Classical ferroelectriclike behavior of highly ordered Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3} studied by dielectric and Brillouin scattering spectroscopy

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The dynamical aspects of the PNRs have been extensively studied in the prototype RFEs such as Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN) and Pb(Zn\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{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 ± 30 K) for most of the Pb-based RFE systems [25].

The 1:1 type ferroelectric relaxors Pb($B'_{1/2}$,$B''_{1/2}$)O\textsubscript{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\textsubscript{3} type compounds exhibit different ferroelectric behavior, depending on the degree of B site ordering [26]. The disordered Pb(Sc\textsubscript{1/2}Nb\textsubscript{1/2})O\textsubscript{3} (PSN) shows a relaxor type ferroelectric behavior, whereas the ordered one exhibits normal ferroelectric 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...
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 \( \text{Pb}(\text{Zr},\text{Ti})\text{O}_3 \) (PZT) and \( \text{BaTiO}_3 \) (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 \( \text{PbO-PbF}_2-\text{B}_2\text{O}_3 \) used in the weight ratio of PSN:\( \text{PbO-PbF}_2-\text{B}_2\text{O}_3 = 0.15:0.40:0.40:0.05 \). 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 °C/h 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.

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\( \theta \approx 19° \) 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 \( S = \left( \frac{I_{111}}{I_{200}} \right)^{1/2} \) was calculated from 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 \( \Delta T = T_m(1 \text{ MHz}) - T_m(1 \text{ kHz}) \) 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 \( \varepsilon_r^{\text{max}} \) in the dielectric spectra can be ascribed to the phase transition from a cubic to rhombohedral structure. It should be noted that \( \varepsilon_r^{\text{max}} \) 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 \( \varepsilon_r^{\text{max}} \) is reduced and that the transition temperature decreased with the increase in the degree of ordering. Perrin et al. also observed two distinct \( \varepsilon_r^{\text{max}} \) values corresponding to the disordered and the

![Graph](image-url)
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 $\varepsilon_{\text{max}}^r$ 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 $\varepsilon_{\text{max}}^r$ with no dielectric dispersion. It can also be noted that there is a small decrease in $\varepsilon_{\text{max}}^r$ 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 $\varepsilon_{\text{max}}^r$ probably suggests that both the ordered and the disordered regions have the same transition temperatures. Figure 2(b) displays $\varepsilon_r$ 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 $T^* = 500$ 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,

![Figure 2](image-url)

**FIG. 2.** (a) Low frequency dielectric dispersion of PSN. (b) Temperature dependence of $\varepsilon_r$ measured during heating and cooling cycles. (c) Plot of $1/\varepsilon_r$ vs temperature $T$. 
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 \( \nu_{LA} \) of the LA phonon mode and its width \( \Gamma \). 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 \( \lambda \) 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 non-vanishing 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 Rb\(_{1-x}\)(NH\(_4\))\(_x\)H\(_2\)PO\(_4\) with \( x = 0.35 \), the temperature dependence of the width of the LA phonon corresponding to quasistatic polarization \( \delta P \), 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 \( \delta P_{st} \). 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 \( \tau \), of the order parameter in the LK mechanism
is given by the following expression [54],
\[
\frac{1}{\tau} = \frac{v^2 - v^2(T)}{\Gamma(T) - \Gamma_{\infty}},
\]
where \(v(\Gamma)\) is the frequency of the LA phonon (width) at a
given temperature and \(v_{\infty}(\Gamma_{\infty})\) 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 \(v\) and \(\Gamma\) in the high temperature limit were used
for \(v_{\infty}\) (54.4 GHz) and \(\Gamma_{\infty}\) (0.5 GHz). The temperature
dependence of the relaxation time \(\tau\) 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],
\[
\frac{1}{\tau} = \frac{1}{\tau_o} \left(\frac{T - T_o}{T_o}\right).
\]

For the cubic phase, \(T_o = 290\,\text{K}\) is the extrapolated
temperature above \(T_c\), where \(1/\tau\) is zero and \(\tau_o = 0.07\,\text{ps}\)
is equal to the relaxation time at \(2T_o\), about 100 K below \(T_B\).
Therefore, \(\tau_o\) is the relaxation time of an uncorrelated dynamic
PNR at a very high temperature. For the rhombohedral phase,
\(T_o = 382\,\text{K}\) is the extrapolated temperature below \(T_c\), where
\(1/\tau\) is zero and \(\tau_o = 0.06\,\text{ps}\) 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 \(\tau\) 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 \(\tau_o\) 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 \( T^* = 500 \text{ K} \), 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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