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Optical and x-ray studies on the low-temperature phase transition of $Ba_2NaNb_5O_{15}$

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Abstract. Low-temperature phase transitions of $Ba_2NaNb_5O_{15}$ with non-stoichiometric composition were investigated using a polarization microscope and x-ray diffractometer. Both apparatuses were equipped with a specially designed low-temperature cryostat which enabled us to measure the birefringence down to 4 K and x-ray reflections down to 20 K. Ferroelastic domain structure was observed to persist even at 4 K. Birefringence Δn_{ab} and pure shear x_{12} show a peak at about 200 K and drop steeply at 110 K but do not vanish below 110 K. These facts indicate that the phase below 110 K is not re-entrant to the tetragonal 4 mm phase. The quite long relaxation process observed in birefringence and the appearance of a new reflection in the x-ray diffraction experiment indicate that the quasi-tetragonal region appears at 110 K and develops with long relaxation time.

1. Introduction

Barium sodium niobate $Ba_2NaNb_5O_{15}$ (abbreviated as BSN hereafter) exhibits two structural phase transitions above room temperature. The upper one at 833 K is known to be a ferroelectric transition associated with the onset of a spontaneous polarization along the c-axis [1]. The point group changes from tetragonal $4/mmm$ to tetragonal $4mm$ on cooling [2]. At the lower transition temperature of 573 K, the point group changes from $4mm$ to orthorhombic $2mm$ [2]. With this change of symmetry, the spontaneous share strain x_{12} occurs in the a_o–b_o plane [3]. Note that the orthorhombic a_o and b_o axes make an angle of 45° with respect to the tetragonal a_t and b_t axes, with the common c-direction. The transition is classified as ferroelastic, because an application of uniaxial stress along either the a_o or the b_o axis interchanges these two axes (figure 1). The ferroelastic domain structure can be easily observed under the polarization microscope [4]. The existence of a large thermal hysteresis over a range of about 100 K was observed [5, 6]. The orthorhombic phase is simultaneously an incommensurate phase which is characterized by the incommensurate wave vector $1q$ along the a_o axis [7]. The incommensurability δ decreases steeply when the temperature reaches 373 K but does not vanish and holds a constant value of 0.003. Thus the phase below 373 K is termed a 'quasi-commensurate' phase [8–11]. A peculiar memory effect which was observed in birefringence, δ and discommensuration structure was considered to be associated with the incommensurate nature of BSN [12–18]. Regarding the NbO_6 octahedron in these two transitions, an Nb atom in the NbO_6 octahedron is shifted along the c-axis to produce a spontaneous polarization at the ferroelectric transition, while an O atom at an apex of the octahedron connecting two adjacent octahedra displaces along

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the a_o axis in the orthorhombic ferroelastic phase. The displacement of O is incommensurate with the fundamental periodicity of the a_o axis. Thus the movement of O atoms produces the doubling of the periodicity of the c-axis [19].

In addition to the high-temperature phase transitions, it was reported that two more phase transitions occur below room temperature. The first one was found by the birefringence experiment of Schneck *et al* [20]. The birefringence Δn_{ab} appearing at 573 K increases with decreasing temperature and has a peak at about 200 K, then decreases to zero or becomes very small around 110 K. They also observed similar behaviour of pure shear x_{12}. Based on these observations, they concluded that the transition at 110 K is the re-entrant one to the tetragonal 4*mm* phase. However, they also reported that the 're-entrant transition' depends strongly on the sample composition and some samples did not show the re-entrant behaviour [21, 22]. In contrast, Verwerft *et al* made a transmission electron microscopic observation around 105 K and claimed that the low-temperature transition is the transition with the change of the translational symmetry along the b_o axis [23, 24]. They found that streaked satellite reflections appear and the intensity increases with decrease of temperature. According to the observation in the real and reciprocal spaces, they proposed that the low-temperature phase is orthorhombic with the lattice parameters $2a_o$, $2b_o$ and c_o. As a_o and b_o are almost equal, the orthorhombicity decreases at the transition temperature around 110 K. Oliver *et al* reported that BSN exhibits a further phase transition between 40 K and about 10 K [25], but the nature of the transition has not been fully understood.

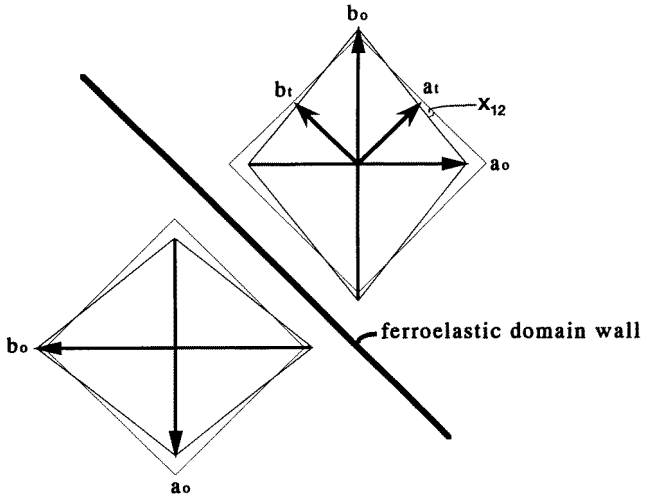

Figure 1. Two configurations of ferroelastic domain in $Ba_2NaNb_5O_{15}$. The relation between the high-temperature tetragonal cell (a_t, b_t) and the low-temperature orthorhombic cell (a_o, b_o) is also indicated.

The purpose of the present paper is to measure precisely the birefringence Δn_{ab} and lattice constants a_o and b_o of BSN with a specified composition ratio from room temperature down to 4 K (optical works) or 20 K (x-ray work) in order to clarify the nature of the low-temperature phase transitions of BSN. With the same specimens, we also examined the existence of the ferroelastic domain structure at 4 K and of the incommensurate reflections at 20 K.

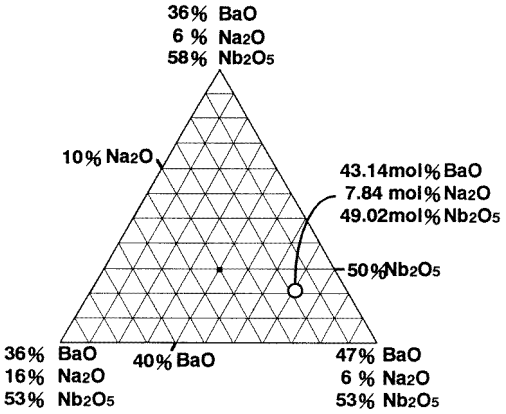

Figure 2. Composition ratio of the present crystal in the three-component phase diagram. The value determined by the inductively coupled plasma method is indicated by an open circle and the stoichiometric composition by a small square.

2. Experimental conditions

Specimens used in the present experiment were cut from a single crystal which was grown by the Czochralski method. The composition ratio of the crystal was determined by using the inductively coupled plasma method. The molar ratio of BaO, Na_2O and Nb_2O_5 was 43.14, 7.84 and 49.02%, respectively. The location of the present crystal in the three-component phase diagram is illustrated in figure 2.

For optical studies, two c_o plates with thicknesses of 196 μm (sample A) and 137 μm (sample B) were prepared. In order to avoid the memory effect, the specimen B was annealed at 725 K in the paraelastic phase for 48 h before measurement, while the sample A was annealed at 550 K in the incommensurate ferroelastic phase for 48 h to examine the memory effect on the low-temperature phase transitions. For x-ray measurement, an a_o (b_o) plate with thickness 800 μm was prepared. Since the sample contained ferroelastic domains, both lattice parameters a_o and b_o could be measured with the same sample orientation. No annealing treatment was carried out on the sample.

The measurement of birefringence was made by the Sénarmont method under the polarization microscope at a wavelength of 546 nm. This enabled us to measure the birefringence of one ferroelastic domain and to observe simultaneously the ferroelastic domain structure. As the angular position of an analyser was determined by a photo-diode detector, the precision of the birefringence reached 1×10^{-5}. The specimen was held in a helium cryostat (Oxford Instruments, CF2102-SA) and the temperature of the specimen was controlled within ± 0.1 K from room temperature down to 4 K. All measurements were made at fixed temperature, so the obtained values are those in the equilibrium state within the temperature fluctuation of ± 0.1 K.

Temperature dependences of lattice parameters a_o and b_o were measured using an x-ray diffractometer with a Ge(111) two-crystal monochromator. The characteristic Cu Kα1 x-ray radiation was used and its line spread $\delta\lambda/\lambda$ was estimated as 4×10^{-4}. The specimen was held in the helium cryostat especially designed for low-temperature x-ray measurement. The temperature of the sample was controlled within ± 0.1 K from room temperature to 20 K. $(1800)_o$ and $(0180)_o$ reflections were used to determine the lattice constants, the precision

being $\pm 1.8 \times 10^{-3}$ Å. Profiles of these reflections were fitted with a mixture function of Gaussian and Lorentzian after smoothing.

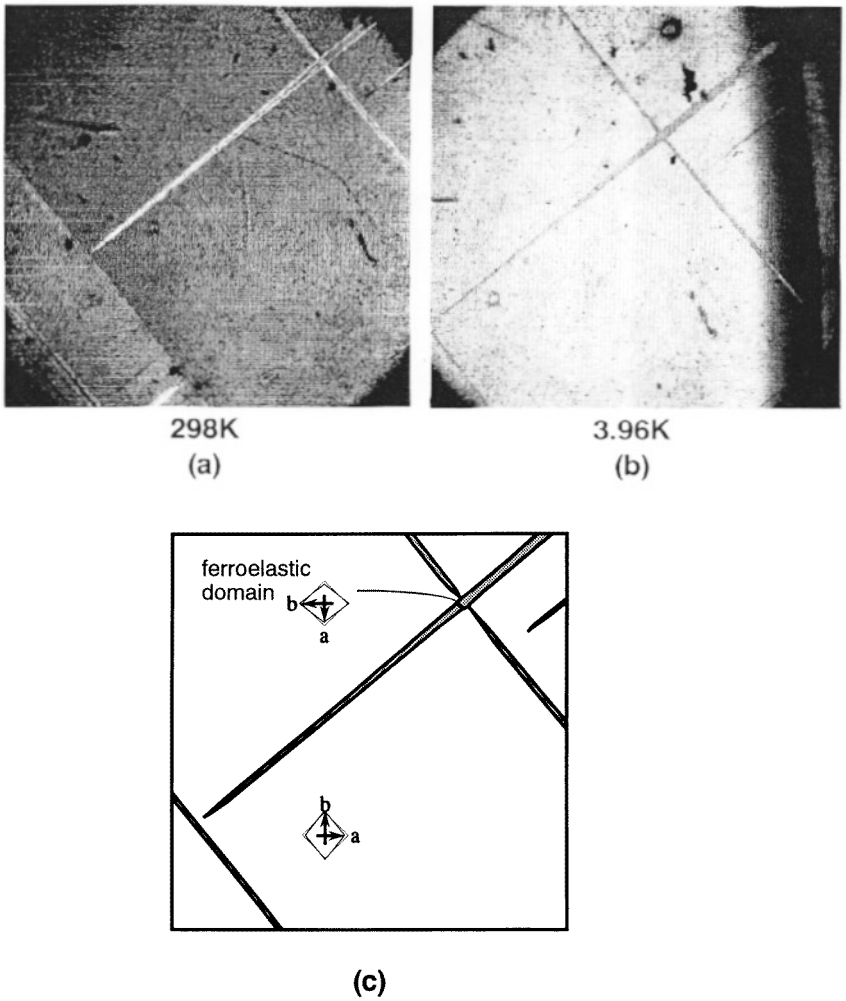

Figure 3. Ferroelastic domain structure of $Ba_2NaNb_5O_{15}$ observed at 298 K (a) and at 4.0 K (b). Corresponding illustration is shown in (c).

3. Experimental results and discussions

3.1. Observation of ferroelastic domain structure and temperature dependence of birefringence

Photographs of domain structures of BSN taken at room temperature and at 4 K are shown in figure 3. The ferroelastic domain structure which was observed at room temperature persists at 4 K without any change of structure. This fact strongly suggests that the 110 K transition is not reentrant. Figure 4 shows the temperature change of Δn_{ab}. Δn_{ab} appears at 573 K, increases with decrease of temperature, exhibits a peak around 200 K, then decreases

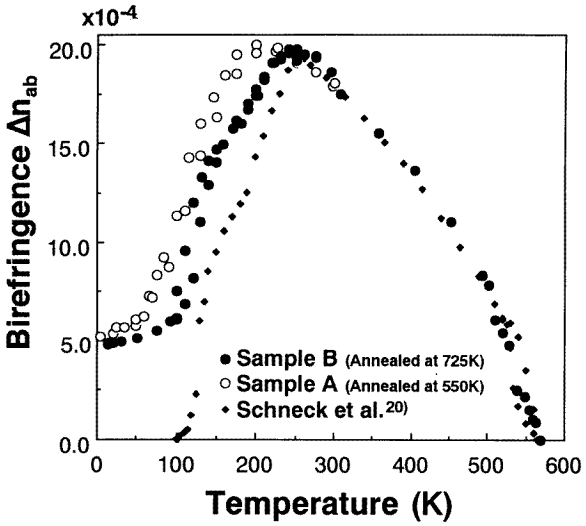

Figure 4. Temperature dependences of birefringence Δn_{ab} of $Ba_2NaNb_5O_{15}$ samples. Values determined by Schneck *et al* [20] are indicated by small squares.

and drops at about 110 K with a thermal hysteresis but does not vanish below 110 K. In the figure, the result of Schneck *et al* [20] is shown for comparison. It is interesting to note that the present result agrees well with that of Schneck *et al* above 200 K but deviates from it below this temperature. Dissimilar temperature dependence below 200 K was also observed in different samples and even in the same sample with different thermal history. The fact possibly comes from the glasslike nature of BSN below 200 K as pointed out by Shobu *et al* [26]. The birefringence measurement indicates that the low-temperature phase is not tetragonal. The existence of thermal hysteresis shows that the transition is first order. No substantial difference was observed between sample A and B, which shows that the memory effect in the incommensurate phase did not affect the nature of the low-temperature phase transition. However, we observed a peculiar behaviour of the birefringence when the sample was treated with a special history at low temperature: the sample was kept at 77 K for 78 h, and Δn_{ab} was measured as a function of time. The result is shown in figure 5, where a small but distinct relaxation of Δn_{ab} can be seen with a quite long relaxation time of 17 h. After this measurement, the sample was heated up to room temperature and cooled down to 4 K. The birefringence was observed to vanish as shown in figure 6. At 4 K, ferroelastic domain boundaries were vaguely observed but interference colours of both domains were pale. If the sample is inclined with respect to the incident beam and the direction coincides with one of the optic axes, the birefringence becomes zero. In this case, the birefringence of another domain should increase and the difference of interference colours of the two domains should be more distinct. This was not the present case and we can reject the possibility of the inclination of the specimen. This fact suggests the orthorhombicity was decreased significantly by the special heat treatment. We shall discuss the origin of the phenomenon later.

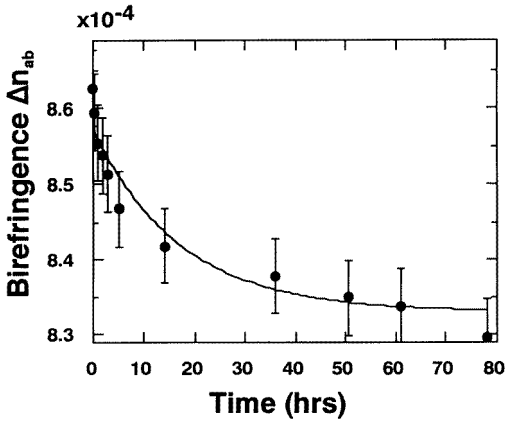

Figure 5. Relaxational change in Δn_{ab} of $Ba_2NaNb_5O_{15}$ observed at 77 K.

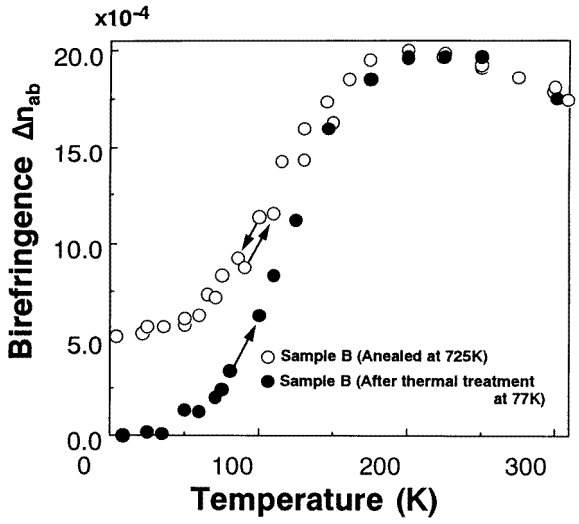

Figure 6. Temperature dependence of Δn_{ab} of sample B with a special thermal treatment at low temperature.

3.2. Super-lattice reflections in the low-temperature phase and temperature dependences of lattice parameters a_o and b_o

Oscillation photographs of the $(h0l)$ plane centred at the $(600)_o$ reflection were taken with an imaging plate at 300 K and 20 K for the purpose of examining the behaviour of super-lattice (incommensurate) reflections at low temperature. As shown in figure 7, the $(h01)_o$ reflections which exhibit doubling of the periodicity along the c_o direction and incommensuration along the a_o direction at room temperature were observed at 20 K. Due to poor spatial resolution of the oscillation photograph, it is difficult to conclude definitely that the observed super-lattice reflections are incommensurate. However, since no drastic changes in the intensity and positions of these reflections were observed, the low temperature phase is probably incommensurate along the a_o-axis.

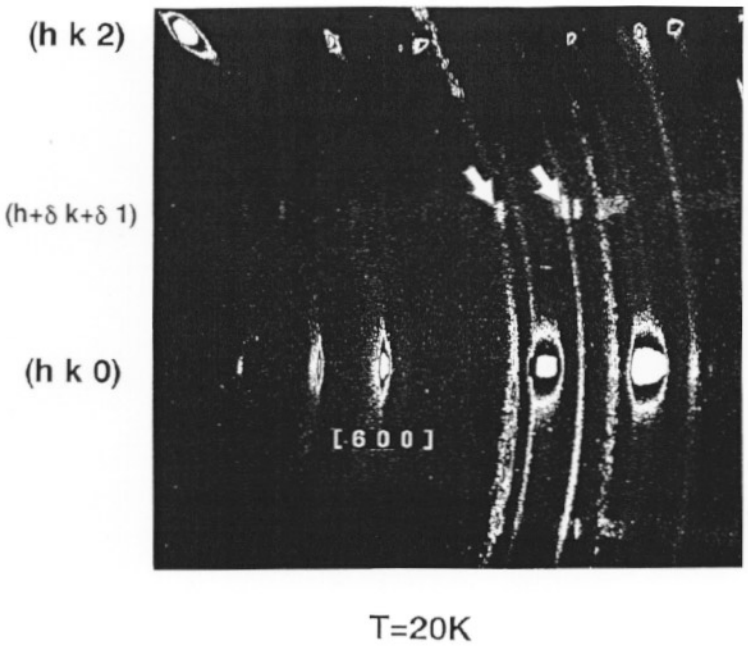

Figure 7. X-ray oscillation photograph of the $(h0l)$ reciprocal plane taken at 20 K. Arrows represent the super-lattice reflections $(h01)_o$. Powder reflection lines from a copper specimen holder overlap the figure.

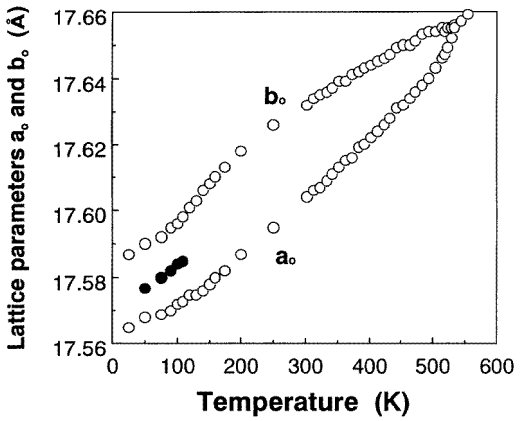

Figure 8. Temperature dependences of orthorhombic lattice constants a_o and b_o of $Ba_2NaNb_5O_{15}$. Solid circles indicate the quasi-tetragonal lattice constant determined by a pattern fitting program.

The temperature dependences of lattice constants a_o and b_o were determined by using $(1800)_o$ and $(0180)_o$ reflections and the result is shown in figure 8. Pure shear x_{12} defined as

$$x_{12} = \frac{b_0 - a_o}{b_o + a_o} \tag{1}$$

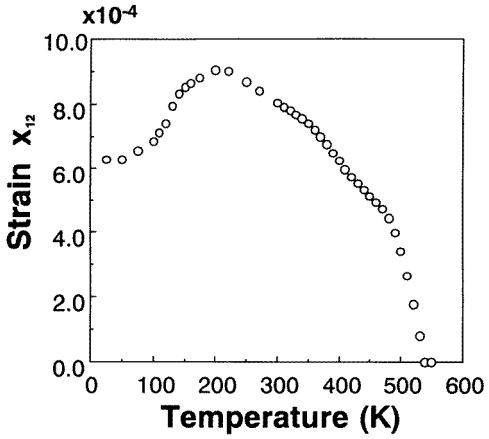

Figure 9. Temperature dependence of pure shear x_{12} of $Ba_2NaNb_5O_{15}$.

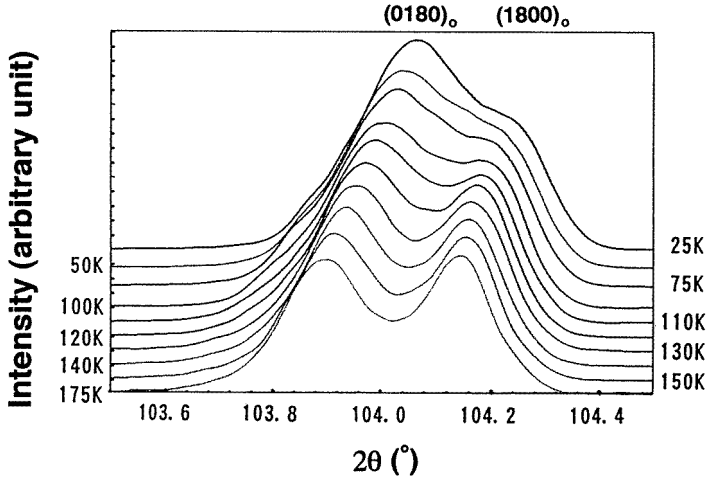

Figure 10. Temperature dependence of x-ray diffraction profiles of $(1800)_o$ and $(0180)_o$ of $Ba_2NaNb_5O_{15}$.

is calculated and its temperature change is shown in figure 9. x_{12} exhibits a quite similar behaviour to Δn_{ab}. It has a peak around 200 K and steeply decreases at about 110 K but does not vanish below 110 K. The temperature change in the profile of these reflections is indicated in figure 10. If we look very carefully at the profile, we notice that another very weak reflection appears between $(1800)_o$ and $(0180)_o$ reflections below 110 K. The position of the third reflection was determined using a profile fitting program with the use of a mixture function of Gaussian and Lorentzian. Under the assumption that the new reflection comes from the quasi-tetragonal phase, the lattice constant was calculated and is shown in figure 8 with solid circles. Recently Mori *et al* have succeeded in observing microstructure below 110 K by transmission electron microscope [27]. If the microstructure can be assigned to the quasi-tetragonal phase, our optical and x-ray observations can be explained as follows. The quasi-tetragonal phase appears first as nuclei at 110 K in the

orthorhombic matrix then increases in area with long relaxation time. The growth rate of the quasi-tetragonal region depends on impurities or defects in a sample and sometimes movement of the nuclei is pinned by these imperfections and average birefringence and pure shear remain at a significant value but the thermal treatment can enhance the development of the quasi-tetragonal region and the birefringence becomes zero. To confirm this idea, further experiments are necessary. We are now making precise x-ray diffraction measurements over the whole reciprocal space at low-temperature.

Between 40 K and 4 K (optical work) or 20 K (x-ray work), we observed no specific changes in birefringence or x-ray profile and intensity. The nature of the transition reported by Oliver *et al* seems to be very weak or of higher order.

Acknowledgments

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