Elastic anomaly and order-disorder nature of multiferroic barium sodium niobate studied by broadband brillouin scattering

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Abstract. The successive phase transitions of multiferroic barium sodium niobate, $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (BNN), were studied by Brillouin scattering. The LA, TA modes, and central peak were measured in a large temperature range from room temperature up to 750 °C. In the vicinity of a ferroelectric phase transition at about $T_C = 585$ °C from the prototypic tetragonal $4/mmm$ to ferroelectric $4mm$ phases, elastic anomaly was observed for LA and TA modes. In addition, the order-disorder nature was observed by the temperature dependence of a central peak. For further cooling another elastic anomaly was also observed in the vicinity of a ferroelastic incommensurate phase transition at about $T_{IC} = 285$ °C into orthorhombic $2mm$ phase with the appearance of incommensurate modulation. The large thermal hysteresis of elastic anomaly near $T_{IC}$ can be attributed the typical feature of the type III incommensurate phase transition predicted recently by Ishibashi and Iwata (2013 J. Phys. Soc. Jpn. 82 044703).

1. Introduction

Ferroic crystals have two or more orientation states without external magnetic, electric and stress fields, and can change from one to another state by the application of external fields [1]. Here any two of orientation states are identical or enatiomorphic in crystal structure, while they are different with the direction of arrangements of atoms or spins. Ferromagnetic, ferroelectric, and ferroelastic crystals possess a spontaneous magnetization, spontaneous polarization, and spontaneous strain, respectively. The term ‘multiferroic’ was originally understood as the simultaneous presence of two or all three primary ferroic properties in the same phase, i.e., ferromagnetism, ferroelectricity and ferroelasticity [2]. Barium sodium niobate $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ (BNN) with tungsten bronze structure (figure 1) is ferroelectric and ferroelastic at room temperature [3,4]. Multiferroic BNN undergoes successive phase transitions on cooling from a prototypic paraelectric and paraelastic tetragonal ($4/mmm$) phase. About 560 °C it transforms into a ferroelectric tetragonal $4mm$ phase with a spontaneous polarization along the $c$-axis (ferroelectric phase transition), and about 300 °C, it transforms into a ferroelastic orthorhombic $2mm$ phase with a spontaneous strain $e_c$. For further cooling the reentrant phase transition into a ferroelectric paraelastic phase with tetragonal $4mm$ occurs at about -168 °C. It was also reported that the lower ferroelastic to paraelastic phase transition temperature increases under high pressure, and at room temperature it occurs at about 2.2 GPa [5,6]. Moreover, in BNN, the incommensurability measured from the point [1/4, 1/4, (1/2)] in the Brillouin zone is known to remain down to very low...
temperatures. Very recently this incommensurate phase transition of BNN is assigned to the new type III incommensurate phase, which is stabilized by the freezing of the soft mode belonging the lower branch induced by the parabolic splitting [7].

Figure 1 shows the tungsten-bronze structure of BNN. The A\textsubscript{1} and A\textsubscript{2} sites are occupied by Na and Ba, respectively. The B\textsubscript{1} and B\textsubscript{2} sites are occupied by Nb, and the C\textsubscript{1} sites are vacancies. The a-axis and b-axis are rotated 45 degrees when the structure changes from tetragonal to orthorhombic system. There is no disorder of cations and vacancy in A\textsubscript{1} and A\textsubscript{2} sites, and BNN undergoes a normal ferroelectric phase transition in contrast to typical uniaxial relaxor Sr\textsubscript{x}Ba\textsubscript{1-x}Nb\textsubscript{2}O\textsubscript{6} in which random quenched fields appears owing to the disorder in A\textsubscript{1} and A\textsubscript{2} sites. As to the mechanism of ferroelectricity, up to the present there is no report of soft optic mode observed by Raman scattering, inelastic neutron and X-ray scattering experiments. The dispersion in the GHz range, which gives the possibility of order-disorder nature, was suggested by ultrasonic study [8]. Nevertheless, there is still no report of critical slowing down near the Curie temperature. Regarding the elastic anomaly, the temperature dependence of elastic properties of BNN was recently studied by the resonant ultrasonic spectroscopy (RUS), and the lock-in transition was detected at -233 °C [9]. However in RUS, it is difficult to measure elastic properties when the acoustic absorption increases markedly near a phase transition temperature or ferroic multi-domains state appears. While in Brillouin scattering it is possible to measure even if the remarkable increase of absorption occurs. In the present work order-disorder nature and elastic anomaly in the GHz frequency range were studied by Brillouin scattering in the large temperature range.

Figure 1. Tungsten-bronze-type structure on the (001) plane. The orthorhombic cell and the tetragonal cell are shown by solid and dotted lines, respectively.

2. Experimental
The colorless and transparent BNN crystal studied was grown by Czochralski method in Tamagawa factory, NEC. The (110) plate with the size of 2.65 × 2.25 × 0.68 mm with two optically polished surfaces was used for Brillouin scattering measurement. Brillouin scattering spectra were measured at the backward scattering geometry using a tandem Fabry-Perot interferometer and a conventional photon counting system. A single frequency green YAG laser (λ = 532 nm) with power of 100 mw was used as an exciting source. The light spot size at a sample surface was about 10 μm using the optical microscope (BX-60) [10]. The temperature of a sample was controlled by the heating stage of a T1500 (high T-Linkam) from room temperature up to 750 °C. All Brillouin scattering spectra were measured in the condition that the free spectral range (FSR) and the scan range are 75 GHz, ± 65 GHz, respectively.
3. Results and Discussion

3.1. Brillouin scattering

By measuring Brillouin scattering, we can study sound velocity of acoustic attenuation of longitudinal acoustic (LA) and transverse acoustic (TA) modes and the relaxation process in the GHz range. The LA and TA sound velocity $V_L$ and $V_T$, and their acoustic attenuation coefficients $\alpha_L$ and $\alpha_T$ were calculated from the Brillouin shift $\nu_B$ and the width $\Gamma_B$ of LA and TA modes, respectively, by the eqs. (1) and (2),

$$V_i = \frac{\lambda_0 \nu_B}{2n \sin(\theta/2)},$$

and

$$\alpha_i = \frac{\pi \Gamma_B}{V_i},$$

where $i$ denotes LA or TA, $n$, $\lambda_0$, $\theta$ is refractive index, the wavelength of incident beam (532 nm), scattering angle (180°), respectively. As to the relaxation process of polarization fluctuations in the GHz frequency range, we can determine the relaxation time $\tau$ by the equation,

$$\tau = \frac{1}{\pi \Gamma_{CP}},$$

where $\Gamma_{CP}$ is the width of a central peak. Therefore, in the study of a phase transition Brillouin scattering is the powerful tool to investigate not only elastic anomaly using LA and TA peaks but also relaxation process related to a central peak [10].

3.2. Ferroelectric phase transition

![Brillouin scattering spectra of BNN. CP, LA, and TA denote a central peak, a longitudinal acoustic mode, and a transverse acoustic mode, respectively.](image)

**Figure 2.** Brillouin scattering spectra of BNN. CP, LA, and TA denote a central peak, a longitudinal acoustic mode, and a transverse acoustic mode, respectively.

Figure 2 shows the temperature dependence of Brillouin scattering spectra. LA and TA modes are clearly observed as sharp peaks at about 58 and 30 GHz, respectively. In addition a central peak (CP) is observed
at zero frequency shift near the ferroelectric phase transition temperature, $T_C = 585 \, ^\circ \text{C}$. The CP appears gradually below $T_C$, and its intensity shows the maximum at $T_C$.

Figure 3. The temperature dependence of the relaxation time of BNN determined by the width of a central peak on heating.

Figure 3 shows the temperature dependence of relaxation time. The critical slowing down is clearly observed near $T_C$. According the IR study, no soft mode was observed down to 15 cm$^{-1}$, while the relaxation mode was not observed in their far IR measurement [11]. This result of figure 3 is the clear evidence to confirm the fact that the ferroelectricity of BNN is not displacive type but order-disorder type.

Figure 4. Sound velocity of longitudinal acoustic (LA) mode and transverse acoustic (TA) mode.
Next, we discuss the elastic anomaly near \( T_c \). Figure 4 shows the temperature dependence of LA and TA sound velocity with the propagation along the [110] direction. Above \( T_c \), the softening of both LA and TA velocities was observed. For further cooling both velocities markedly decrease. In the typical relaxor SBN, such an elastic anomaly shows broadening near \( T_c \) [12]. Figure 5 shows the temperature dependence of sound attenuation coefficient of TA mode with the propagation direction along the [110] direction. The attenuation of TA mode shows the sharp divergence in the vicinity of \( T_c \), and it is the typical behaviour of a nearly second order phase transition.

![Figure 5. Temperature dependence of the attenuation coefficient of TA mode.](image)

3.3. Ferroelastic incommensurate phase transition

BNN undergoes the incommensurate phase transition at about 300 °C, and spontaneous shear strain appears perpendicular to the \( c \)-axis [4]. In figure 4 the LA velocity shows the broad minimum near \( T_{IC} = 285 \) °C, and the attenuation of TA mode shows a broad peak on the heating near \( T_{IC} \) as shown in figure 5. In contrast, on cooling from high temperatures, it is almost constant near \( T_{IC} \). Such a large thermal hysteresis cannot be occurred in a normal ferroelastic phase transition. It is attributed to the typical nature of incommensurate phase transition. The lattice instability of the incommensurate phase occurs near the point [1/4, 1/4, 1/2] at the Brillouin zone, while the soft mode instability occurs at the M-point [1/2, 1/2, 0] which is far from [1/4, 1/4, 1/2]. On heating the incommensurate modulation disappears easily, while on cooling it needs a long time to form the incommensurate modulation. Since the incommensurate structure is connected to macroscopic shear strain in the new type III incommensurate phase, the thermal hysteresis appears strongly in attenuation of TA mode, while not remarkable in that of LA mode.

4. Conclusion

The Brillouin scattering of a multiferroic \( \text{Ba}_2\text{NaNb}_5\text{O}_{15} \) crystal was studied to clarify the dynamical properties on both ferroelectric and ferroelastic phase transitions. The LA, TA modes, and central peak were measured in a large temperature range from room temperature up to 750 °C. In the vicinity of a ferroelectric phase transition at about \( T_c = 585 \) °C from the prototypic tetragonal \( 4/mmm \) to ferroelectric \( 4mm \) phases, elastic anomaly was observed for LA and TA modes. In addition, the order-disorder nature was confirmed by the observation of critical slowing down. For further cooling elastic anomaly was also observed in the vicinity of a ferroelastic incommensurate phase transition at about \( T_{IC} = 285 \) °C into orthorhombic \( 2mm \) phase with the incommensurate modulation. The large thermal hysteresis of elastic
anomaly of TA mode near $T_{ic}$ can be attributed the typical feature of the type III incommensurate phase transition predicted recently by Ishibashi and Iwata.

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References

[1] Aizu K 1970 Phys. Rev. B 2 754
[2] Schmid H 1994 Ferroelectrics 162 665
[3] Aizu K 1976 J. Phys. Soc. Jpn. 41 880
[4] Toledano J C, Schneck J and Erradonea G: Ed. Blinc R and Levanyk A P, Incommensurate phases in dielectrics, North-Holland, Amsterdam, 1986. P.233.
[5] Kojima S, Asaumi K, Nakamura T and Minomura S 1978 J. Phys. Soc. Jpn. 45 1433
[6] Kojima S, Nkamura T, Asaumi K, Takashige M and Minomura S 1979 Solid State Commun. 29 779
[7] Ishibashi Y and Iwata M 2013 J. Phys. Soc. Jpn. 82 044703
[8] Yamada T, Iwasaki H and Niizeki N 1970 J. Appl. Phys. 41 4141
[9] Herrero-Albillos J, Marchment P, Salje E K H, Carpenter M A and Scott J F 2009 Phys. Rev. B 80 214112
[10] Kojima S 2010 Jpn. J. Appl. Phys. 49 07HA01
[11] Buixaderas E, Kamba S, Petzelt J, Wada M, Ando S and Tsukamoto T 2000 Ferroelectrics 239 17
[12] Jiang F M and Kojima S 2002 Phys. Rev. B 66 184301