Anomalous behavior of acoustic phonon and central peak in $Pb[(In_{1/2}Nb_{1/2})_{0.65}Ti_{0.35}]O_3$ single crystal

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The temperature dependences of acoustic phonon mode and the central peak have been investigated in $Pb[(In_{1/2}Nb_{1/2})_{0.65}Ti_{0.35}]O_3$ single crystal by Brillouin scattering. Longitudinal acoustic phonon begins to show marked softening below the Burns temperature $T_B \sim 700$ K. The longitudinal acoustic phonon mode exhibits clear anomalies at the cubic-tetragonal phase transition temperature of 540 K and at the tetragonal-rhombohedral one of 460 K. Below 600 K, the relaxation time calculated from the phonon mode agrees well with that of the broad central peak, suggesting a coupling between the local polarization and strain fluctuations of polar nanoregions. This temperature has been identified as another characteristic temperature T^* besides T_B, where the formation of long-lived polar nanoregions accompanied by the local strain fields governs the relaxation dynamics. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3058606]

I. INTRODUCTION

Relaxor ferroelectric materials with general formula $Pb(B'B'')O_3$ and their solid solution with $PbTiO_3$ (PT) have been extensively investigated due to the exotic physical phenomena they display and ultrahigh piezoelectric responses they exhibit at the morphotropic phase boundary (MPB).[1–3] Relaxor ferroelectrics are distinguished by a broad and frequency dependent maximum in the dielectric susceptibility as a function of temperature, broad distribution, and divergence of relaxation time on cooling with no macroscopic change in the crystal structure. Several theoretical models have been proposed in order to understand the microscopic origin of the complex behavior of relaxor ferroelectric materials.[4–6] The main features that are central to the complex phenomena in these materials are the nucleation and the growth of the polar nanoregions (PNRs), which are nanometer-scale regions having local, randomly oriented, ferroelectric polarizations. PNRs begin to appear at very high temperature, known as Burns temperature T_B above the temperature of dielectric maximum T_{max}.[7] Below T_B, the deviation from Curie–Weiss behavior, change in the thermal expansion coefficient, and specific heat anomalies were observed in relaxor ferroelectric systems.[8–10] Extensive studies on the dynamical aspects of PNRs have been carried out in $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), PMN-PT, PZN-PT, and $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN)-PT systems through neutron and light scattering studies.[11–17] Brillouin scattering studies in these systems clearly revealed interesting features of the PNRs, such as the softening of the acoustic phonon mode and the appearance of central peak (CP) below T_B and slowing down of their relaxation time and the coupling between the polarization fluctuations and acoustic phonon modes.[14–17]

$Pb(In_{1/2}Nb_{1/2})O_3$ (PIN) belongs to the class of $Pb(B'B'')O_3$ compounds in which the degree of ordering of In^{3+} and Nb^{5+} ions can be altered by thermal treatment. Disordered PIN in which the *B* site is randomly occupied by In and Nb ions exhibits relaxor-type ferroelectric behavior. Ordered PIN on the other hand shows antiferroelectric behavior.[18] Recently PIN-PT solid solution system has generated a lot of interest due to the high electromechanical coupling factor k_p along with high dielectric constant and high transition temperatures at MPB.[19,20] The phase diagram of $(1-x)$PIN-xPT solid solution system shows the sequence of structural phases with temperature and PT content, and MPB is found to exist for $x=0.37$.[21] The dielectric studies on the composition near MPB show cubic-tetragonal (T_{ct}) and tetragonal-rhombohedral (T_{tr}) phase transitions that are similar to PMN-PT and PZN-PT systems.[14,22] However unlike PMN-PT and PZN-PT systems, the studies on the dynamical aspects of PNRs have not yet been carried out in PIN-PT solid solution system. Such studies on broader compositional system will help in the better understanding on the various physical aspects of PNRs. In the present study, we report the Brillouin scattering studies on $Pb[(In_{1/2}Nb_{1/2})_{0.65}Ti_{0.35}]O_3$ single crystal over a wide temperature range to understand the dynamical aspects of PNRs.

II. EXPERIMENTAL DETAILS

Single crystals of $Pb[(In_{1/2}Nb_{1/2})_{0.65}Ti_{0.35}]O_3$ (0.65PIN-0.35PT) were grown by flux method with Pb_3O_4 and B_2O_3 as fluxes. The flux and charge were taken in 59 (Pb_3O_4): 1 (B_2O_3): 40 (0.65PIN-0.35PT) wt %. The crystals were grown by cooling from 1250 to 950 °C at the rate of 2 °C/h and then at 100 °C/h to room temperature. Electron probe microanalysis (EPMA) was carried out to determine the stoichiometry of the composition. Brillouin spectra were measured at backscattering geometry using a high contrast 3+3 pass Sandercock tandem Fabry–Pérot interferometer. The free spectral range (FSR) of the spectrometer was 75 and 400 GHz. Scattering was excited by a diode pumped solid-state

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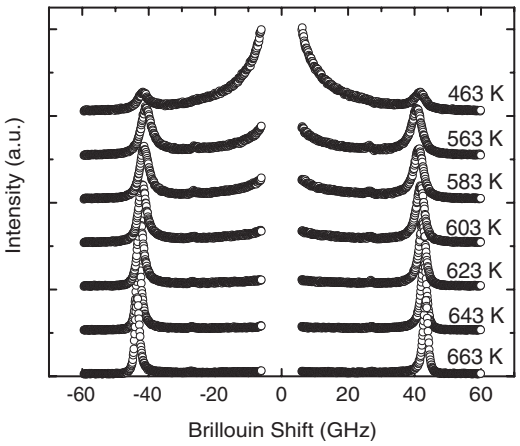

FIG. 1. Brillouin spectra of $Pb[(In_{1/2}Nb_{1/2})_{0.65}Ti_{0.35}]O_3$ measured with a FSR of 75 GHz at some selected temperatures.

laser (Coherent Compass 532). The spectra were recorded from 873 to 300 K using a Linkam hot stage (Linkam THMS 600).

III. RESULTS AND DISCUSSION

Although the PIN-PT composition at MPB ($x=0.37$) was used for the growth of single crystals, EPMA analysis indicated that the composition of the grown crystals was $x=0.35$. Figure 1 shows the Brillouin spectra in the FSR range of 75 GHz at some selected temperatures. The Brillouin doublet of longitudinal acoustic (LA) phonon can be seen clearly. A faint and broad transverse acoustic (TA) phonon mode could also be observed in the cubic phase. The TA mode however could not be followed for all the temperature and hence is not further discussed in the present study. Figure 2(a) shows the Brillouin shift of LA mode and its full width at half maximum (FWHMγ) as a function of the temperature. The Brillouin shift and FWHM of LA mode exhibit a small change above 700 K, indicating that the normal anharmonic process governs the lattice dynamical behavior in the high temperature. Below 700 K, LA mode shows substantial softening, followed by a strong increase in its width on approaching T_{ct}. The frequency and the width of LA mode show clear anomalies at T_{ct} as well as at T_{tr}. The intensity of LA phonon mode as shown in Fig. 2(b) exhibits clear anomalies at T_{ct} and T_{tr} along with a shallow plateau at 600 K and a strong change at 700 K. In relaxor ferroelectric materials, the PNRs, which begin to form below T_B, have been suggested to be the origin of the anomalous behavior of acoustic phonon modes. In the present study, the observation of anomalous behavior, the Brillouin shift, and the width of LA phonon together with the change in its intensity 700 K clearly suggest that $T_B \sim 700$ K. The implication of the shallow plateau in the intensity of LA phonon mode at 600 K will be discussed later.

As also shown in Fig. 1, a narrow CP begins to appear at about 620 K and grows further substantially upon cooling. Figure 3 shows the Brillouin spectra measured in the FSR range of 400 GHz. A broad CP begins to grow below T_B. Assuming a Debye relaxation process, both narrow and broad components of the CP could be independently fitted

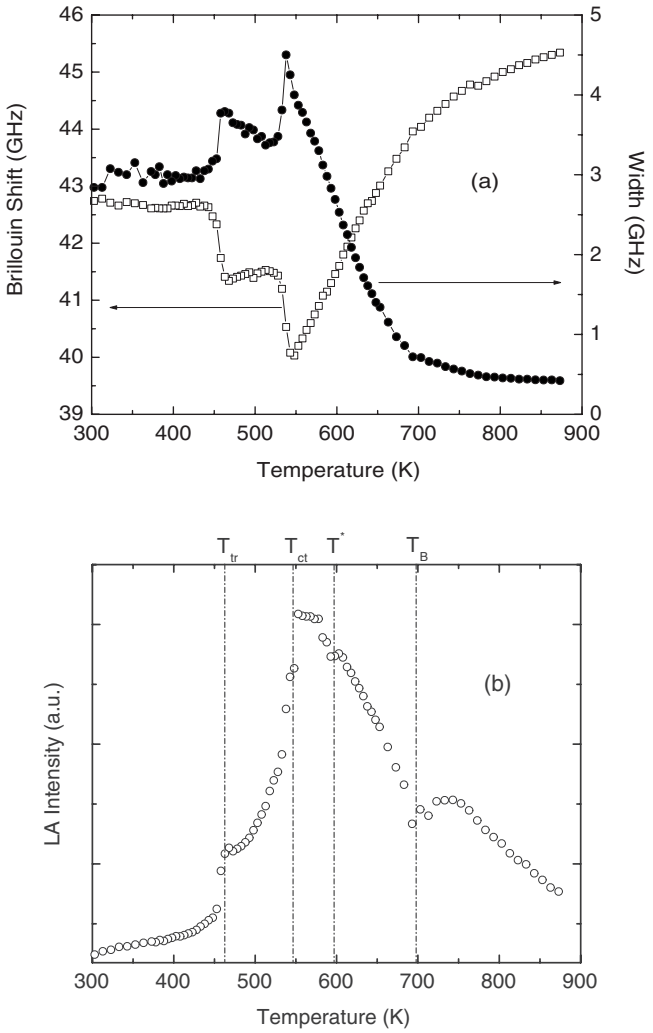

FIG. 2. (a) Temperature dependences of Brillouin shift (squares) and width (Γ) (circles) of the LA phonon mode of $Pb[(In_{1/2}Nb_{1/2})_{0.65}Ti_{0.35}]O_3$ single crystal. (b) Temperature dependence of the intensity of LA phonon mode.

with a single Lorentzian function centered at zero frequency. The temperature dependence of the width and the integrated intensity of the CPs are shown in Figs. 4(a) and 4(b). The width of both CPs decreased upon cooling toward T_{ct}, reflecting the slowing down of the relaxation time associated

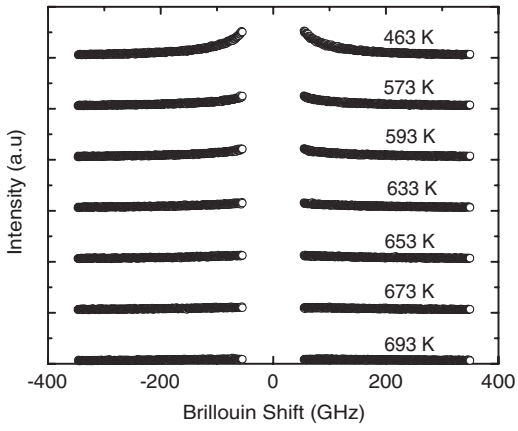

FIG. 3. Brillouin spectra of $Pb[(In_{1/2}Nb_{1/2})_{0.65}Ti_{0.35}]O_3$ measured with a FSR of 400 GHz at some selected temperatures.

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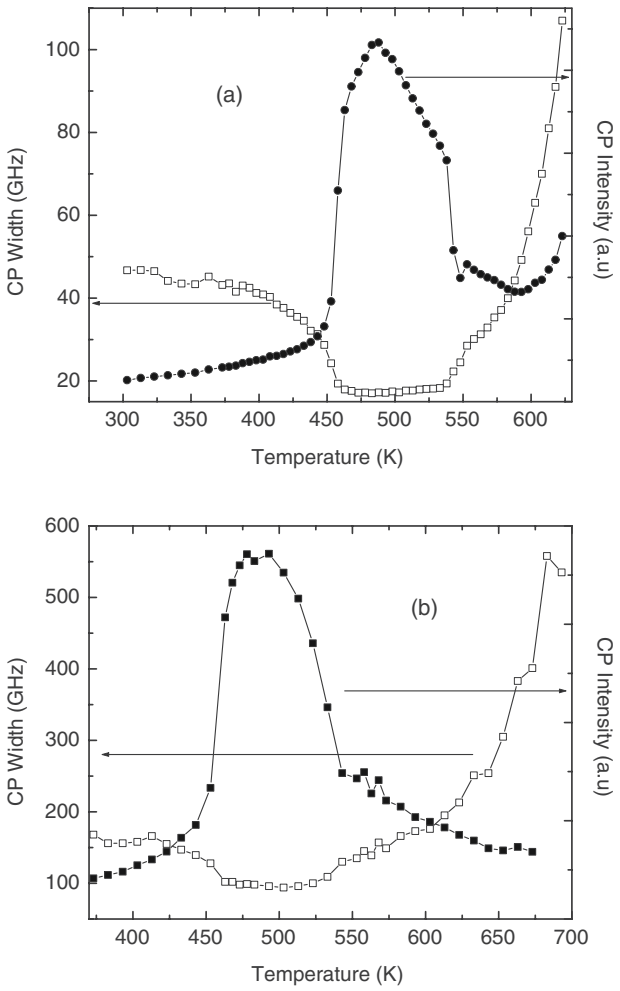

FIG. 4. (a) Temperature dependences of width of narrow CP (squares) and the intensity (circles). (b) Temperature dependences of width of broad CP (squares) and the intensity (closed squares).

with the relaxation process that contributes to CP. The integrated intensity of both CPs shows marked anomalies at T_{ct} and T_{tr}. The softening of LA mode below T_B can be likely attributed to the strain fluctuations associated with PNRs since the polarization fluctuations of PNRs can couple to the strain through $\Delta x_{jj}=(Q_{11}+2Q_{12})P_s^2$, where Q_{11} and Q_{12} are the electrostrictive coefficients and P_s is the local polarization ($\langle P_s\rangle=0$, while $\langle P_s^2\rangle\neq 0$). The relaxation time of the strain fluctuations can be calculated from LA phonon mode assuming the Debye relaxation process for the complex elastic stiffness coefficient (c) as[23–25]

$$c(\omega)=c(\infty)-\frac{\Delta c}{1-i\omega\tau_{\mathrm{LA}}(T)}. \tag{1}$$

The expression for the relaxation time is given as

$$\tau_{\mathrm{LA}}=\frac{\frac{\Delta\Gamma_c}{\Delta\Gamma}\omega_c-\sqrt{\left(\frac{\Delta\Gamma_c}{\Delta\Gamma}\omega_c\right)^2-\omega^2}}{\omega^2}, \tag{2}$$

where $\Delta\Gamma=\Gamma(T)-\Gamma_\infty$, Γ is the width of the LA phonon, and ω_c is the Brillouin shift of LA phonon at T_c. Γ_∞ is the additional decay or attenuation channels not included in Eq. (1). The details of the derivation of Eq. (2) are given in Ref. 25.

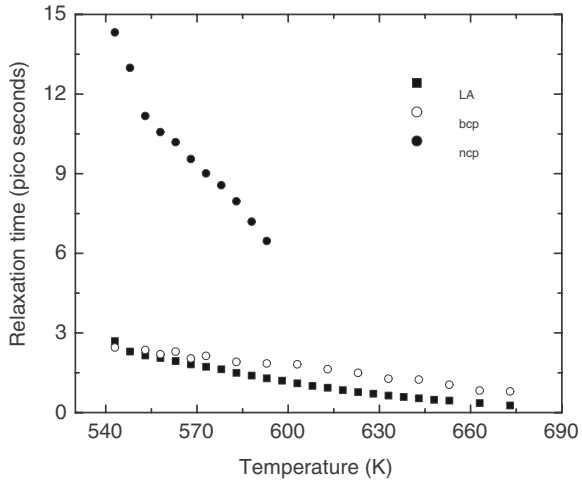

FIG. 5. Temperature dependences of relaxation time of LA phonon mode, τ_{LA} (closed squares), broad (τ_{bcp}) (open circles), and narrow (closed circles) CPs.

It can be seen from Fig. 2(a) that the width of LA mode is nearly constant above 700 K. It is commonly observed in relaxor ferroelectric materials that Γ is nearly independent of temperature above T_B. Hence we use the highest temperature (at 873 K) value of the width of the LA mode for Γ_∞. The value of ω at cubic-tetragonal phase transition temperature is used for ω_c. The calculated value of the relaxation time from the above expression along with the relaxation times ($\tau=1/\pi\Delta f$) obtained for the narrow (τ_{ncp}) and broad CPs (τ_{bcp}) above T_{ct} is shown in Fig. 5. Below 600 K, a good agreement between the relaxation time of the strain (as determined by LA phonon mode, τ_{LA}) and the polarization fluctuations (as determined by broad CP, τ_{bcp}) of PNRs can be seen. This result implies that below 600 K, the relaxation process of PNRs is determined by the polarization fluctuations coupled with the local strain fluctuations through LA phonon. It is difficult to discuss relaxation process below T_{ct}; it is complicated by the structural phase transition. It is instructive to compare the present results of CP with that of the other type of relaxor ferroelectric materials. A narrow CP coupled with transverse acoustic phonon mode has been reported for the composition near MPB in PMN-PT system well below T_B.[14] On the other hand, a broad CP has been observed near T_B for the composition near MPB in PZN-PT solid solution system.[15] A coupling between LA phonon and the broad CP has been reported for 0.71PNN-0.29PT system below T_B.[17]

Based on the systematic Raman studies on PZN and PZN-xPT with $x=0.045$, Toulouse *et al.*[26] recently suggested that there exists another characteristic temperature, denoted as T^*, which is located below T_B. This temperature has been characterized by the strong anomalies of frequency and the intensity of optic modes and CPs. According to Toulouse *et al.*,[26] the Burns temperature T_B can be identified with the formation of short lived correlations between the off-centered ions, which results in the formation of dynamic PNRs, whereas T^* can be associated with the long-lived or permanent correlations between the atomic displacements of off-center ions, which results in the formation of static PNRs. The permanent correlation between the off-centered

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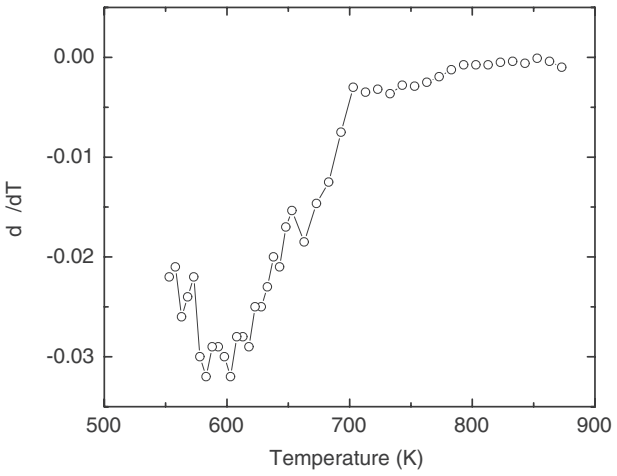

FIG. 6. Temperature derivative of the width of the LA phonon mode.

ions results in the local ferroelectric phase transitions and generates local strain fields. The recent acoustic emission studies revealed the existence of this intermediate temperature T^* and also a local ferroelectric phase transition below this temperature in PZN and PZN-PT systems.[27,28] A further corroborative evidence for T^* could be obtained from the derivative spectra of the frequency and the width of LA phonon.[17] It has been suggested that the temperature T^* should correspond to the extremum of temperature derivative of frequency and the width of LA phonon. The derivative spectrum of the LA phonon as shown in Fig. 6 exhibits a minimum at 600 K. Additionally, the shallow plateau at 600 K in the intensity of the LA phonon shown in Fig. 2(b) could also be possibly taken as the evidence for the existence of T^*. These findings suggest that the temperature of 600 K in the present study can be identified with T^* where the static PNRs begin to form. The present study also reveals that the dynamics of relaxation process is governed by the electrostrictive coupling between the local polarization fluctuations in permanent PNRs and the strain (Fig. 5). The anisotropic electrostrictive coupling between the local polarization and strain fluctuations below T^* has been recently reported in the Brillouin spectroscopic investigations of PZN-PT single crystals.[29] In the present study, though broad CP appears below T_B, its coupling with LA phonon occurs only below T^*. In 0.71PNN-0.29PT system also, the narrow CP begins to appear around T^*.[17] In this context, the present results closely follow the PNN-PT solid solution system except that the coupling of the CP with LA phonon occurs below T^*. In fact the appearance of narrow CP in PMN-PT system well below T_B could be taken as the evidence for the existence of T^*.[14] In the present study also, the appearance of narrow CP and the coupling of the broad CP with LA phonon mode below T^* indeed support the existence of T^* where the long-lived PNRs begin to form. The existence of T^* has also been established in another class of relaxor ferroelectric systems such as PST and PBST through Raman spectroscopic studies.[30] Therefore the present study together with the reported evidence on the existence of T^* in other relaxor ferroelectric systems strongly suggests that T^* below T_B is indeed the common characteristic in the temperature evolution of PNRs in relaxor ferroelectric systems.

IV. CONCLUSIONS

To summarize, the temperature dependences of acoustic phonon and CP of $Pb[(In_{1/2}Nb_{1/2})_{0.65}Ti_{0.35}]O_3$ single crystal have been investigated in the wide temperature range between 300 and 900 K by Brillouin light scattering. Below T_B, (~700 K), a significant softening of frequency of LA phonon mode, followed by an increase in its width is observed. The frequency and the width of the LA phonon exhibited clear anomalies at cubic-tetragonal and tetragonal-rhombohedral phase transition temperatures. The narrowing of the width of CPs with temperature reflects the slowing down of the relaxation time of PNRs. The present study suggests a clear evidence for the existence of intermediate characteristic temperature T^* (~600 K) below T_B, where electrostrictive coupling between the polarization and strain fluctuations of PNRs begins to take place. This suggests that below 600 K, the relaxation dynamics is governed by the long-lived PNRs.

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