Condensed Matter Physics, 2022, Vol. 25, No. 4, 43702: 1–8
DOI: 10.5488/CMP.25.43702
http://www.icmp.lviv.ua/journal

CONDENSED MATTER PHYSICS

Broadband Brillouin scattering study of ferroelectric instability of barium sodium niobate

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Received July 18, 2022

The barium sodium niobate (BNN) with tungsten-bronze structure is one of well-known optical crystals for electro-optic and nonlinear optic applications. This paper reviews the ferroelectric instability of BNN crystals. BNN is a uniaxial ferroelectric with a spontaneous polarization along the tetragonal c-axis. There is no report on the observation of an optical soft mode responsible for a ferroelectric phase transition. In the vicinity of the Curie temperature, $T_C = 560$°C, an intense central peak (CP) related to the polarization fluctuations along the c-axis was observed by the broadband Brillouin scattering experiment. The relaxation time determined by the CP width shows the critical slowing down towards T_C. This fact indicates that the ferroelectric instability of BNN is an order-disorder type.

Key words: *Brillouin scattering, ferroelectric, order-disorder, central peak, barium sodium niobate*

1. Introduction

Ferroelectricity is defined by the existence of switchable spontaneous polarization by an external electric field. Ferroelectric phenomenon was identified for the first time in 1920 by Valasek on the study of Rochelle salt [1]. The microscopic origin of ferroelectricity has two typical cases, namely, the displacive type and order-disorder type. In the displacive type, an infrared active soft optic mode exists in a paraelectric phase, and the freezing of a soft mode displacement induces a spontaneous polarization [2, 3]. The softening of a soft mode frequency has been observed by far-infrared spectroscopy, Raman scattering, and neutron inelastic scattering. On the other hand, in the order-disorder type, the relaxation time of the polarization fluctuations of polar molecules along a ferroelectric axis diverges at the Curie temperature, and the aligned polar molecules induce a spontaneous polarization. Rochelle salt belongs to this type. The critical slowing down towards a Curie temperature has been observed by dielectric spectroscopy. In $NaNO_2$, Hatta observed the divergence of the relaxation time of the flipping motion of each NO_2 ion toward a Curie temperature due to the thermodynamical slowing down process of the correlated fluctuation of polarization [4]. The critical slowing-down of the polarization relaxation process was also observed in triglycine sulfate [5] and $Ca_2Sr(C_2H_5CO_2)_6$ above the Curie temperature [6]. Another method to observe the critical slowing down is the low-frequency inelastic light scattering. The polarization fluctuations along a ferroelectric axis are observed as a central peak (CP). In the vicinity of a Curie temperature, the divergence of CP intensity and the narrowing of CP width are observed for an order-disorder phase transition. In a $K(Ta_{0.68}Nb_{0.32})O_3$ crystal, the relaxation time determined by the CP width clearly shows a critical slowing down towards the Curie temperature, $T_C = 258$ K, indicating an order-disorder feature of the ferroelectric phase transition [7, 8]. Up to the present, the critical slowing down has been studied by the observation of a CP in ferroelectric phase transitions of 12 mol% KF substituted $BaTiO_3$ [9], $LiTaO_3$ [10], KNN [11], $MAPbCl_3$ [12], $BaTi_2O_5$ [13], and $K_2MgWO_2(PO_4)_2$ [14].

For the ferroelectric phase transitions of relaxor ferroelectrics, the diffusive nature was observed in the critical slowing down [15]. In $0.70Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.30PbTiO_3$ (PZN–7PT), the slowing down

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was suppressed below the intermediate temperature T^* and the typical critical slowing down was not observed near T_C. The local transition from dynamic to static PNRs at T^* stops the farther slowing down. To describe such a suppressed slowing down by random fields, the empirical equation of the stretched slowing down was used in the vicinity of T_C as given by the following equation,

$$\frac{1}{\tau_{CP}} = \frac{1}{\tau_0} + \frac{1}{\tau_1}\left(\frac{T - T_C}{T_C}\right)^{\beta}, \quad (T > T_C), \tag{1.1}$$

where β is the stretched index. In the case of $\beta = 1.0$, the equation (1.1) gives a critical slowing down of normal ferroelectrics without random fields. In the case of $\beta > 1.0$, the slowing down of relaxation time is suppressed and/or stretched by an increase of the strength of random fields. In PZN–7PT, it is found that the value of $\beta = 3.0$ gives a good reproduction of slowing down [16].

In some ferroelectrics, the mechanism of the ferroelectricity is not simple. The coexistence of both mechanisms or the crossover from displacive to order-disorder nature has been reported. In $LiNbO_3$, two-stage process involving a displacive transition in the Nb–O cages and an order-disorder transition in the Li–O planes was reported at the Curie temperature [17]. The unified model theory describing both the "order-disorder" and "displacive" ferroelectric phase transitions was proposed by introducing the model pseudospin-phonon Hamiltonian [18]. For such phase transitions, the study of the lowest frequency soft optic modes by Raman scattering or infrared spectroscopy is also necessary.

2. Ferroelectrics with tungsten-bronze structure

Ferroelectricity has been observed in various kinds of organic and inorganic materials. Regarding inorganic ferroelectrics, the oxygen octahedra ferroelectrics are the most popular. One of this family is the ferroelectrics with tungsten-bronze structure. It is technologically important in the field of telecommunications due to its superior electro-optical, photorefractive, and nonlinear optical properties such as second harmonic generation, and its resistance to optical damage is high. The ferroelectricity was reported at first in lead metaniobate, $PbNb_2O_6$ with $T_C = 570$°C [19]. Its piezoelectric constant is the same order of magnitude as that of barium titanate, $BaTiO_3$ with $T_C = 120$°C. The useful nonlinear coefficients and low optical damage were reported in barium sodium niobate, $Ba_2NaNb_5O_{15}$ (BNN), with $T_C = 560$°C [20]. Nowadays, a lot of tungsten-bronze type ferroelectrics are known [2].

Figure 1 shows the projection of tungsten bronze structure on the c-plane. In BNN, the A_1 and A_2 sites are fully filled by Na and Ba, respectively, and there is no vacancy. The B_1 and B_2 sites are fully occupied by Nb, while the C sites are vacant. BNN is called a filled tungsten-bronze structure with no charge disorder at A_1 and A_2 sites. BNN undergoes successive phase transitions at 560, 300, and −163°C [21].

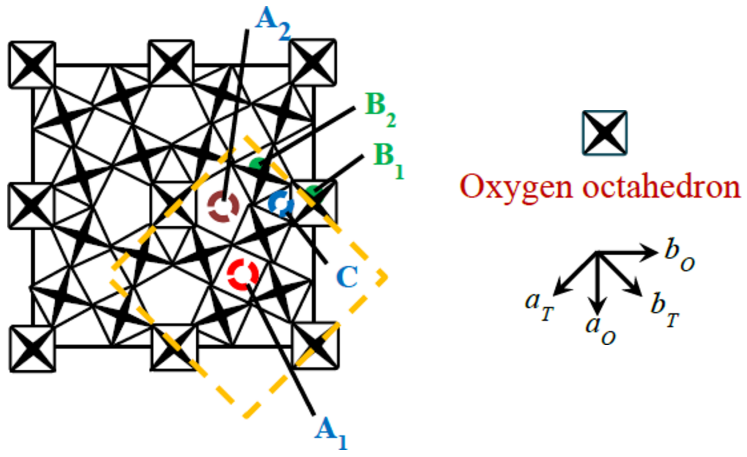

Figure 1. (Colour online) Projection of tungsten bronze structure on the c-plane. Tetragonal and orthorhombic unit cells are shown by dotted and solid lines, respectively.

The higher one is associated with the ferroelectric Curie temperature at 560°C, and its crystal symmetry changes from prototypic $4/mmm$ to ferroelectric tetragonal $4mm$ with a spontaneous polarization P_3 along the c-axis. The symmetry changes from tetragonal to incommensurate (IC) orthorhombic mmm systems at 300°C, the a and b axes are rotated for 45° along the c-axis as shown in figure 1. The modulation direction of the IC wave vectors is along a and b axes of the orthorhombic coordinate [22]. The lowest temperature phase transition at −163°C is the reentrant ferroelastic phase transition into the tetragonal $4mm$ phase. The pressure induced reentrant ferroelastic phase transition was also observed at 2.2 GPa and at room temperature [23, 24]. Recently, a new type of the IC phase transition was proposed by Ishibashi [25]. This new type of phase transition is referred to as type III, and it is characterized by the parabolic splitting of the doubly degenerate modes at the Brillouin zone boundary. The related macroscopic change in the IC phase transition was studied by Brillouin scattering [26]. Regarding a ferroelectric instability, the accurate measurement of low-frequency polaritons was performed on the optical phonon branch of $A_1(z)$ symmetry. However, any evidence of displacive nature was not found down to 18 cm^{-1} [27].

Since the T_C of $Ba_2NaTa_5O_{15}$ (BNT) is −233°C, the high tunability of the T_C of the temperature width of about 800°C was reported for $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ (BNNT), and this is technologically important [28, 29]. The ferroelectric phase transition of the BNNT single crystals with $x = 0.57$ at $T_C = 115$°C was studied by broadband dielectric spectroscopy up to 4 GHz. The order-disorder nature of the proper ferroelectric phase transition was observed, and its origin is attributed to the anharmonic motion of the Nb (Ta) atoms in a double well potential of oxygen octahedra [30].

Up to the present, no soft optic mode was observed in the tungsten-bronze ferroelectrics by vibrational spectroscopy. Recent theoretical studies reported the local pseudo-Jahn–Teller effect (PJTE) in transition metal B ion center of ABO_3 perovskite crystals. The vibronic coupling between the ground and excited electronic states of the local BO_6 center results in dipolar distortions, leading to an eight-well adiabatic potential energy surface [31]. Such a situation may also occur in tungsten bronze ferroelectrics and the order-disorder nature of ferroelectricity may exist. Therefore, the order-disorder nature of a ferroelectric phase transition of BNN has been examined by the broadband Brillouin scattering spectroscopy, which is a powerful tool to observe a critical slowing down in the vicinity of an order-disorder type phase transition temperature. In this paper, we review the broadband Brillouin scattering study on the ferroelectric instability of a BNN crystal [32].

3. Broadband Brillouin scattering and ferroelectric instability

Vibrational spectroscopy i.e., infrared spectroscopy and Raman scattering observes the vibrational modes of atoms, molecules, and crystal lattice. In the vibrational study of inorganic ferroelectric crystals, it is possible to observe not only the internal modes of octahedra or tetrahedra but also the external modes such as a soft optic mode. The spectral resolution of vibrational spectroscopy is usually 1 cm^{-1} = 30 GHz or more, and it is sufficient to detect the change of mode frequency related to a phase transition. The resolution of 1 cm^{-1} is sufficient to measure the temperature dependence of a ferroelectric soft optic mode. However, in the study of a ferroelectric phase transition of order-disorder type, the resolution of 1 cm^{-1} is not sufficient to measure the critical slowing down of the relaxation time towards the Curie temperature [33].

Polarization fluctuations related to a ferroelectric instability are detected as a broad CP in an inelastic scattering spectrum. The colorless and transparent BNN crystal studied was grown by Czochralski method in Tamagawa factory, NEC, Japan. The (100) plate with the size of 2.65 × 2.25 × 0.68 mm with two optically polished surfaces was used for Brillouin scattering measurements. Brillouin scattering spectra were measured at the backward scattering geometry using a 3 + 3 tandem multi-pass 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) [33]. 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 the Brillouin scattering spectra were measured in the condition that the free spectral range (FSR) and the scan range are 300 and 600 GHz, respectively. An intense polarized CP of BNN was observed in the

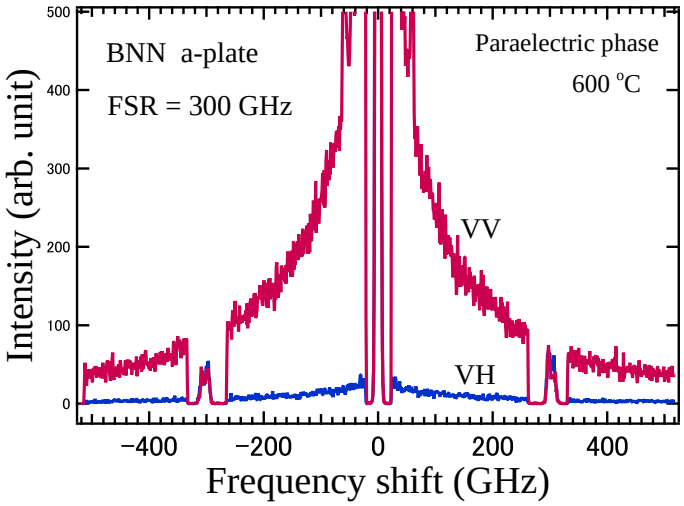

Figure 2. (Colour online) Broadband VV and VH Brillouin scattering spectra of a BNN crystal at 600°C observed by $a(cc)\bar{a}$ and $a(cb)\bar{a}$ back scattering geometry, respectively.

vicinity of the Curie temperature, T_C = 560°C, in the broadband Brillouin scattering spectra as shown in figure 2 [34]. In the polarized VV spectrum observed at $a(cc)\bar{a}$, backward scattering geometry shows an intense broad CP with $A_1(z)$ symmetry, while in the depolarized VH spectrum observed at $a(cb)\bar{a}$, backward scattering geometry does not show an intense CP with B_2 symmetry. Therefore, the polarization fluctuations along a ferroelectric c-axis are the origin of an intense broad CP.

4. Critical slowing down on a ferroelectric phase transition of barium sodium niobate

For the detailed analysis of the width of a CP, the temperature dependence of broadband Brillouin scattering spectra of a BNN crystal was measured at the backward scattering geometry with the free spectral range of 300 GHz as shown in figure 3.

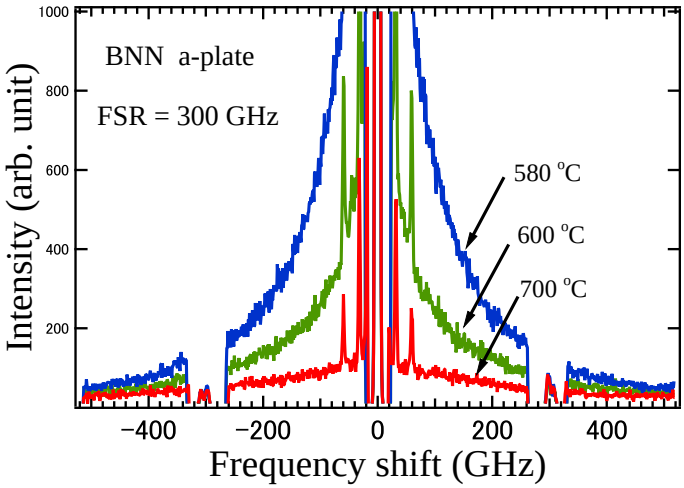

Figure 3. (Colour online) Broadband VV Brillouin scattering spectra of a BNN crystal in a paraelectric phase.

Under the assumption of a single Debye relaxation process, the relaxation time τ_{CP} was determined

by the relation $\pi \times$ (CP width) $= \tau_{CP}^{-1}$. The relaxation process related to the order-disorder nature of a ferroelectric phase transition has been observed as a CP with a zero frequency shift in an inelastic scattering spectrum. In the order-disorder phase transition, the relaxation time τ of the fluctuations of the order parameters increases toward the phase transition point and was called the critical slowing down. The relaxation time determined from the CP width shows a critical slowing down in the vicinity of $T_C = 560$°C as shown in figure 4 [34]. The temperature dependence of the relaxation time is given by the following equation of the case of $\beta = 1.0$ in equation (1.1) for a first order phase transition:

$$\frac{1}{\tau_{CP}} = \frac{1}{\tau_0} + \frac{1}{\tau_1}\left(\frac{T - T_1}{T_1}\right), \quad (T > T_C > T_1). \tag{4.1}$$

For example, in the ferroelectric phase transition at $T_C = 500$ K of the relaxor ferroelectric $0.70Pb(Sc_{1/2}Nb_{1/2})O_3$–$0.30PbTiO_3$ with the perovskite structure, the values of the fitting parameters are $\tau_0 = 14$ ps and $\tau_1 = 0.47$ ps, and $T_1 = 500$ K [35]. The temperature dependences of T/I_{CP} of a BNN crystal are shown in figure 5. In BNN, the fitting parameters of $1/\tau$ are $\tau_0 = 1.29$ ps, $\tau_1 = 0.73$ ps, and $T_1 = 555$°C. The intensity of a CP I_{CP} obeys the following equation in a paraelectric phase [36]:

$$\frac{T}{I_{CP}} \propto \left[\int_0^\infty \frac{\chi''(\omega)}{\omega}\,\mathrm{d}\omega\right]^{-1} \propto \frac{1}{\chi'(0)} = \frac{T - T_1}{C}, \quad (T > T_C > T_1). \tag{4.2}$$

Here, for the first order phase transition, $T_C > T_1$, because the ferroelectric phase transition of BNN is the first order. In the ferroelectric phase transition at $T_C = 500$ K of the $0.70Pb(Sc_{1/2}Nb_{1/2})O_3$–$0.30PbTiO_3$, the Curie–Weiss law also holds for I_{CP}/T above T_C [35].

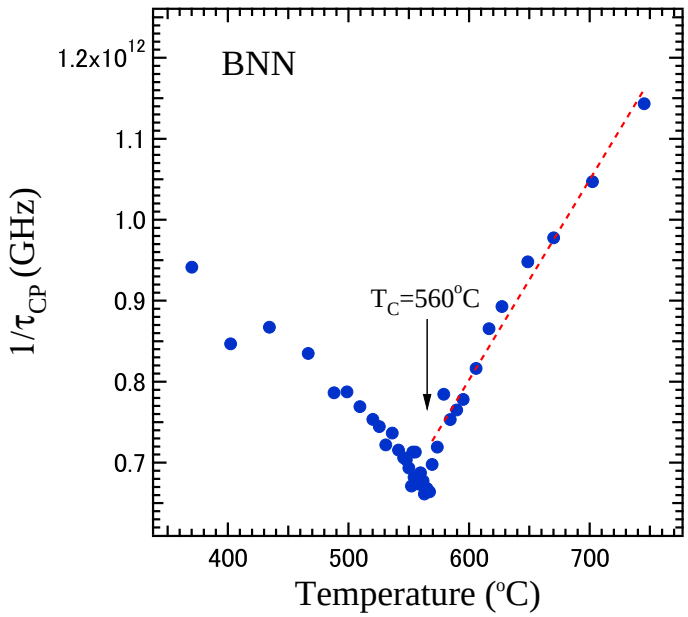

Figure 4. (Colour online) Temperature dependence of the inverse relaxation time. The dotted line is the fitted line by the equation (4.1) above $T_C = 560$°C.

The experimental results of the critical slowing down of relaxation time and the Curie–Weiss behavior of the CP intensity indicate the order-disorder nature of a ferroelectric phase transition of BNN. In the study of the order-disorder phase transition, Brillouin scattering is a powerful tool to detect the critical slowing down [37].

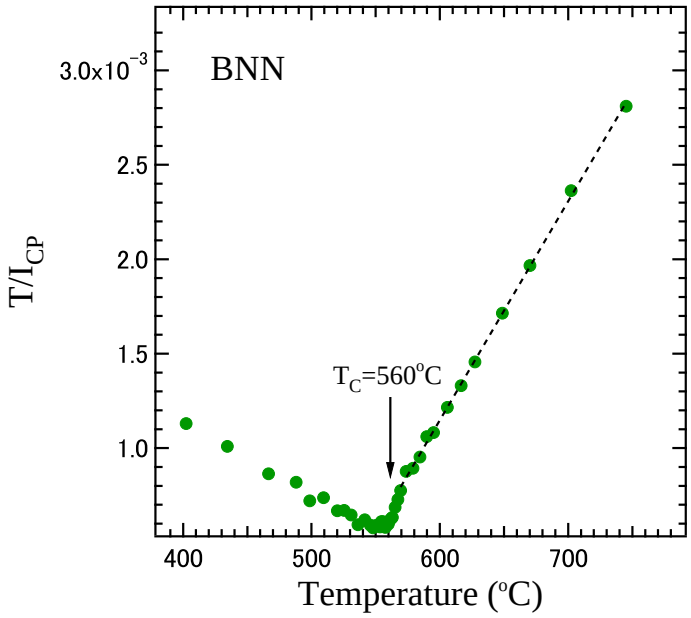

Figure 5. (Colour online) Temperature dependence of temperature divided by the intensity of a central peak. The dotted line is the fitted line by the equation (4.2) above T_C = 560℃.

5. Conclusions

For the study of the lattice instability of ferroelectrics, vibrational spectroscopy is a powerful tool to discuss not only displacive but also order-disorder nature. This paper reviews the experimental studies on the ferroelectric instability of a ferroelectric phase transition of barium sodium niobate (BNN) crystals with tungsten-bronze structure. BNN is one of well-known optical crystals for electro-optic and nonlinear optic applications. It shows a uniaxial ferroelectricity with a spontaneous polarization along the tetragonal c-axis. In the vicinity of the Curie temperature, T_C = 560℃, an intense central peak (CP) was observed by the broadband Brillouin scattering experiment. The CP has a strong polarization dependence, which originates from the polarization fluctuations along the ferroelectric c-axis. The CP intensity shows a maximum at T_C. The relaxation time determined by the CP width shows a critical slowing down towards T_C. The temperature dependence of the CP intensity shows the Curie–Weiss behavior. These experimental results are the evidence of the order-disorder nature of the ferroelectric instability of BNN.

Acknowledgements

Author thanks to Prof. J. Grigas, Prof. J. Banys, Prof. M. Maczka for the collaboration and S. Ohta, Y. Christy, K. Matsumoto, K. Suzuki, and M. Aftebuzzamann for the discussion and experiments.

Funding

This research was funded in part by JSPS KAKENHI, Grant No. JP17K05030.

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Дослідження сегнетоелектричної нестійкості в ніобаті барію-натрію методами широкосмугового розсіювання Бріллюена

С. Коджіма

Відділення матеріалознавчих наук, Університет Цукуби, Цукуба, Ібаракі 305-8573, Японія

Ніобат барію-натрію (BNN) зі структурою вольфрамової бронзи є одним з добре відомих оптичних кристалів, які використовуються для електрооптичних досліджень та у нелійнійній оптиці. У даній роботі розглядається сегнетоелектрична нестійкість в кристалах BNN. BNN є одновісним сегнетоелектриком, в якому спонтанна поляризація напрямлена вздовж тетрагональної осі c. У літературі немає згадок про спостереження оптичної м'якої моди, відповідальної за сегнетоелектричний фазовий перехід у цьому кристалі. В околі температури Кюрі $T_C = 560$°C в спектрах широкосмугового розсіювання Бріллюена спостерігається інтенсивний центральний пік, пов'язаний з флуктуаціями поляризації удовж осі c. Час релаксації, який визначається шириною центрального піка, виявляє критичне сповільнення при наближенні до T_C. Цей факт свідчить про те, що сегнетоелектрична нестійкість у BNN-сполуках є типу "лад-безлад".

Ключові слова: *розсіювання Бріллюена, сегнетоелектрик, лад-безлад, центральний пік, ніобат барію-натрію*