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Evolution of a ferroelastic domain structure in an incommensurate phase of barium sodium niobate ($Ba_2NaNb_5O_{15}$)

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Features of a ferroelastic domain structure in an incommensurate phase of barium sodium niobate [$Ba_2NaNb_2O_{15}$ (BSN)] that appear in the cooling process were investigated by means of a transmission electron microscope. The *in situ* observation revealed that there exists an abrupt change in the domain structure around 503 K. The ferroelastic domain structure above 503 K basically consists of two types of $1q$ ferroelastic microdomains with a size of about 20 nm while below it large ferroelastic domains with flat domain boundaries are formed.

Barium sodium niobate (BSN, $Ba_2NaNb_5O_{15}$) is known to show some peculiar phenomena in the incommensurate phase such as the memory effect, which are closely related to a phase transition from a normal tetragonal phase (space group $I4mm$) to an incommensurate one at 573 K.[1-8] Note that an incommensurate phase is characterized by the $1q$ incommensurate structure with a period of about $2a$ along the $[100]_0$ direction, where a is the lattice parameter of the orthorhobmic structure in the $[100]_0$ direction. An important feature of the transition is that Landau theory predicts a change in point symmetry from $4mm$ to $mm2$ in the transition.[2,3,9,10] Then, an orthorhombic distortion appears in the incommensurate phase. The incommensurate transition results in the appearance of a ferroelastic domain with orthorhombic symmetry.

Hebbache and Errandonea examined the change in elastic constants of C_{11} and C_{12} in the incommensurate phase by means of Brillouin scattering and found that in the cooling process from the normal tetragonal phase the constants exhibit anomalous behavior between 573 and 500 K.[11] Particularly, when the temperature is lowered in the incommensurate phase, two components of C_{11} and C_{22} start to be split around 543 K. Birefringence and optical experiments made by Kiat *et al.* further showed that the incommensurate structure has a tetragonal symmetry in the temperature range between 573 and 543 K.[12] Very recently, an x-ray-diffraction experiment revealed that fundamental peaks still appear at positions expected for the normal tetragonal structure in the temperature range between 573 and 543 K.[13]

In spite of the prediction based on Landau theory, the above-mentioned data suggest that an incommensurate phase between 573and 543 K on cooling has tetragonal symmetry, which results in a $2q$ incommensurate structure characterized by modulations along two $\langle 110 \rangle_t$ directions, where t denotes the normal tetragonal system. Note that the tetragonal structure has an orientation relation to the orthorhombic one, $[1\bar{1}0]_t \| [100]_0$, $[110]_t \| [010]_0$, and $[001]_t \| [001]_0$. However, details of the $2q$ incommensurate structure have not been sufficiently understood so far. In order to understand the features of the $2q$ incommensurate structure in BSN, we made an *in situ* observation of the microstructures in the incommensurate phase by means of a transmission electron microscope. As a result, we found both a unique ferroelastic domain structure in the $2q$ incommensurate structure and an abrupt change in the domain structure around 503 K, which basically corresponds to a transition from the $2q$ structure to the $1q$ one. In this paper, then, we describe details of the evolution of the ferroelastic domain structure in the incommensurate phase on cooling, which have been experimentally obtained by the present *in situ* observation, and discuss the origin of the sudden change between two types of the ferroelastic domain structures. Note that the present work is focused on the incommensurate phase appearing in the cooling process.

BSN single crystals made by the Czochralski method were used in the present work. In order to erase the previous hysteresis, a sample crystal was first annealed at 723 K in the high-temperature tetragonal phase for 24 h. Thin-film samples for transmission-electron-microscope observations were then prepared as follows: BSN single crystals were polished mechanically down to a thickness of about 50 μm and subsequently thinned to about 100 nm thick by an Ar-ion beam. The observation was made by a JEM-200CX electron microscope equipped with a

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double-tilt heating holder. In the present observation, dark field images were obtained mainly by using satellite reflection spots characterizing the incommensurate structure in order to examine features of the ferroelastic domain structures. Although a way of taking satellite dark field images in BSN was in detail described in Ref. 8, let us explain it briefly here. There are two types of satellite reflection spots in electron diffraction patterns obtained from the incommensurate phase, which are due to two types of $1q$ ferroelastic domains with orthorhombic symmetry. These two types of the domains consist of the twin structure. We call these spots (α)- and (β)-type spots, respectively. In addition, because of weak satellite reflection spots just below the transition temperature of 573 K, it is hard to obtain a conspicuous contrast in conventional films. Thus, in order to obtain a strong contrast, we took satellite dark field images by using imaging plates with high sensitivity in the present work.

BSN exhibits a normal-to-incommensurate phase transition at 573 K on cooling from the normal tetragonal phase. Figure 1 shows a satellite dark field image at room temperature, which was obtained from a sample cooled from the normal tetragonal phase. The image was taken by using only the (α)-type spot. In the image, bright and dark contrasts are observed with a flat boundary parallel to the $(110)_0$ plane. Because a satellite dark field image taken by the (β)-type spot exhibits a reversed contrast, the bright and dark contrasts in Fig. 1 are understood to be due to two types of $1q$ ferroelastic domains, respectively. Note that in each ferroelastic domain modulation takes place along the $[100]_0$ direction. In the ferroelastic domain giving rise to the bright contrast, wavy dark line contrasts are also seen. As pointed out in our previous work, the line contrast is due to a discommensuration with a phase slip of $2\pi/4$.[14] It is worth noticing that the domain size at room temperature is estimated to be about 1 μm as an average.

In order to elucidate the change in microstructures during the cooling process, which results in the domain structure shown in Fig. 1 at room temperature, the *in situ* observation of the evolution of the ferroelastic domain structure in the incommensurate phase was performed. Figure 2 shows a change in microstructures obtained during the cooling process from the normal tetragonal phase. Figure 2(a) is a satellite dark field image taken at 553 K by using only the (α)-type spot. Note that according to the previous work the sample at 553 K has the $2q$ incommensurate structure.[7,12,13,15] In the image, a characteristic contrast is observed. This contrast can be called a "mazy pattern" and was already reported in Ref. 16. When the temperature is lowered in the incommensurate phase, the intensities of the satellite reflection spots are increasing and the wavy contrast becomes conspicuous. Figures 2(b) and 2(c) show satellite dark field images taken at 543 and 533 K by using the (α)-type spot, respectively. The contrast exhibiting a mazy pattern is clearly observed. Around 533 K elongated rectangular domains are seen in some regions of the specimen, as marked by an arrow in Fig. 2(c). The present *in situ* observation showed that an elongated rectangular domain is formed by a gradual change from the mazy pattern. On further cooling in the incommensurate phase, a ferroelastic domain structure shown in Fig. 1 suddenly appears around 503 K. That is, there exists an abrupt change in the domain structure in the incommensurate phase of BSN. From a comparison with the previous data, this change is basically understood to correspond to the $2q$-to-$1q$ transition.[2,11,13,15]

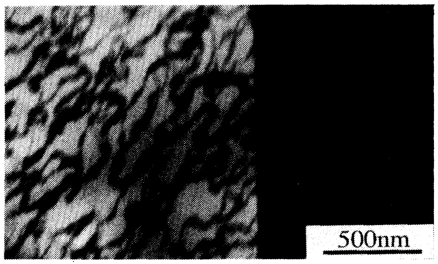

FIG. 1. Satellite dark field image taken at room temperature by using the (α)-type spot. In the image, two types of ferroelastic domains are observed as bright and dark regions, respectively.

In order to investigate the details of the characteristic contrasts of the mazy pattern, a satellite dark field image was taken by using a (β)-type spot. Figures 3(a) and 3(b)

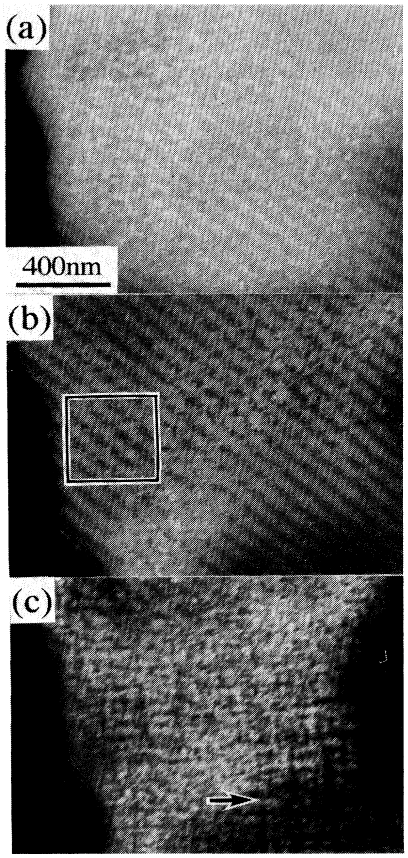

FIG. 2. Series of satellite dark field images showing the change in microstructures during the cooling process from the normal tetragonal phase. The images are taken at (a) 553 K, (b) 543 K, and (c) 533 K, respectively.

are satellite dark field images in the same region taken at 543 K by using the (α)- and (β)-type spots, respectively, which were obtained from the region indicated by the rectangular part in Fig. 2(b). Figure 3(c) is a contrast reversed image of Fig. 3(a), which was made by the computational method in order to easily compare the images shown in Figs. 3(a) and 3(b) with each other. From a comparison between Figs. 3(a) and 3(b), it is found that the bright-contrast regions in Fig. 3(a) correspond to dark-contrast ones in Fig. 3(b). These facts clearly imply that the regions with the bright and dark contrasts are understood to be two types of the $1q$ ferroelastic domains with modulation only along the $[100]_0$ direction, respectively. That is, the incommensurate structure in the temperature range between 573 and 543 K is constituted of a complicated array of ferroelastic microdomains with a size of about 20 nm. Note that the modulation in each microdomain occurs only along the $[100]_0$ direction. In other words, the $2q$ incommensurate structure with tetragonal symmetry is just an average structure consisting of two types of $1q$ ferroelastic microdomains with orthorhombic symmetry. In addition, the bright-contrast regions in Fig. 3(a) are cut by dark-contrast stripes running along the $\langle 110 \rangle_0$ direction. Because the stripe is not observed in the dark-contrast region of Fig. 3(b), these contrasts should be due to the discommensurations.

On the basis of the present *in situ* observation, here we summarize the evolution of the ferroelastic domain structure in the incommensurate phase of BSN, which was formed in the cooling process. Figure 4 is a schematic description showing the ferroelastic domain structures at three temperatures. Figure 4(a) shows the domain structure appearing in the incommensurate phase around 553 K below the transition temperature of 573 K. Note that the incommensurate phase at 553 K is identified as the $2q$ incommensurate phase on the basis of physical properties such as the elastic constants.[2,11,12] As found from Fig. 3, the ferroelastic domain structure, which can be called the mazy domain structure, is observed and is understood to be constituted of a complicated array of two types of $1q$ ferroelastic microdomains with a size of about 20 nm. A feature of the domain structure is that the boundary between two microdomains is not clear, but diffuse and wavy. When the temperature is lowered to 533 K, the domain structure exhibits two different continuous changes. One is the decrease in volume of one of the two types of microdomains, and the other is the formation of an elongated rectangular domain structure, as shown in Fig. 4(b). That is, it is understood that the domain structure around 533 K is constituted of both the mazy and elongated rectangular domains. When the temperature is further lowered to around 503 K, the domain structure abruptly changes into a large scaled domain structure of the ferroelastic phase with the orthorhombic symmetry. The size of the domain was estimated to be about 1 μm on average. In each ferroelastic domain, modulation occurs only along the $[100]_0$ direction, as in the case of microdomains. Eventually these experimental results indicate that the domain structure drastically changes around 503 K, although the continuous change in the domain structure takes place between 573 and 503 K.

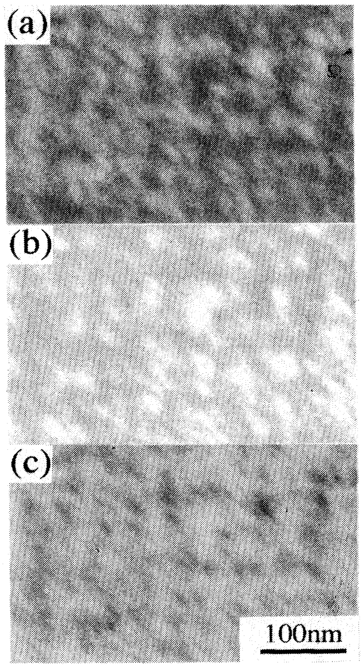

FIG. 3. (a), (b) Satellite dark field images taken at 543 K using (α)- and (β)-type spots, respectively. Image (c) is a contrast reversed one of image (a) by a computational method.

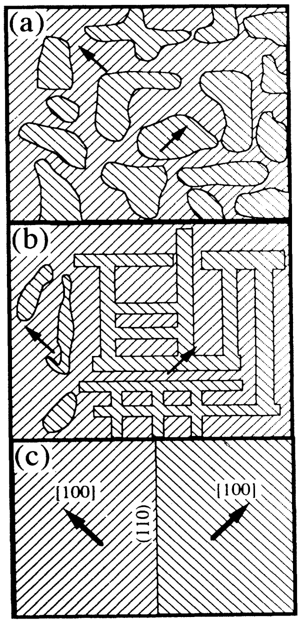

FIG. 4. Schematic description showing the evolution of the ferroelastic domain structure in the incommensurate phase of BSN. The domain structures at (a) 543 K, (b) 533 K, and (c) room temperature are depicted schematically. Arrows represent the direction of the modulation along the $[100]_0$ direction in each ferroelastic domain.

It is time to discuss the origin of the sudden change in the ferroelastic domain structure around 503 K in the incommensurate phase of BSN. The most important feature of this change is that the domain-structure change never accompanies a change in point group symmetry. That is, both the $2q$ and $1q$ incommensurate phases consist of $1q$ ferroelastic domains with orthorhombic symmetry. It should be noticed that Barre, Mutka, and Roucau found a ferroelastic microdomain structure appearing around 503 K in the heating process from room temperature.[15] This means that a large ferroelastic domain structure with a flat domain boundary at room temperature changes into a ferroelastic microdomain structure around 503 K during the heating process. Our recent work revealed that the microdomain structure found by Barre *et al.* is basically the same as that for the $2q$ incommensurate phase, although the observed images are not shown here. This fact indicates that the domain-structure change takes place reversibly around 503 K during the cooling and heating processes. From the reversibility, the domain-structure change around 503 K could be called "the domain-structure transition." The following point should be made. We analyzed the properties of the incommensurate phase in BSN on the basis of the Ginzburg-Landau theory.[14] Our theory predicts an incommensurate-to-commensurate transition at 500 K, although the transition has not been observed experimentally.[14] Actually, a characteristic pattern playing an important role in the incommensurate-to-commensurate transition is observed in the $1q$ incommensurate phase below about 503 K.[8,15,17] We call the characteristic pattern a jellyfish pattern, which is a defect of a discommensuration lattice. From a comparison between the experimental data and the theoretical consideration, the transition temperature of the domain-structure transition is surprisingly found to coincide with the predicted one of the incommensurate-to-commensurate transition. This fact suggests that a domain-structure transition should originate from the incommensurate-to-commensurate transition.

Our Ginzburg-Landau theory predicts that the incommensurate-to-commensurate transition is of first order. Because of the first-order transition, a discrete change in the order parameter should occur at the transition temperature. Note that the order parameter in this case is an amplitude of a modulated wave. In addition, there exists a coupling term between the order parameter and the spontaneous strain characterizing the orthorhombic distortion in a free energy, as pointed out by Toledano and co-workers.[2,3,9,10] It is obvious that the coupling term results in a discrete change in the spontaneous strain in the transition, corresponding to a discrete change in the order parameter. It then seems that this discrete change in the spontaneous strain in the incommensurate-to-commensurate transition produces a drastic and discrete change in the domain structure around 503 K. Thus we believe that the coincidence between the experimentally obtained transition temperature and the predicted one in the Ginzburg-Landau theory is a key factor in order to understand the origin of the abrupt change in the domain structure. As was understood in our previous paper, the memory effect is directly related to the elongated rectangular microdomain stabilized by annealing a sample.[8] Because the annealing of the sample produces a redistribution of the mobile Na ion, the stability of two kinds of microdomain structures should depend on the history of the sample. From this fact, the history of the sample is expected to affect the domain-structure transition. Hence our future task on the incommensurate-to-commensurate transition of BSN is then to clarify this speculation.

In summary, the present data obtained by means of the transmission electron microscope clearly show that the domain structures in both the $2q$ and $1q$ incommensurate phases of BSN consist of $1q$ ferroelastic domains with orthorhombic symmetry, and then the $2q$-to-$1q$ transition around 503 K on cooling never accompanies a change in point group symmetry. On the other hand, an abrupt change in the ferroelastic domain structure was found around 503 K. Because of the reversible change in the domain structure during the cooling and heating processes, the change could be called "the domain-structure transition." Our Ginzburg-Landau theory proposed previously suggests that the domain-structure transition should originate from a discrete change in the spontaneous strain in the incommensurate-to-commensurate transition.

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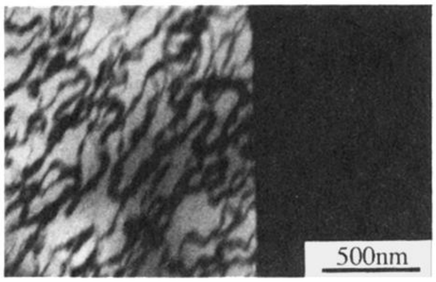
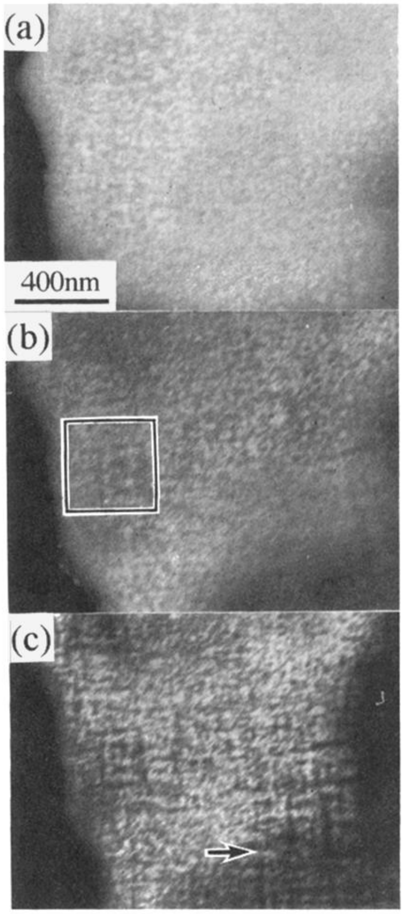


FIG. 1. Satellite dark field image taken at room temperature by using the (α)-type spot. In the image, two types of ferroelastic domains are observed as bright and dark regions, respectively.



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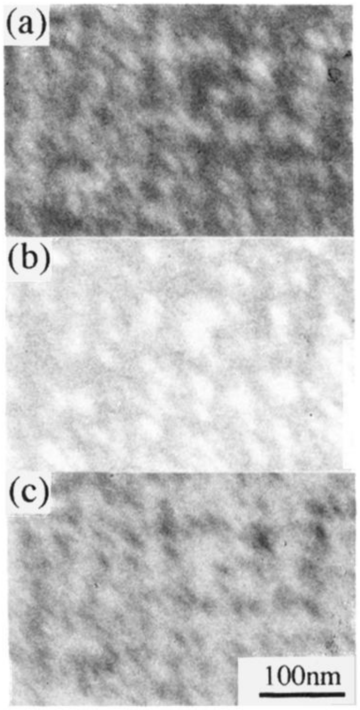

FIG. 3. (a), (b) Satellite dark field images taken at 543 K using (α)- and (β)-type spots, respectively. Image (c) is a contrast reversed one of image (a) by a computational method.