Classical ferroelectriclike behavior of highly ordered $Pb(Sc_{1/2}Nb_{1/2})O_3$ studied by dielectric and Brillouin scattering spectroscopy

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The ferroelectric phase transition behavior in the highly ordered $Pb(Sc_{1/2}Nb_{1/2})O_3$ has been investigated by the dielectric and Brillouin spectroscopy. The dielectric permittivity ε_r exhibits a sharp maximum without any frequency dispersion at its Curie temperature T_c. In the temperature range far above T_c, it was noted that the dielectric permittivity exhibits a noticeable deviation from the Curie-Weiss law below the characteristic intermediate temperature $T^* = 500\,\text{K}$, which is common to most of the Pb-based oxide perovskite relaxors. Upon cooling, the frequency of the longitudinal acoustic phonon mode exhibits a remarkable softening towards T_c. The relaxation time of the order parameter calculated using the Landau-Khalatnikov approach was determined to be more than one order of magnitude lower than that of the disordered $Pb(Sc_{1/2}Nb_{1/2})O_3$ and is very close to that observed in the paraelectric phase of the classical ferroelectric, $BaTiO_3$. The observed dielectric and relaxation features are qualitatively discussed in terms of the difference in the strength of the random electric fields.

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I. INTRODUCTION

The classical ferroelectrics, such as $PbTiO_3$, undergo a normal ferroelectric phase transition with the divergence of the dielectric permittivity, which obeys the Curie-Weiss law [1]. The relaxor behavior exhibited by the lead-based complex perovskites $Pb(B'_xB''_{1-x})O_3$ have been the subject of intense investigation due to both fundamental and technological interest. Relaxor ferroelectrics (RFEs) present a diffuse and frequency dependent dielectric anomaly with a high dielectric permittivity value. In these materials, the dielectric maximum temperature T_m and the corresponding maximum of the dielectric permittivity, $\varepsilon_r^{\max}$ depends on the frequency of the applied field. The $\varepsilon_r^{\max}$ decreases, while the T_m increases with increase in the frequency [2,3]. It is generally accepted that the origin of the complex behavior exhibited by the RFEs is related to the nucleation of fluctuating polar nanoregions (PNRs) below the Burns temperature T_B [4], which is considerably higher than T_m. The observed change in the thermal expansion, deviation from the Curie-Weiss law and the specific heat anomaly below T_B, is related to the dynamics of the PNRs [2,5,6]. It has been argued that the quenched random electric fields (REFs) arising from the random distribution of the B site heterovalent cations play central role in stabilizing the relaxor phase [7–10].

The dynamical aspects of the PNRs have been extensively studied in the prototype RFEs such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) and other related systems through Brillouin light scattering studies [11–17]. Raman scattering studies revealed the existence of the intermediate temperature T^*, in which the PNRs undergo local structural transformation. Below T^*, the PNRs become larger and long lived, giving rise to large local strain fields [18–22]. Three important temperatures are associated with the temperature evolution of the PNRs: T_B, T^* (intermediate temperature), and T_f (freezing temperature) [18–22]. Between T^* and T_f, the dynamics of the PNRs considerably slow down, and the local polarization enters into the quasistatic region [21,22]. Below the freezing temperature T_f, the PNRs become static. Acoustic emission (AE) studies also confirmed the existence of the intermediate temperature T^* and revealed that the corresponding local structural transformations are accompanied by changes in the local strain fields [23,24]. X-ray diffraction studies showed that the T^* is the same ($500 \pm 30\,\text{K}$) for most of the Pb-based RFE systems [25].

The 1:1 type ferroelectric relaxors $Pb(B'_{1/2}B''_{1/2})O_3$ are of special interest because the degree of the B site order can be controlled by thermal annealing. $Pb(B'_{1/2}B''_{1/2})O_3$ type compounds exhibit different ferroelectric behavior, depending on the degree of B site ordering [26]. The disordered $Pb(Sc_{1/2}Nb_{1/2})O_3$ (PSN) shows a relaxor type ferroelectric behavior, whereas the ordered one exhibits normal ferroelectriclike behavior. In the disordered PSN, a spontaneous relaxor to the ferroelectric phase transition accompanied by a change in the structure from cubic to rhombohedral at the temperature T_c below T_m has also been observed [26,27]. With an increase in the degree of B site ordering, the relaxor behavior gets suppressed, and the transition temperature decreases [27]. The polarization between the disordered and the ordered regions of PSN as revealed by nuclear magnetic resonance (NMR) is substantially different, suggesting that the dynamics of PNRs are influenced by the degree of ordering and that the long range polar order is set only in the ordered region of the crystal [28,29].

Despite numerous experimental studies of this important class of materials, the role of degree of B site ordering on the phase transition behavior of PSN is still unclear. Generally, the observed dielectric behavior in PSN has been theoretically accounted by the REF model [9,30]. Grinberg *et al.* [31] characterized relaxor behavior of various relaxors in terms of

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the difference in the strength of REFs. Using the parametrized form of the Landau phenomenological model, the degree of the dielectric dispersion was analyzed in terms of the average B site ion displacement from the high symmetry cubic position $\bar{D}_B$, and the second moment of the valence of the two B site ion nearest neighbors of each oxygen atom, $\langle V^2 \rangle$ [31] $\langle V^2 \rangle$, is characterized as the measure of the REF strength [32]. The greater the REFs, the larger the dielectric dispersion. The prototype relaxors such as PMN and PZN belong to the strong REF limit in which $\langle V^2 \rangle$ is high, while the classical ferroelectric systems such as $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) and $BaTiO_3$ (BT), in which $\langle V^2 \rangle$ is rather low, represent the case of weak REFs [31,32]. The comparative study of the relaxor PMN-PT and ferroelectric PZT by various combinations of techniques revealed that the dynamics of the polarization are strongly influenced by the strength of the REFs [32].

The PSN is a unique Pb-based system that exhibits both strong and weak REF limits. Disordered PSN, which has a high $\langle V^2 \rangle$, belongs to the case of strong REFs, while that of the ordered PSN, in which $\langle V^2 \rangle = 0$, represents weak the REF case [31]. Though the local condensation temperature T^* for both the disordered and ordered PSN is nearly same [25], the dynamics of the PNRs below T^* in the highly ordered PSN are expected to be quite different from that of the disordered PSN due to the difference in the strength of the REFs. To shed more insight into the influence of the degree of B site ordering on the relaxation behavior of the PNRs, we examined the relaxor to ferroelectric phase transition behavior of the highly ordered PSN crystal by dielectric and Brillouin scattering spectroscopy. Previously, the coupling of acoustic phonons with the PNRs and the critical slowing down of the relaxation time have been reported for a disordered PSN crystal [33].

II. EXPERIMENT

Single crystals of PSN were grown by the flux method [34]. The flux was a mixture of $PbO\text{-}PbF_2\text{-}B_2O_3$ used in the weight ratio of $PSN:PbO:PbF_2:B_2O_3 = 0.15:0.40:0.40:0.05$. The employed thermal cycle was heating to 1250 °C and soaking at this temperature for 4 hours. The single crystals were grown by cooling from 1250 °C to 900 °C at the rate of $2\,^{\circ}\mathrm{C}\,\mathrm{h}^{-1}$ and then at 100 °C to room temperature. The degree of B site 1:1 order was determined from the powder x-ray diffraction study using the Philips X'pert Multipurpose Diffractometer (MPD) of the crushed single crystals. Dielectric and Brillouin light scattering studies were performed on the same single crystal with typical size of 2 mm × 2 mm × 1 mm. Low frequency dielectric measurements at various frequencies were carried using a digital inductance-capacitance-resistance (LCR) meter in the temperature range of 295–690 K. Brillouin light scattering measurements were performed on the (100) surface of the crystal in the back scattering geometry using a high contrast 3+3 pass Sandercock tandem Fabry-Pérot interferometer. A diode pumped solid-state laser of 532 nm wavelength was used as the excitation source. Measurements were carried out in the free spectral range of 75 GHz in the temperature range of 873–200 K using a Linkam FTIR600 heating/cooling stage.

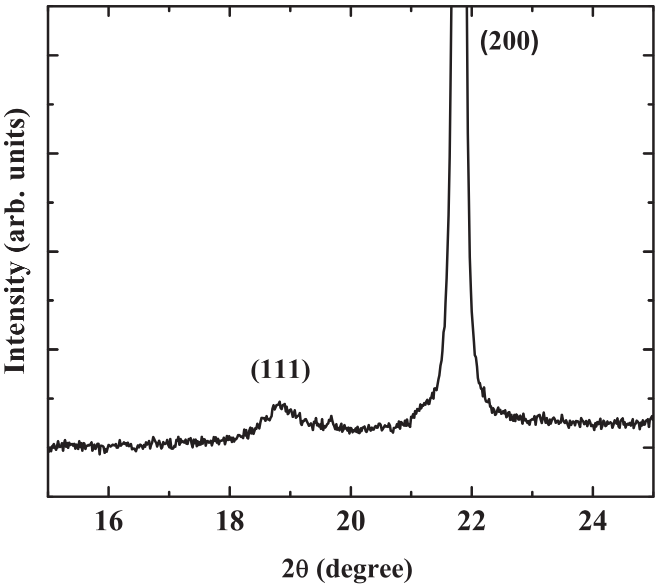

FIG. 1. Powder x-ray diffraction pattern of PSN.

III. RESULTS AND DISCUSSION

A. Degree of *B* site ordering

The powder x-ray diffraction pattern of PSN is shown in Fig. 1. The super structure peak at $2\theta \approx 19^{\circ}$ corresponding to the B site ordering is clearly observed, which shows that the as-grown single crystals are ordered. The degree of the B site 1:1 ordering $S = (\frac{I_{111}}{I_{200}})^{1/2}_{\mathrm{exp}}/(\frac{I_{111}}{I_{200}})^{1/2}_{\mathrm{theo}}$ was calculated from the comparison of the integrated intensities of the superstructure (111) and the adjacent fundamental (200) reflections [35]. For the completely ordered PSN, the theoretical intensity ratio I_{111}/I_{200} is 0.09 [36]. The degree of the B site ordering of the as-grown single crystal was determined to be $S = 0.80$. The average size of the ordered region calculated from the width of the superstructure peak using the Debye-Scherrer formula was about 13 nm, which is much larger than the size of the PNRs of the Pb-based relaxors.

B. Temperature dependence of dielectric permittivity

The low frequency dielectric dispersion of PSN measured during heating is shown in Fig. 2(a). In the vicinity of $T_c = 346$ K, the dielectric peak is very sharp and does not exhibit any frequency dispersion. The strength of the dielectric dispersion $\Delta T = T_m(1\,\mathrm{MHz}) - T_m(1\,\mathrm{kHz})$ was determined to be equal to zero. Dielectric and differential scanning calorimetry (DSC) studies of a similarly ordered PSN indicate that at 346 K, a cubic-rhombohedral phase transition takes place [36]. Therefore, the sharp $\varepsilon_r^{\max}$ in the dielectric spectra can be ascribed to the phase transition from a cubic to rhombohedral structure. It should be noted that $\varepsilon_r^{\max}$ is significantly reduced and the transition temperature is decreased with respect to the disordered PSN [26,27,36]. Malibert *et al.* [27] and Perrin *et al.* [36] studied the influence of ordering on the dielectric behavior of a ceramic PSN. They observed that $\varepsilon_r^{\max}$ is reduced and that the transition temperature decreased with the increase in the degree of ordering. Perrin *et al.* also observed two distinct $\varepsilon_r^{\max}$ values corresponding to the disordered and the

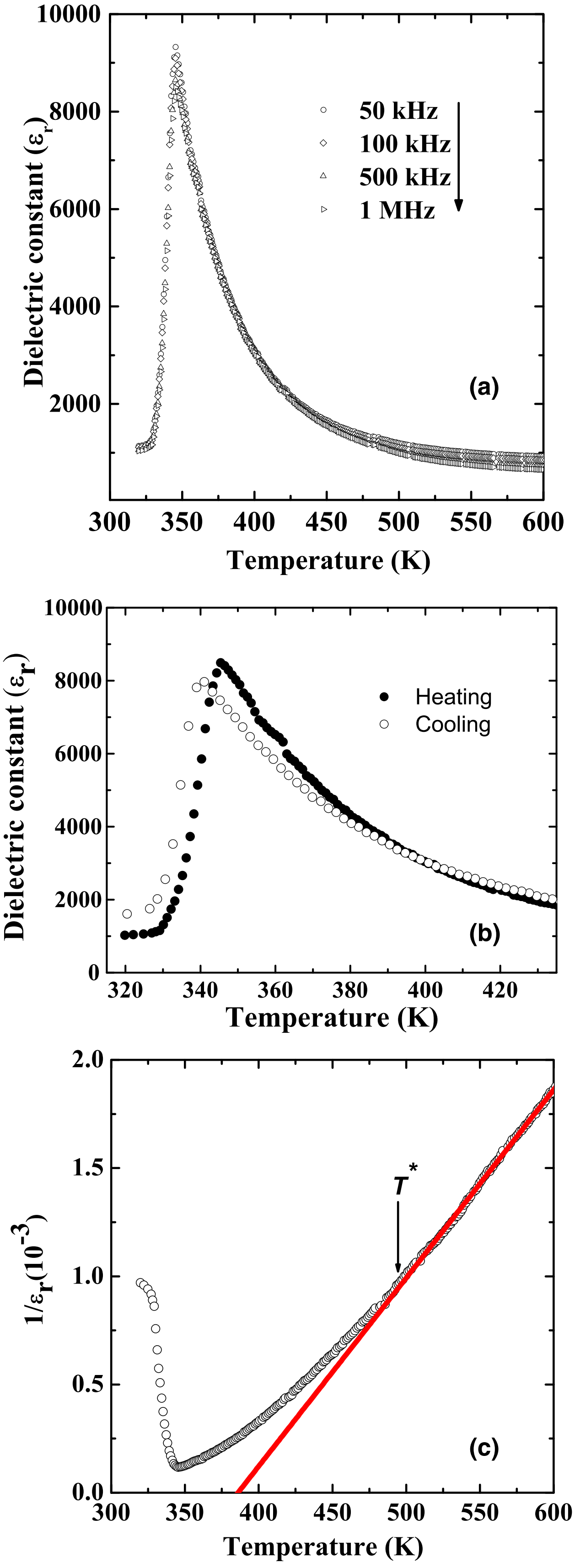

FIG. 2. (a) Low frequency dielectric dispersion of PSN. (b) Temperature dependence of ε_r measured during heating and cooling cycles. (c) Plot of $1/\varepsilon_r$ vs temperature T.

ordered regions of PSN [36]. They observed that for the ordered PSN ($S = 0.60$ and 0.85), the presence of the ordered region lowers the T_c of the disordered region. The observed $\varepsilon_r^{\max}$ in the present study is almost close to the ordered region of PSN reported by Perrin *et al.* for $S = 0.85$ [36]. However, we observed only single $\varepsilon_r^{\max}$ with no dielectric dispersion. It can also be noted that there is a small decrease in $\varepsilon_r^{\max}$ with the increase in frequency, suggesting the presence of the disordered region similar to that observed for $S = 0.85$ by Perrin *et al.* [36]. The observed single $\varepsilon_r^{\max}$ probably suggests that both the ordered and the disordered regions have the same transition temperatures. Figure 2(b) displays ε_r measured at 1 MHz during the heating and cooling cycles. A clear difference in the T_c of 5 °C observed between the heating and cooling cycles indicates the first order nature of the phase transition. It has been reported that the disordered PSN exhibits a first order ferroelectric phase transition below T_m with a large thermal hysteresis in T_c of about 10 °C between the heating and cooling cycles [26]. The thermal hysteresis of the transition temperature of the ordered PSN was found to be lower than that of the disordered PSN. In the plot of $1/\varepsilon_r$ vs T, as shown in Fig. 2(c), a clear departure from the Curie-Weiss behavior is observed at $T^* = 500\,\mathrm{K}$, the characteristic intermediate temperature. This means that the highly ordered PSN, while exhibiting a normal ferroelectric type transition at T_c, shows characteristic relaxor behavior far away from T_c. Based on the x-ray diffraction studies, it was observed that the disorder (static or dynamic) in the position of the Pb, Sc, and Nb ions, as well as the cooperative shifts of these ions relative to the oxygen network, remains the same for both the disordered and ordered PSN over a broad temperature range [27]. The polarization within the PNR, however, is predominantly caused by the dynamic disorder of the Pb ions [37,38]. The observed difference in the dielectric behavior between the disordered and ordered PSN, therefore, lies in the length scale and the time scale over which the correlation of such dynamic disorder of Pb ions occur. In other words, the difference in the low frequency dielectric behavior between the disordered and the ordered PSN essentially arises from the difference in the dynamic behavior of the PNRs.

The sharp dielectric anomaly observed at T_c in the highly ordered PSN is quite similar to that observed in the classical ABO_3 type ferroelectrics such as BT. It is well known that ABO_3 type ferroelectrics exhibit a first order ferroelectric phase transition with a sharp, frequency independent dielectric maxima at T_c. Although these systems are known to exhibit the soft mode behavior in the paraelectric phase, the Raman scattering and infrared reflectivity studies clearly showed that the cubic to tetragonal phase transition was not driven by the low frequency soft mode [39–42]. The IR reflectivity studies showed that the frequency of the soft mode does not drop to zero at T_c but saturates at a finite value well above T_c. It was also found that the soft mode alone could not account for the observed low frequency dielectric response in these systems. The cubic to tetragonal phase transition was found to be an order-disorder type associated with the relaxation dynamics of pretransitional polar clusters formed in the paraelectric phase [39–42]. The existence of such pretransitional polar clusters in these systems was clearly revealed through various studies [43–46]. Relaxor like properties of these polar clusters,

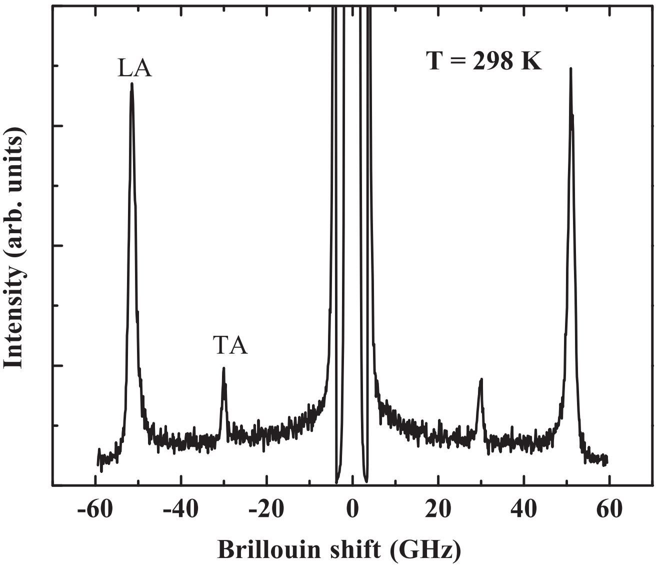

FIG. 3. Brillouin scattering spectrum of PSN at 298 K.

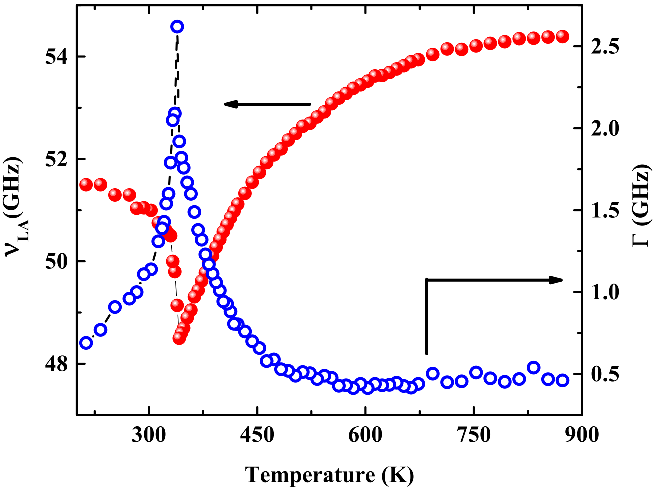

FIG. 4. Temperature dependences of Brillouin shift υ_{LA} (closed circles) and width Γ (open circles) of the LA phonon mode of PSN.

such as the existence of T_B and the intermediate temperature T^*, were revealed by AE studies in the paraelectric phase [47]. The acoustic phonon anomalies, the appearance of a strong central peak, and the critical slowing behavior have also been observed in the paraelectric phase of BT [48]. However, the size of the polar clusters in these systems is smaller, and their dynamics are much faster than that of the Pb-based relaxors [49]. Since the highly ordered PSN has weak REFs like that of BT, not only the low frequency dielectric behavior but also the dynamics of the PNRs in the relaxor phase are expected to be quite similar to that observed in the paraelectric phase of BT. This is indeed found to be the case, as shown by the Brillouin light scattering studies.

C. Brillouin scattering

The Brillouin scattering spectrum of the ordered PSN crystal at 298 K is shown in Fig. 3. The measurement was carried out upon cooling from 873 K. An intense longitudinal acoustic (LA) phonon peak around 50 GHz and a weak transverse acoustic (TA) mode at 30 GHz can be seen. The TA mode appears in the back scattering geometry as the room temperature structure of PSN is rhombohedral. However, the features of the TA mode are not discussed further, as it does not exhibit any systematic temperature dependence. Figure 4 shows the temperature dependence of the Brillouin shift υ_{LA} of the LA phonon mode and its width Γ. The frequency of the LA phonon exhibits a sharp minimum followed by a sharp maximum in width at $T_c = 342$ K, which is same as that seen in the dielectric anomaly measured during cooling. The width of the LA phonon shows a typical λ type behavior in the vicinity of T_c, similar to the disordered PSN [33]. As shown in Fig. 4, below 700 K, the frequency of the LA phonon mode begins to exhibit significant softening. This temperature in fact corresponds to T_B, where the PNRs begins to nucleate [25]. Therefore, the most likely origin of the softening of the LA phonon below T_B is due to the coupling of local polarization fluctuations of the PNRs with strain. The strong increase in the coupling between polarization and strain is clearly manifested at T^*, at which the width of the LA phonon begin to rise.

Depending on the nature of the coupling between the acoustic phonon and polarization, it is usual to distinguish between (a) the relaxation and (b) the fluctuation mechanisms of anomalous changes in the frequency and width of the LA phonon [50]. The relaxation mechanism arises due to the linear coupling of strain with polarization and is manifested only in the ordered phase below T_c where $\langle P\rangle \neq 0$. The relaxation mechanism, also known as the Landau-Khalatnikov (LK) mechanism, can qualitatively explain the relaxation behavior of the order parameter (polarization in the present case) in a material below T_c. The fluctuation mechanism, originating from the quadratic coupling of the polarization with strain, leads to the anomalies both above and below T_c. However, in the ordered phase below T_c, the fluctuation damping is much weaker than the damping due to the relaxation mechanism [50]. The ferroelectric state below T_c in PSN is characterized by a nonvanishing macroscopic spontaneous polarization ($\langle P\rangle \neq 0$) along the $\langle 111\rangle$ direction [27]. In this case, linear coupling, linear in the order parameter and strain, seems to be the dominant term in the coupling free energy F_c [50].

In the Brillouin scattering studies of the relaxorlike system $\mathrm{Rb}_{1-x}(\mathrm{NH}_4)_x\mathrm{H}_2\mathrm{PO}_4$ with $x = 0.35$, the temperature dependence of the width of the LA phonon corresponding to quasistatic polarization δP_s was shown to be equivalent to the LK type mechanism [51]. In the relaxor phase of the PSN, the rapid increase in the width of the LA phonon below T^* evidently arises due to the development of the quasistatic part δP_s. Moreover, since the local structure inside the PNR is noncentrosymmetric [52,53], a linear coupling between the polarization and strain can be allowed [54]. Hence, it is possible to use the LK relaxation mechanism in the quasistatic region below T^* for analyzing the relaxation time of the order parameter. We therefore calculated the relaxation time of the order parameter both in the ferroelectric phase below T_c and in the quasistatic region below T^* (in the temperature range between T^* and T_c) using the LK relaxation mechanism. The relaxation time τ, of the order parameter in the LK mechanism

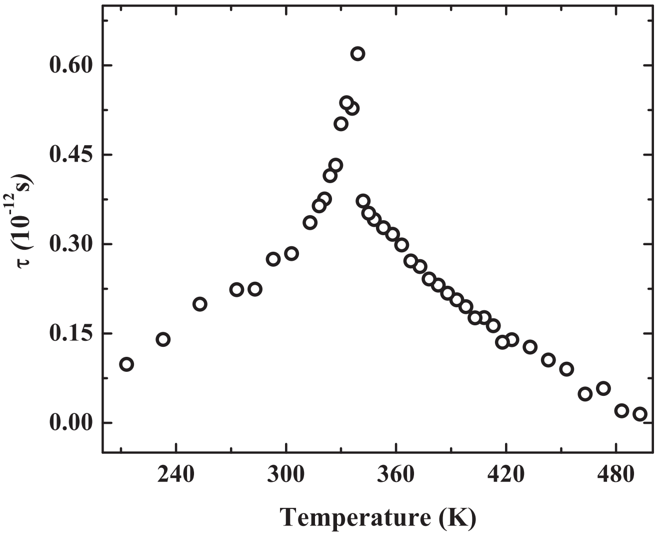

FIG. 5. Temperature dependence of relaxation time τ.

is given by the following expression [54],

$$\frac{1}{2\pi\tau} = \frac{\upsilon_\infty{}^2 - \upsilon^2(T)}{\Gamma(T) - \Gamma_\infty}, \tag{1}$$

where $\upsilon(\Gamma)$ is the frequency of the LA phonon (width) at a given temperature and $\upsilon_\infty(\Gamma_\infty)$ is the frequency of the LA phonon (width) not affected by the structural phase transition. The details of the derivation of Eq. (1) are given in Refs. [50] and [54]. For the calculation of the relaxation time, constant values of υ and Γ in the high temperature limit were used for υ_∞ (54.4 GHz) and Γ_∞ (0.5 GHz). The temperature dependence of the relaxation time τ of the order parameter is shown in Fig. 5. In the ferroelectric as well as the relaxor phase, the relaxation time of the order parameter exhibits a critical slowing down on approaching T_c. The temperature dependence of the relaxation rate shown in Fig. 6 exhibits an approximately linear behavior, where $1/\tau$ is found to satisfy the following relation [55,56],

$$\frac{1}{\tau} = \frac{1}{\tau_o}\frac{|T - T_o|}{T_o}. \tag{2}$$

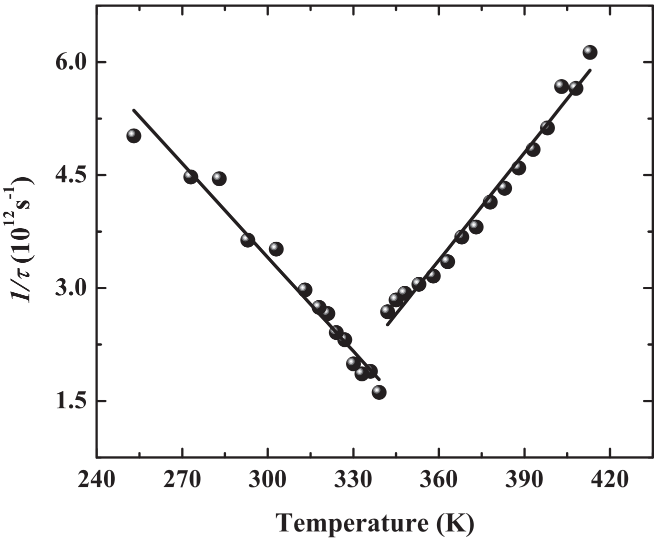

FIG. 6. $1/\tau$ as a function of temperature T. Points are the experimental data, and the solid line is the fit of Eq. (2).

For the cubic phase, $T_\text{o} = 290\,\text{K}$ is the extrapolated temperature above T_c, where $1/\tau$ is zero and $\tau_\text{o} = 0.07$ ps is equal to the relaxation time at $2T_\text{o}$, about 100 K below T_B. Therefore, τ_o is the relaxation time of an uncorrelated dynamic PNR at a very high temperature. For the rhombohedral phase, $T_\text{o} = 382\,\text{K}$ is the extrapolated temperature below T_c, where $1/\tau$ is zero and $\tau_\text{o} = 0.06$ ps is equal to the relaxation time at 0 K. However, the quantum fluctuations may suppress such a linear dependence at very low temperatures.

It is interesting to note that τ for the highly ordered PSN is more than one order of magnitude (30 times near T_c) shorter than that of the disordered PSN (Fig. 2 of Ref. [33]). It is also very interesting to note that the relaxation rate $(1/\tau)$ is very close to that obtained for BT [$1/\tau_{LA}$ in Fig. 9(a) of Ref. [48]] not only in terms of the order of the magnitude but also in the numerical value. The value of τ_o obtained in the present study above T_c is found to be comparable to that of BT (0.09 ps above T_c) [57]. This suggests that the dynamic behavior of the PNRs in the highly ordered PSN is quite similar to that in BT. The observed difference (with disordered PSN) and similarity (with BT) in the relaxation time can be qualitatively discussed in terms of the difference and the similarity in the strength of the REFs. In the case of BT, which has weak REFs, below T^*, as previously discussed in Sect. III.B, the correlations between the polar clusters are weak, and their dynamics are much faster than that of the typical Pb-based relaxors [49,58]. In the highly ordered PSN, the NMR study clearly shows that the local quasistatic polarization appears not at T^* but very close to T_c. The first principle calculation also shows that for the disordered PSN, the local quasistatic polarization begins to appear around T^*, while for the ordered PSN such a polarization of comparable magnitude appears very close to T_c, which is well below T^* [25]. This means that the correlation between the PNRs gets weaker for the ordered PSN than that of the disordered one below T^*. Moreover, according to the random field model [9,30] as well as the theoretical analysis by Grinberg *et al.* [31], the correlations between the PNRs decrease due to the weakening of the random fields. All these studies suggest that in the case of the highly ordered PSN, correlations between the PNRs decrease due to weakening of the REFs below T^*. The decrease in the correlations between the PNRs results in the weakening of the coupling between the polarization and strain that could lead to the faster relaxation of the order parameter than that observed for the disordered PSN. The observed similarity in $1/\tau$ clearly indicates that the size and hence the dynamics of the PNRs in the ordered PSN are similar to that of BT.

As in the case of BT, a soft mode-like behavior of the low frequency optical phonon mode is observed in PSN both above and below T_c [59,60]. The anomalous softening of a localized Pb vibrational mode takes place in the temperature range of 800–500 K and levels off in the temperature range of 500–300 K. Once again, the same mode exhibits a softening behavior towards T_c upon heating from 100 K [60]. The linear decrease in the square of the frequency of this mode in the ferroelectric phase is consistent with the behavior of the ferroelectric soft mode [59]. However, it is not the soft mode but the dynamics of the PNRs that dominate the low frequency dielectric response of the PSN [59]. Therefore, in terms of the observed similarities in the dielectric anomalies at T_c, the first order nature of the phase transition, and the relaxation dynamics of PNRs in the relaxor phase and along with the existence of the soft mode, it appears that the phase transition behavior of the highly ordered PSN is very similar to that of BT. In both cases, it is not the soft mode, but the order-disorder process associated with the relaxation dynamics of the PNRs that drives the phase transition. Similarly to BT, the size of the PNRs in the ordered PSN appears to be smaller, their relaxation takes place at much higher frequencies, and hence the low frequency dielectric anomaly near T_c does not exhibit any frequency dependence.

IV. CONCLUSION

We have examined the ferroelectric phase transition behavior in the highly *B* site ordered PSN crystal by dielectric and Brillouin spectroscopy. The temperature dependence of the dielectric permittivity is found to exhibit a sharp and dispersionless peak at the Curie temperature T_c. The ordered PSN exhibits a first order phase transition from the cubic relaxor to rhombohedral ferroelectric phase. Above T_c, the dielectric permittivity showed a noticeable deviation from the Curie-Weiss behavior at $T^* = 500\,\mathrm{K}$, the characteristic intermediate temperature. The LA phonon frequency exhibits a sharp minimum in the frequency followed by the sharp maximum of the width at T_c. The relaxation time of the order parameter below and above T_c was found to be more than one order of magnitude shorter than that of the disordered PSN. The critical slowing down of the relaxation time observed in the quasistatic phase below T^* is found to be very close to that observed in the paraelectric phase of the classical ferroelectric BT. The observed similarity in the dielectric behavior and the relaxation time of the order parameter suggests that the phase transition behavior of the ordered PSN is quite similar to that of BT.

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