PHYSICAL REVIEW B VOLUME 55, NUMBER 17 1 MAY 1997-I

Low-temperature transition in barium sodium niobate $Ba_2NaNb_5O_{15}$

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(Received 28 October 1996)

In order to examine a low-temperature transition in barium sodium niobate $Ba_2NaNb_5O_{15}$ (BSN), an *in situ* observation was made in the temperature range between room temperature and 25 K by a transmission electron microscope. It was revealed that satellite reflection spots characterizing the incommensurate structure, which appear around 573 K, do not disappear even around 25 K. On the other hand, it was found that microdomains elongating along the [010] direction with a width of about 10 nm appear around 200 K, together with the appearance of both new satellite spots at the $(h,k,l+1/2)$ points with h,k,l integers and new faint diffuse streaks through the $(h,k+1/2,l+1/2)$ points along the [100] direction. It is concluded that the low-temperature transition in BSN is a transition from the $1q$ quasicommensurate state to the $2q$ one in which two modulated waves arise along the [100] and [010] directions. [S0163-1829(97)02317-5]

I. INTRODUCTION

Barium sodium niobate [$Ba_2NaNb_5O_{15}$ (BSN)] has been reported to undergo a transition from a high-temperature tetragonal phase to an incommensurate one around 573 K in the cooling process.[1–4] This transition is characterized by the appearance of a modulated wave with a period of about $2a_o$ along the $[100]_o$ direction, which gives rise to satellite reflection spots characterizing the incommensurate structure. Note that a subscript o denotes an orthorhombic system. In addition, an orthorhombic distortion characterized by a spontaneous strain $[e_{11}-e_{22}]$ appears in this transition, and the point symmetry changes from $4mm$ to $mm2$.[2] As a result, a ferroelastic domain structure is formed in the incommensurate structure.[1–6]

The incommensurate phase in BSN has been studied so far both experimentally and theoretically.[1–10] One of the important features in the incommensurate phase is that the incommensurability (δ) characterizing an incommensurate structure exhibits a large thermal hysteresis for the cooling and subsequent heating processes. When the temperature is lowered in the incommensurate phase, δ decreases continuously from $\delta=0.031$ at the transition temperature of 573 K to 0.003 at about 373 K and keeps constant below 373 K. Note that a state with the constant value of $\delta=0.003$ is called a quasicommensurate state. According to the previous work, it was found that the transition to the quasicommensurate state results in the appearance of two types of ferroelastic domains with a modulated wave only along the $[100]_o$ direction.[5–10] This means that the quasicommensurate state is characterized as a $1q$ incommensurate one. Recently we revealed that the quasicommensurate state should be regarded as a metastable one in which the discommensurations are pinned during the incommensurate-to-commensurate transition around 500 K.[8,10]

In addition to the transition mentioned above, Schneck *et al.* made a birefringence measurement in the temperature range between room temperature and 77 K and found that a birefringence characterizing the orthorhombic structure starts decreasing at about 200 K as the temperature is lowered from room temperature and vanishes around 110 K.[11] They pointed out that the $4mm$ point-group symmetry of the high-temperature tetragonal phase is restored in the low-temperature region below 110 K.[11] On the other hand, recently Fujishiro and Uesu made both a birefringence measurement and x-ray-diffraction experiment in the temperature range between room temperature and 20 K and suggested that the $4mm$ point-group symmetry of the high-temperature tetragonal phase is not restored in the low-temperature region below 110 K.[12] Verwerft *et al.* investigated the microstructure of BSN around 105 K by means of a transmission electron microscope and found a streaked satellite reflection spot along the $[110]_o$ direction in reciprocal space.[13] In addition, microdomains with several nanometer size were observed in the dark-field image using the streaked satellite reflection spot. However, the nature of the microdomain structure appearing by the low-temperature transition in BSN has not been sufficiently understood so far.

In the present work, an *in situ* observation was made using a transmission electron microscope in the temperature range between room temperature and 25 K, in order to study the origin of the microdomain structure and the distribution of the diffuse scattering characterizing the low-temperature transition in BSN. In addition, both the nature of the low-temperature transition in BSN and the correlation between the microstructure and physical properties such as the birefringence are considered on the basis of the present experimental results.

II. EXPERIMENTAL METHOD

Single crystals of BSN grown by the Czochralski method were used in the present work. In order to erase a previous hysteresis, all the samples were kept at 723 K in the high-temperature tetragonal phase for 24 h and cooled down to room temperature. Thin-film samples for the transmission-electron-microscope observation were prepared in the following two techniques. One technique is that the BSN single crystals are polished mechanically down to about 50 μm in thickness and subsequently thinned by an Ar-ion beam. The other technique is that the BSN single crystals are crashed into fine fragments and then dispersed on holey carbon films supported by molybdenum grids. The observation was made in a JEM-200CX electron microscope equipped with both liquid N_2 and He cooling stages. Dark-field images were taken by using both satellite reflection spots characterizing the incommensurate structure and new faint diffuse streaks appearing around 200 K. Diffraction patterns were taken by using the imaging plates with the 25-μm pixels in order to measure intensities of both new satellite spots and new faint diffuse streaks appearing below 200 K quantitatively.

III. EXPERIMENTAL RESULTS

First of all, the $1q$ quasicommensurate structure was reexamined by taking both diffraction patterns and dark-field images, in order to confirm the incommensurate structure at room temperature. Figure 1 shows diffraction patterns taken with incident beams parallel to the $[010]_o$ and $[011]_o$ directions and a dark-field image taken by using a satellite reflection spot characterizing the $1q$ quasicommensurate structure. In the diffraction pattern of Fig. 1(a), both fundamental spots due to the orthorhombic tungsten bronze-type structure and satellite reflection spots are seen clearly. As shown in the diffraction pattern of Fig. 1(b) taken with the $[011]_o$ incidence, on the other hand, only fundamental reflection spots due to the orthorhombic tungsten bronze-type structure are seen. Figure 1(c) shows a typical dark-field image taken at room temperature by using a satellite reflection spot characterizing the incommensurate structure. In the image, two neighboring ferroelastic domains are seen as bright and dark regions on the left and right sides, respectively. Note that the orientations of two neighboring ferroelastic domains are different from each other by a rotation of about 90° around the $[001]_o$ direction and the ferroelastic domain boundary is parallel to the $\langle 110\rangle_o$ direction. In the bright-contrast region, black line contrasts regarded as the discommensurations with the phase slip of $2\pi/4$ are seen clearly. It is confirmed from an analysis of the diffraction patterns and dark-field images that the quasicommensurate state at room temperature consists of two types of ferroelastic domains with an incommensurate period of about $2a_o$ only along the $[100]_o$ direction, as has been reported in the previous work.[1–10]

In order to examine the low-temperature transition in BSN, a change in the diffraction pattern was observed in the temperature range between room temperature and 25 K. Figure 2 shows diffraction patterns from a single ferroelastic domain taken at 120 K. Note that incident beam directions in Figs. 2(a) and 2(b) are parallel to the $[010]_o$ and $[011]_o$ directions, respectively. As shown in Fig. 2(a), new satellite reflection spots indicated by an arrow are seen at the $(h,k,l+1/2)$ points with $h,k=2n$ (n integer), in addition to fundamental spots of the orthorhombic tungsten bronze-type structure and satellite reflection spots which characterize the $1q$ quasicommensurate structure. It should be noticed that the satellite reflection spots characterizing the $1q$ quasicommensurate structure do not disappear in the cooling process down to around 25 K. This means that the $4mm$ point-group symmetry of the high-temperature tetragonal phase is not restored in the low-temperature region, unlike as Schneck *et al.* pointed out.[11] On the other hand, characteristic faint

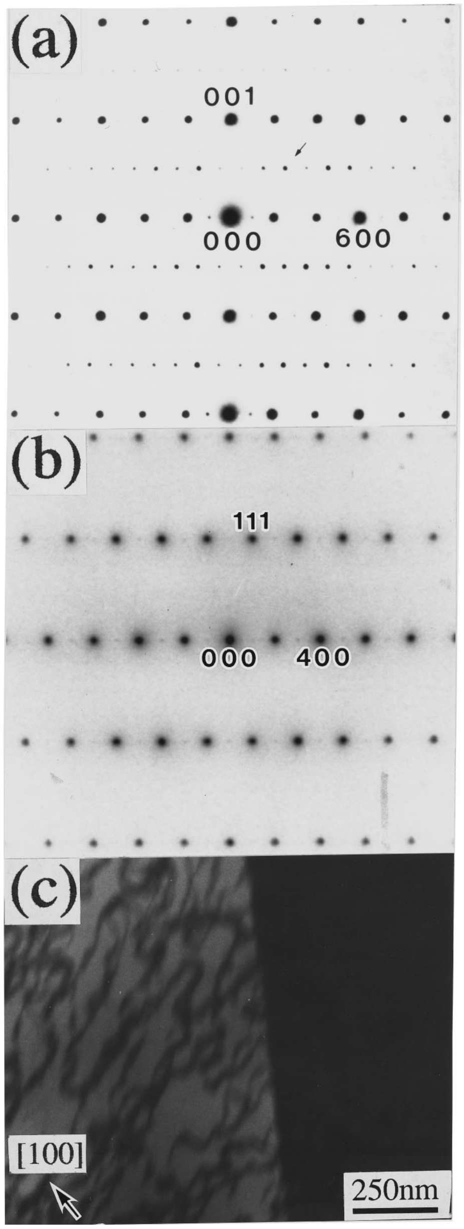

FIG. 1. Diffraction patterns with the incident beams parallel to the $[010]_o$ (a) and $[011]_o$ (b) directions and satellite dark-field image (c) at room temperature. Note that the satellite reflection spot, which is marked by an arrow in (a), is located at the $(5/2-\delta, 0, 1/2)$ point, where the value of δ is estimated to be about 0.003.

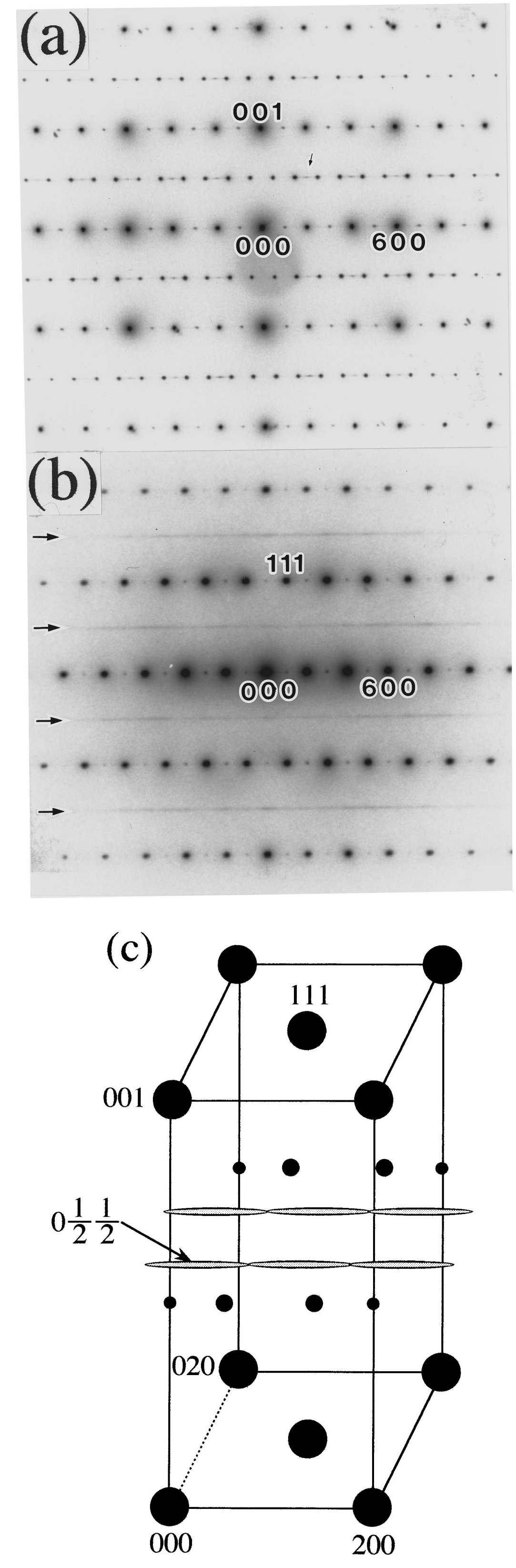

FIG. 2. Diffraction patterns with the incident beams parallel to the $[010]_o$ (a) and $[01\bar{1}]_o$ (b) directions at 120 K. (c) The distribution of the diffuse scattering and satellite reflection spots appearing with the low-temperature transition. Large solid circles represent fundamental spots due to the tungsten bronze structure, while small solid circles and rods denote new satellite reflection spots and faint diffuse streaks, respectively.

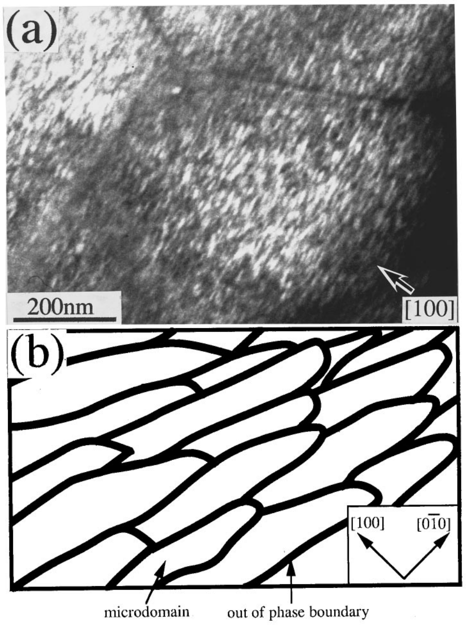

FIG. 3. (a) Microstructure obtained at 25 K by using a part of the faint diffuse streak appearing around 200 K. (b) Schematic description of the microdomain structure.

diffuse streaks through the $(h,k+1/2,l+1/2)$ points along the $[100]_o$ direction are seen, as indicated by arrows in Fig. 2(b). Figure 2(c) shows schematically the distribution of the diffuse scatterings found in the present work. As seen in Fig. 2(c), two types of diffuse scattering were found in the present work. One is a new faint satellite reflection spot at the $(h,k,l+1/2)$ point and the other is a new diffuse streak through the $(h,k+1/2,l+1/2)$ points along the [100] direction. Then a change in intensity of the new satellite reflection spot and new faint diffuse streak on cooling was measured by using the imaging plates quantitatively. It was found that the satellite reflection spots appear at the $(h,k,l+1/2)$ point around 200 K, as the specimen temperature is lowered from room temperature. The intensity of the satellite spot increases gradually on cooling. The faint diffuse streaks also appear around 200 K in the cooling process from room temperature. The intensity increases continuously, but the intensity distribution along the streak does not change even at 25 K. These data obviously suggest that a structural change in BSN occurs around 200 K on cooling. Then the microstructure in the low-temperature region of BSN was examined in the dark-field method.

Figure 3(a) shows a dark-field image of a microstructure obtained at 25 K by using a part of the streak appearing around 200 K. In the image, characteristic bright regions elongating along the $[010]_o$ direction with a width of about 10 nm on average are observed. One of the important features of the regions is that the boundary between two neighboring bright regions is not straight, but wavy. Because the bright contrast is diffraction contrast, as mentioned by Verwerft *et al.*,[13] they can be attributed to the microdomains formed by a structural change in the low-temperature region. We took both diffraction patterns and dark-field images and examined the details of the microdomains. The microdomain structure model proposed in the present work is shown schematically in Fig. 3(b). The microdomain structure consists of

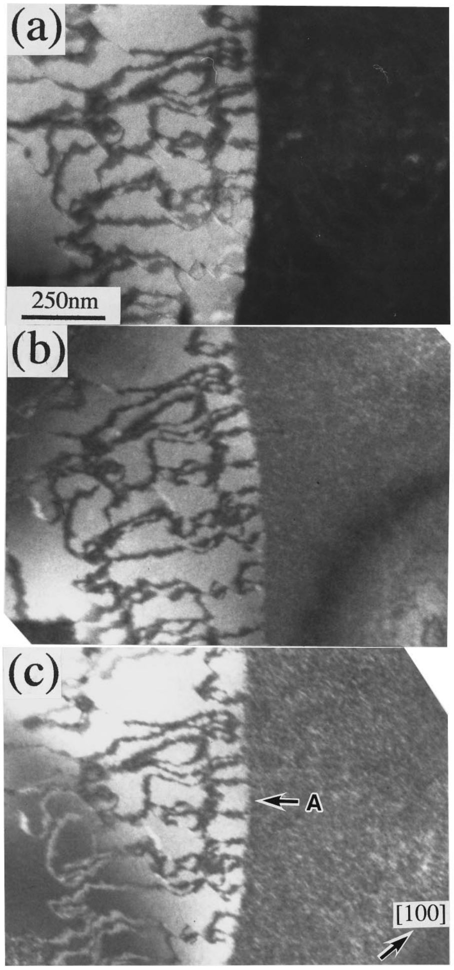

FIG. 4. Change in microstructures characterizing the low-temperature transition in BSN. The images are taken at (a) room temperature, (b) 190 K, and (c) 120 K, respectively.

both microdomains elongating along the $[010]_o$ direction with a width of about 10 nm and the out-of-phase boundaries between two neighboring microdomains. The out-of-phase boundaries are oriented nearly parallel to the $(100)_o$. This clearly indicates that the diffuse streak found in Fig. 2(b) originates from the characteristic arrangement of the out-of-phase boundaries.

In order to investigate a change in a microstructure in the low-temperature region, an *in situ* observation was made by the transmission electron microscope. Figure 4 shows a change in microstructure observed in the cooling process from room temperature. As shown in the dark-field image of Fig. 4(a) taken at room temperature using a $(h+1/2,k,l+1/2)$ satellite reflection spot, the ferroelastic domains characterizing the $1q$ quasicommensurate structure are seen as bright and dark regions. In the bright-contrast region, the discommensurations with a phase slip of $2\pi/4$ are seen clearly. When the temperature was lowered from room temperature, characteristic bright regions due to the microdomains were observed in the dark-field image taken by using a part of the faint diffuse streak appearing around 200 K. Note that because the two neighboring ferroelastic domains are different in orientation from each other by rotation of about 90° around the $[001]_o$ direction, the diffuse streaks elongating in one direction through the $(h+1/2,k,l+1/2)$ points appear in the bright ferroelastic domain and those elongating in the perpendicular direction appear in the dark ferroelastic domain. Therefore, the position at which the $(h+1/2,k,l+1/2)$ spots appear in one ferroelastic domain coincides with a position through which diffuse streak runs in the other ferroelastic domain. Figures 4(b) and 4(c) show microdomain structures observed around 190 and 120 K, respectively. As indicated by an arrow in Fig. 4(b), characteristic bright regions due to the microdomains are faintly seen in the dark ferroelastic domain, while dark line contrasts due to the discommensurations are seen in the bright ferroelastic domain. It should be noticed that on cooling the ferroelastic domain boundary becomes zigzag by the appearance of the microdomains, which is marked by an arrow (A) in Fig. 4(c), while the shape of the discommensuration does not change on cooling, as seen by comparing Fig. 4(a) with Fig. 4(c). This indicates that the appearance of the microdomain structure has no influence on the discommensurations. The structural change around 200 K is characterized by the appearance of the microdomain structure consisting of the microdomains and the out-of phase boundaries between the microdomains.

The details of the microdomain structure appearing around 200 K were examined by the dark-field method. Figure 5 shows dark-field images of a microstructure in BSN taken at 120 K. Figures 5(a) and 5(b) show microstructures of the same area, which were obtained by using the satellite reflection spot characterizing the incommensurate structure and a part of the diffuse streak appearing around 200 K, respectively. In Fig. 5(a), only the wavy black line contrasts regarded as the discommensurations are seen. On the other hand, the microdomains are observed with a bright contrast in Fig. 5(b) taken by using the part of the diffuse streak. These observations show that both the discommensurations and the microdomains coexist in the same region without any appreciable interaction. In other words, the microdomains appearing around 200 K in Fig. 5(b) produce both the satellite reflection spot and the diffuse streak in the diffraction pattern. In addition, Fig. 5(c) is a dark-field image taken by using the fundamental spot of the tungsten bronze structure. No characteristic contrast associated with the microdomains is seen. This suggests that a lattice distortion is not induced by the appearance of the microdomain structure.

IV. DISCUSSION

It is confirmed that the $1q$ quasicommensurate structure in BSN consists of two types of ferroelastic domains with an incommensurate period of about $2a_o$ along the $[100]_o$ direction. The present *in situ* observation of the low-temperature transition in BSN revealed that the microdomain structure consisting of microdomains elongating along the $[010]_o$ direction with a width of about 10 nm appears around 200 K and exists even at 25 K. Moreover, both new satellite reflection spots at $(h,k,l+1/2)$ points and new diffuse streaks through the $(h,k+1/2,l+1/2)$ points along the $[100]_o$ direction were found. In addition, the microdomain produces the satellite reflection spots associated with the $1q$ quasicommensurate structure in the diffraction pattern. The present observation shows that the microdomain should be regarded

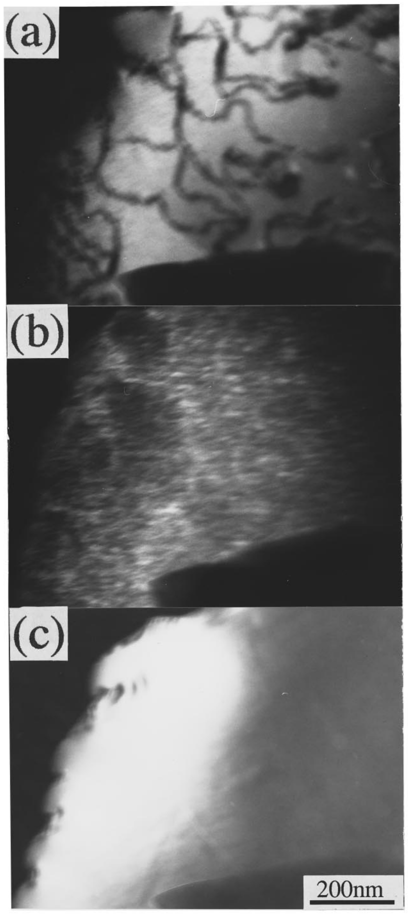

FIG. 5. Microstructures taken at 120 K. The images are taken by using (a) a satellite reflection spot characterizing the incommensurate structure, (b) a part of faint diffuse streak appearing around 200 K, and (c) a fundamental spot due to the tungsten bronze structure.

as the $2q$ state with two modulations along both the $[100]_o$ and $[010]_o$ directions.

We first discuss an origin of the appearance of both the new satellite spot at the $(h,k,l+1/2)$ point and the new faint diffuse streak elongating along the $[100]_o$ direction found in the present work. The previous work revealed that the incommensurate transition around 573 K exhibits a soft-phonon mode behavior.[1,2] The neutron diffraction experiment made by Schneck *et al.* actually showed that the incommensurate transition accompanys a softening of a double-degenerate phonon mode related to a modulation consisting of a collective shearing of the oxygen octahedra involved in the tungsten bronze structure and one of the double-degenerate phonon mode is condensed around 573 K.[1] The modulation vector related to the condensed phonon mode is $k=1/2(1+\delta)(a_t+b_t)+1/2c_t$, with $\delta=0.031$ at the transition temperature of 573 K. Note that a subscript t denotes the high-temperature tetragonal system, where the high-temperature tetragonal structure has an orientation relation to the orthorhombic one as follows: $[100]_o \| [110]_t$, $[010]_o \| [1\bar{1}0]_t$, and $[001]_o \| [001]_t$. The important features in the low-temperature structure is that the microdomain appearing around 200 K gives rise to the $(h,k,l+1/2)$ spot in the diffraction pattern. It can be considered from an analysis of the diffraction patterns that the appearance of the $(h,k,l+1/2)$ spots is explained by the existence of both the $(h+1/2,k,l+1/2)$ and the $(h,k+1/2,l+1/2)$ spots. It should be noted that the $(h,k+1/2,l+1/2)$ spots are produced by the condensation of the other double-degenerate phonon mode with $k=1/2(a_t-b_t)+1/2c_t$ though these spots are immersed into the diffuse streaks in the observed diffraction pattern due to the microdomains. That is, it is suggested that the structure in the microdomain is characterized by the condensation of the double-degenerate phonon modes at both the $(h,k+1/2,l+1/2)$ and $(h+1/2,k,l+1/2)$ points in the reciprocal space of the orthorhombic system. Because of this, it is considered that the diffuse streak along the $[100]_o$ direction consists of two types of diffuse scatterings; that is, one is the faint satellite reflection spots at $(h,k+1/2,l+1/2)$ points associated with the structure in the microdomain and the other is the diffuse streaks associated with the irregular arrangement of out-of-phase boundaries between the microdomains. From this consideration, the low-temperature phase below 200 K is concluded to have the structure in which the new unit cell is $2a_o \times 2b_o \times c_o$.

The nature of the low-temperature transition in BSN is discussed on the basis of the present experimental results. As shown in Fig. 4, the microdomain structure characterizing the low-temperature phase in BSN appears homogeneously around 200 K. As mentioned above, the low-temperature transition in BSN is characterized by the appearance of new modulated waves along the $[010]_o$ direction. That is, the transition accompanies a structural change from the $1q$ quasicommensurate structure to the $2q$ one with two modulated waves along the $[100]_o$ and $[010]_o$ directions. It should be noted that the intensity of the satellite reflection spots characterizing the incommensurate structure is much stronger than that of the streaks appearing around 200 K. This suggests that amplitude of the modulated waves along the $[100]_o$ direction is much larger than that of the new modulated waves along the $[010]_o$ direction. It should be remarked that coupling terms between amplitudes of the modulation waves and a spontaneous strain are involved in the free energy proposed by Toledano and co-workers.[1–3] This means that the appearance of the modulated waves gives rise to a strain through the coupling term. From the fact that the ferroelastic domain structure is seen in Fig. 4(c) taken at 120 K, orthorhombic distortion appearing around 573 K does not disappear perfectly in the low-temperature phase below 200 K, while the ferroelastic domain boundary becomes zigzag and unclear by the appearance of the microdomains. This suggests that the orthorhombic distortion is relaxed in the low-temperature phase. It is understood from this consideration that the decrease in the birefringence (Δn_{ab}) below 200 K originates from the relaxation of the orthorhombic distortion by the appearance of the microdomains. That is, the microdomain structure appearing below 200 K has strong influence on physical properties such as the birefringence in the low temperature phase of BSN.

V. CONCLUSION

The present *in situ* observation revealed that the low-temperature transition in BSN is characterized by the appearance of the microdomain structure consisting of the microdomains elongating along the $[100]_o$ direction with a width of about 10 nm around 200 K. Because each microdomain structure gives rise to two types of satellite reflection spots, each of the microdomain is characterized as the $2q$ state with two modulations along both the $[100]_o$ and $[010]_o$ directions. It is therefore concluded from the analysis of these data that the $4mm$ symmetry of the high-temperature tetragonal phase is not restored in the low-temperature phase, but the symmetry is orthorhombic with a new lattice constant for the b axis, which is twice that of the orthorhombic phase above 200 K.

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