

Intrinsic and extrinsic central peaks in the Brillouin light scattering spectrum of the uniaxial ferroelectric relaxor $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$

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Broadband Brillouin scattering of $\text{Sr}_{0.61}\text{Ba}_{0.39}\text{Nb}_2\text{O}_6$ uniaxial ferroelectric relaxors has been investigated. One broader central peak (CP) appeared at all temperatures and was ascribed to light-induced charge carriers, while the other narrower CP began to appear near the Burns temperature suggesting its origin from the formation of polar nanoregions. Temperature evolution of both CPs indicated one characteristic temperature near 450 K at which the volume and/or density of polar clusters with broken inversion symmetry began to increase resulting in a substantial increase of the intensities of both CPs and coupling between them. © 2007 American Institute of Physics. [DOI: 10.1063/1.2772771]

Strontium barium niobate, $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (SBN), has attracted increasing attention for many applications due to their superior pyroelectric, piezoelectric, photorefractive, and nonlinear optic properties.¹ Congruently melting SBN with $x=0.61$, abbreviated as SBN-61, belongs to the unfilled tetragonal tungsten bronze (TTB) ferroelectric oxide family. Since 1/6 of the 12-fold and 15-fold coordinated A sites are empty in the TTB structure, charge disorder in the cation distribution, which is expected to become sources of the quenched random electric fields, provides the ferroelectric phase transition of SBN-61 from paraelectric $4/mmm$ to polar $4mm$ symmetry with diffuse relaxor characteristics. In contrast to the quasicontinuous order parameter in cubic relaxors such as lead magnoniobate,² SBN is characterized by a one-component order parameter parallel to the tetragonal polar axis. Owing to the uniaxial nature of the order parameter and the existence of random fields, the diffuse phase transition of SBN-61 has been interpreted in the framework of a three-dimensional random-field Ising model.³

The formation of polar nanoregions (PNRs) at a certain temperature, the so-called Burns temperature (T_B), has been suggested as a common feature of ferroelectric relaxors. The existence of PNRs has been indicated by unusual properties such as deviations of the index of refraction and the strain from high-temperature linearities,⁴⁻⁶ appearance of diffuse neutron scattering,⁷ quasielastic central peaks (CPs) observed in the light scattering spectrum,⁸ etc. The estimated T_B of SBN-61 is in the range of 620–750 K.⁴⁻⁶ Inelastic Brillouin light scattering can be a very useful tool for probing the dynamics of PNRs because the characteristic time scale of CPs related to the dynamics of PNRs can be located in the Brillouin frequency window. Jiang *et al.*⁹ reported detailed Brillouin study on SBN-61 including polarization analysis of acoustic modes and quasielastic CPs. The CP was observed in a wide temperature range, which was the strongest at the polarized $x(zz)\bar{x}$ scattering geometry, where x and z denote tetragonal axes. This result is consistent with the uniaxial character of the order parameter in TTB SBN-61. However,

the temperature dependence of the relaxation time estimated from the width of CP showed an abnormal behavior that could not be understood exactly.¹⁰

The purpose of the present letter is to report CP behaviors of SBN-61 in wide temperature and frequency ranges and thus to reveal a clear correlation between the dynamics of PNRs and temperature evolution of CPs in SBN-61.

Striation-free single crystals of tetragonal SBN-61 were grown with the Czochralski method. The Brillouin scattering system with a 3+3 pass Sandercock-type tandem Fabry-Perot interferometer combined by a diode-pumped solid state laser at a wavelength of 532 nm has been used to measure the Brillouin spectra of SBN-61. Since the elastic scattering is very strong at a backward scattering geometry, a special right-angle scattering geometry was used for the measurement without any significant disturbance of the elastic scattering.¹¹ In this scattering geometry, the vertically polarized (VV) spectrum was obtained at the $\bar{a}(zz)\bar{b}$ scattering geometry, where \bar{a} and \bar{b} denote the directions of the incident and scattered light in the plane perpendicular to the z axis. \bar{a} and \bar{b} were inclined 45° with respect to the tetragonal x and y axes, and the phonon propagation direction was along the tetragonal $x(=y)$ axis. In order to cover a frequency range for probing CP as wide as possible, two free spectral ranges (FSRs) of 300 and 50 GHz were chosen and used.

Figure 1 shows two Brillouin spectra of SBN-61, one at the highest measurement temperature of 873 K above T_B and the other at 698 K near T_B . Although the intensity is quite small, a weak CP can be seen even at 873 K at which no PNR is expected to exist. CP at this temperature can be fitted by a single Lorentzian function centered at zero frequency. Similar CPs were also discovered by neutron scattering study on SBN-70 and SBN-45.¹² The full width was approximately 6 meV which corresponds to ~ 1450 GHz, and the origin was ascribed to the anharmonic hopping motion of Ba/Sr atoms. It is well known that ionic hopping can give rise to quasielastic CP in light scattering spectrum.¹³ However, this interpretation is questionable because hopping processes of A-site ions in SBN would destroy the quenched charge disorder, which is essential for the relaxor nature of SBN-61.

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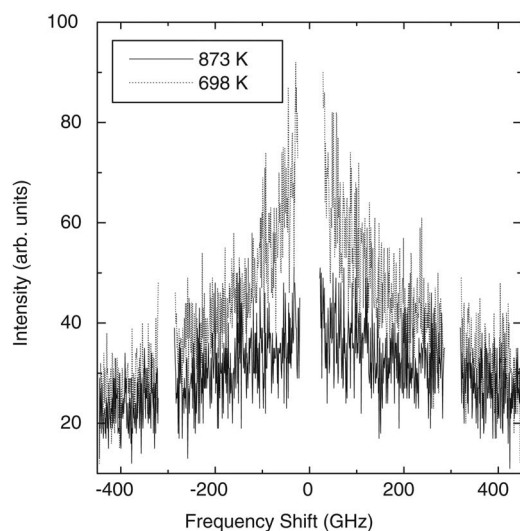


FIG. 1. Polarized (VV) Brillouin spectra of SBN-61 measured at 873 and 698 K.

Upon cooling, CP does not show significant changes down to about 750 K, below which an additional contribution to the quasielastic spectrum develops, as can be seen in Fig. 1. Figure 2 shows Brillouin spectra of SBN-61 recorded at three selected temperatures. Each spectrum consists of two acoustic modes overlapped on broad CPs. All spectra below 750 K could be fitted by two Lorentzian functions; one for the narrower CP and the other for the broader CP. The white circles represent experimental data and the solid line is the fitted result. Two dashed lines denote two CPs obtained from the fitting procedure. The other two fitting lines for the acoustic modes were omitted for better clarity. The ordinate scale of three figures is the same, and hence, it is clear that

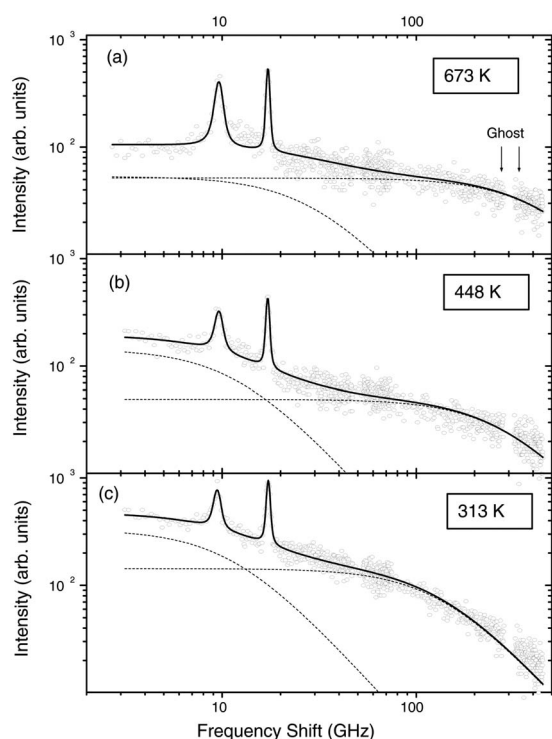


FIG. 2. Polarized Brillouin spectra measured at (a) 673 (b) 448, and (c) 313 K. Solid lines denote the full fitted line for the spectrum while the two dashed lines correspond to two CPs. The ordinate scale is the same for the three figures.

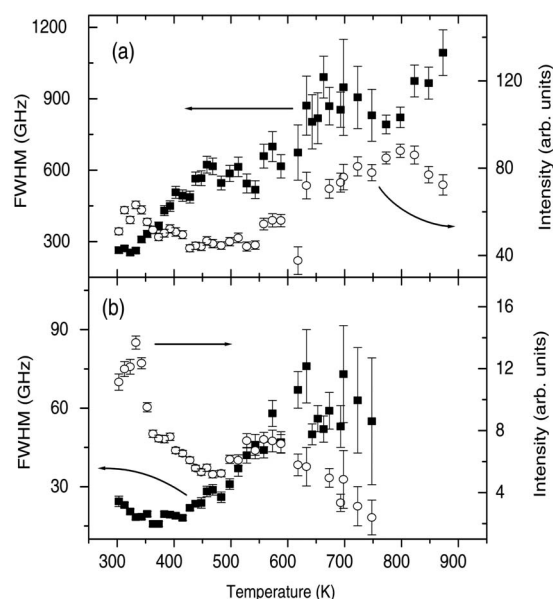


FIG. 3. Temperature dependences of the full width at half maximum (FWHM) and the integrated intensity of (a) the wide CP and (b) the narrow CP.

the intensities and half width of both CPs are changing substantially with decreasing temperature.

Figures 3(a) and 3(b) summarize the fitted results, i.e., the temperature dependences of the full width at half maximum (FWHM) and the integrated intensity for broader and narrower CPs, respectively. At temperatures above $T_B \sim 750$ K, only one weak CP appears. Near and below $T_B \sim 750$ K, additional CP appears in a narrower spectral range, which can thus be correlated to the formation of PNRs. The FWHM of this component decreases with lowering temperature toward the diffuse phase transition temperature (T_m), reflecting the slowing down of the dynamics of PNRs. The FWHM of the broader CP also decreases in the temperature range between 700 and 450 K, but the change seems to be mild compared to that of the narrower CP. Upon further cooling, the integrated intensity of both components begins to increase and the FWHM of the wider CP decreases abruptly at about 450 K. The intensity of the narrow CP shows a sharp increase at T_m and both components show intensity maxima at about 332 K. Concomitant decrease in the intensity of both CPs at lower temperatures suggest progressive arrest or freezing of dynamical degrees of freedom related to both CPs.

In order to reveal whether the origin of the broader CP is intrinsic or extrinsic, the intensity of this component was monitored as a function of the laser power at selected temperatures. Figure 4 shows the CP intensity at 200 GHz, where the contribution from narrow CP is negligible, measured at 373 K, but almost the same dependence has been observed at other temperatures. The solid line in this figure is a guide to the eye for the case where the intensity of the broad CP is exactly proportional to the laser power. It is clear from this figure that the CP intensity at 200 GHz grows much faster than the increase of the laser power. This result indicates that the density of the scattering centers is changing with the laser power and thus the origin of the broad CP is, in part, extrinsic. Considering the photorefractive properties and nonlinear intensity dependence of photoconductivity on the light intensity in SBN,¹⁴ probably, light-induced charge

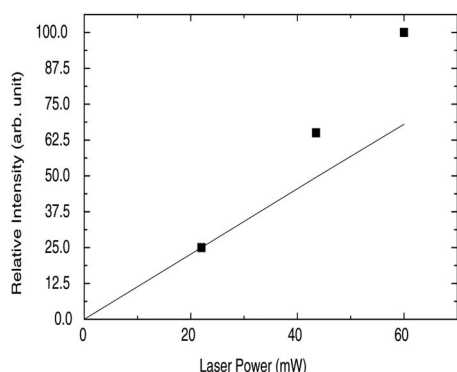


FIG. 4. Laser-power dependence of the light scattering intensity at 373 K at the frequency shift of 200 GHz where the contribution from narrow CP is negligible. The solid line is a guide to the eyes for the case where the intensity of the broad CP is linearly proportional to the laser power.

carriers such as conduction electrons and their trapping by A-site ions seem to be responsible for the polarization fluctuations contributing to the appearance of the broad CP rather than the hopping processes of A-site ions suggested by Prokert.¹² However, contribution from hopping processes of A-site ions may not completely be discarded at high temperatures far above T_B because the dc conductivity exhibits a substantial increase and the A-site vacancies seem to redistribute by thermal energies above T_B .^{15,16} Accurate separation of these two effects could not be carried out from the present study, which needs a more sophisticated approach.

From the above results, several noteworthy findings can be derived as follows. First, thanks to the wide spectral range, it was revealed that the detailed spectral shape of the broad quasielastic spectrum could be explained by assuming two CPs indicating two microscopic origins for the observed polarization fluctuations. The broader CP exists at all measuring temperatures from 873 to 300 K. It is tentatively ascribed to the polarization fluctuations by the photoexcitation of charge carriers, their transfer and trapping by A-site ions in the unfilled TTB structure. The narrow CP begins to appear at about 700–750 K around T_B , which indicates that its origin is the dynamic relaxation of PNRs. Broadband dielectric studies on SBN revealed distribution of relaxation times, which showed splitting of the relaxation spectrum into at least two relaxation processes upon cooling,^{17,18} and the present study suggests a possible correlation between the narrow CP and the high-frequency relaxation process observed in the dielectric spectrum.

Second, both CP components exhibit slowing down with decreasing temperature. The FWHM of the wide CP can be related to the hopping rate or time of flight of the charge carriers between sites, which is expected to become smaller upon cooling resulting in the decrease in FWHM. On the other hand, the FWHM of the narrow CP is inversely proportional to the relaxation time of the PNRs and thus decreases, reflecting the slowing down of PNRs.

Third, substantial changes in the spectral features of both CPs can be seen at ~ 450 K, at which the integrated intensities of both CPs increase and the FWHM of the wide CP decreases significantly. This temperature is the same one at which the intensity of the second harmonic generation signal suddenly increases upon cooling.¹⁹ These results clearly indicate that the volume and/or density of polar clusters with broken inversion symmetry begins to increase substantially at about 450 K. Therefore, this temperature may be said to

be the temperature at which the PNRs become long lived and more correlated than at higher temperatures. This result is also consistent with the growing signal of the second harmonic nonlinear susceptibility below ~ 400 K.²⁰ It is worth noting that in other lead-based perovskite relaxors, additional characteristic temperature other than T_B has also been suggested by Raman and Brillouin studies.^{21,22}

To summarize, the Brillouin scattering of SBN-61 has been investigated in wide frequency and temperature ranges. It was found that the quasielastic light scattering spectrum consisted of two-component CPs, the wider one existing at all temperatures and the narrower one appearing near T_B . The former was ascribed to the photoexcitation of charge carriers and trapping by A-site ions occurring in the unfilled TTB structure, while the latter was to the dynamics of PNRs. From the temperature dependences of the FWHM and the intensity of CPs, one characteristic temperature ~ 450 K much lower than T_B was identified at which the volume and/or density of polar clusters with broken inversion symmetry began to increase resulting in a substantial increase of the intensities of two CPs and the coupling between them.

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