT is characterized by two characteristic temperatures, $T_B \sim 610$ K and $T_C=521$ K. Above T_B , the dielectric permittivity ϵ follows the CW law and there is no substantial change in acoustic properties. Between T_B and T_C , ϵ deviates from the CW law and follows the quadratic scaling relationship similar to other typical relaxors, and a strong central peak grows upon cooling accompanied by substantial softening of the LA mode. At T_C , the Brillouin shift of the LA mode shows a discontinuous change in addition to the appearance of the TA mode, indicating a typical structural phase transition. All these results indicate that dynamic PNRs still persist even in PMN-55%PT without CORs, which is responsible for the relaxorlike behavior observed in the high-temperature phase ($T_C < T < T_B$), even though a long-range ferroelectric phase is achieved due to the weakened random fields and the enhanced anisotropy with increased PT content.

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