Absence of interaction between ferroelectric and incommensurate transitions in $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$

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Features of both the ferroelectric and incommensurate transitions in $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ were investigated by means of a transmission electron microscope in order to find the relationship between these transitions. An *in situ* observation of the transitions revealed that the ferroelectric transition takes place around 373 K in $x=0.57$ while the incommensurate transition occurs around 543 K. Because the ferroelectric transition does not basically accompany a change in microstructures related to the incommensurate lattice modulation, there is no interaction between these two transitions.

Barium sodium niobate ($Ba_2NaNb_5O_{15}$: BSN) has been reported to undergo two successive phase transitions in the cooling process.[1,2] One is a ferroelectric transition with a change in point symmetry from $4/mmm$ to $4mm$ around 833 K and a spontaneous polarization appears along the [001] direction in the ferroelectric phase. The other is a phase transition from a tetragonal phase (space group: $I4mm$) to an incommensurate one; that is, an incommensurate transition, around 573 K, which is related to a peculiar phenomenon called the memory effect.[3–8] A feature of the incommensurate transition is that the transition accompanies a point symmetry change from $4mm$ to $mm2$ and results in the appearance of ferroelastic domains in the orthorhombic phase. As for atomic displacements in these two transitions, a Nb atom involved in the NbO_6 octahedron is displaced along the [001] direction in the ferroelectric transition, while the incommensurate transition is due to atomic displacements which consist of a collective shearing of apex O atoms in the octahedron along the [100] direction.[1,2] From these displacements, an interaction between the ferroelectric and incommensurate transitions should be expected in BSN.

Recently Takashige *et al.* examined the change in transition temperatures of the ferroelectric and incommensurate transitions in $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ (BSNT) with substitution of Nb by Ta and found that the former transition temperature drastically decreases with an increment of Ta content x.[9,10] As a result of the decrease in ferroelectric transition temperature, the ferroelectric transition actually occurs around 35 K at the end component of $Ba_2NaTa_5O_{15}$ (BST).[11,12] On the other hand, the transition temperature of the incommensurate transition in BSNT was found to be almost independent of x. From these facts, the ferroelectric transition can take place in the incommensurate phase of BSNT. In this case, when the temperature is lowered from the high-temperature tetragonal phase, a point symmetry first changes from $4/mmm$ to mmm in the incommensurate transition and then to $mm2$ in the ferroelectric one. Then, in order to clarify the influence of the ferroelectric transition on the incommensurate one, we have investigated microstructures in the successive transitions in $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ with $x=0.57$ and then report experimentally obtained data on it in the present paper. The reason of the choice of $x=0.57$ is that the transitions in $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ with $x=0.57$ were, respectively, reported to be 488 K for a change related to the incommensurate transition and 373 K for the ferroelectric one.[13] That is, because the latter temperature is by 115 K lower than the former one, it is possible to easily examine a change in microstructures in the incommensurate phase, which is related to the ferroelastic transition. Previous work has revealed features of microstructures in the incommensurate phase of BSN.[1,4,7,8,14–19] It should be noted that the incommensurate transition in BSN takes place in the ferroelectric phase while the incommensurate transition in $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ with $x=0.57$ occurs in the paraelectric phase. In the present work, the ferroelectric transition in the incommensurate phase of $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ with $x=0.57$ was investigated in order to elucidate the relation between the incommensurate and ferroelectric transitions.

Single crystals of $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ ($x=0.57$; BSNT) are used in the present work. The details of the preparation of the single crystal were already described in the previous paper.[9,10] Thin-film samples for the transmission electron microscope were prepared by crashing in the BSNT single crystals and then dispersing on holey carbon films supported on molybdenum grids. The observation of the ferroelectric and incommensurate transitions was made mainly by taking dark field images, using a JEM-200CX electron microscope equipped with a double-tilt heating holder. Concretely, we examined features of the ferroelectric domains by taking dark field

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images using fundamental reflections and those of both the ferroelastic domain and discommensurations in the incommensurate phase by taking images using satellite reflections. A way of taking satellite dark field images was reported in Ref. 7.

For the reasons mentioned earlier, we here describe features of both the ferroelectric and incommensurate transitions for $x = 0.57$ among oxides examined in the present work. Figure 1 shows an electron diffraction pattern of BSNT with $x = 0.57$, taken at room temperature. Note that the direction of the incident beam is parallel to the [010] direction. In the diffraction pattern, there are both fundamental reflection spots due to the orthorhombic structure and satellite reflection spots indicated by an arrow. It is found that the satellite reflection spots are located around $\frac{1}{2}+\delta\ 0\ \frac{1}{2}$ type positions in the reciprocal space of the orthorhombic structure, where an incommensurability δ is defined as the magnitude of a deviation from a $\frac{1}{2}\ 0\ \frac{1}{2}$ type position in the reciprocal space. From a careful analysis of the diffraction pattern, the value of δ is estimated to be about 0.005. This means that BSNT has an incommensurate structure with the modulation along the [100] direction at room temperature, as in the case of BSN. Figures 2(a) and 2(b) are dark field images of an area showing the diffraction pattern of Fig. 1, which were taken by a satellite reflection spot characterizing the incommensurate structure and a fundamental spot of the orthorhombic structure, respectively. Note that the satellite dark field image was taken by using only an (α)-type spot of the satellite reflections, where there are two types of satellite reflection spots, (α)-type and (β)-type spots, which are related to two types of ferroelastic domains, respectively.[7] In Fig. 2(a), ferroelastic domains are observed with bright and dark contrasts, which are regarded as diffraction contrast. Note that the ferroelastic domain boundary indicated by an arrow (A) is perpendicular to the [110] direction. In the bright-contrast regions, wavy black line contrasts identified as the discommensurations with a phase slip of $2\pi/4$ are clearly seen. In the fundamental dark field image of Fig. 2(b), ferroelastic domains are also seen as bright and dark contrasts, as in the satellite dark field image. In addition, in both ferroelastic domains, characteristic zigzag line contrasts are seen, as is marked by an arrow (B). From the g-vector dependence of the contrasts, the characteristic contrasts are found to be due to the existence of ferroelectric domains. These results mean that both the ferroelectric and incommensurate phases coexist at room temperature in BSNT.

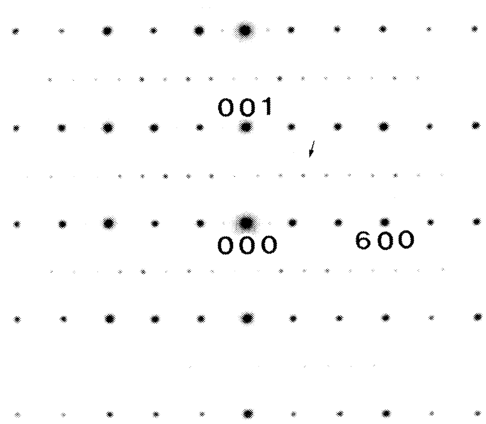

FIG. 1. Electron diffraction pattern of $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ with $x = 0.57$ taken at room temperature. An incident direction is parallel to the [010] direction.

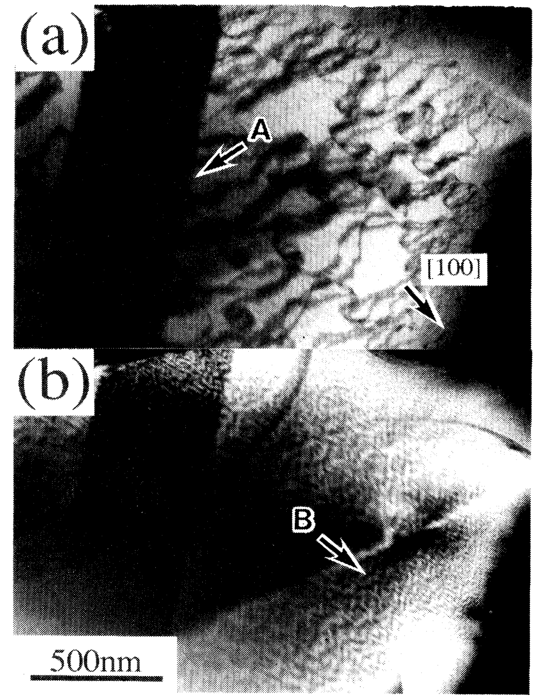

FIG. 2. Microstructures of BSNT with $x = 0.57$ obtained at room temperature. The images (a) and (b) were taken by using a satellite reflection spot characterizing the incommensurate structure and a fundamental reflection spot due to the orthorhombic structure, respectively.

In order to examine both the ferroelectric and incommensurate transitions, an *in situ* observation of the transitions was made. Figure 3 shows changes in both the fundamental and satellite dark field images, which are related to the ferroelectric transition. Figures 3(a) and 3(b) first show the fundamental and satellite dark field images taken at room temperature, respectively. The characteristic zigzag contrasts due to the ferroelectric domains are seen in Fig. 3(a), while in Fig. 3(b) wavy black line contrasts identified as the discommensurations are clearly seen. When the temperature is raised from room temperature, the zigzag contrasts become faint and disappear around 373 K. The fundamental and satellite dark field images taken at 393 K are shown in Figs 3(c) and 3(d), respectively. No characteristic contrast is observed in Fig. 3(c). This means that the ferroelectric transition on heating occurs around 373 K, as was reported by Takashige *et al.*[9,10] On the other hand, in the satellite dark field image of Fig. 3(d), the wavy black line contrasts identified as the discommensurations are still left. Although a gradual change in the line contrasts is detected on heating, there is no special change in the contrast at the ferroelectric

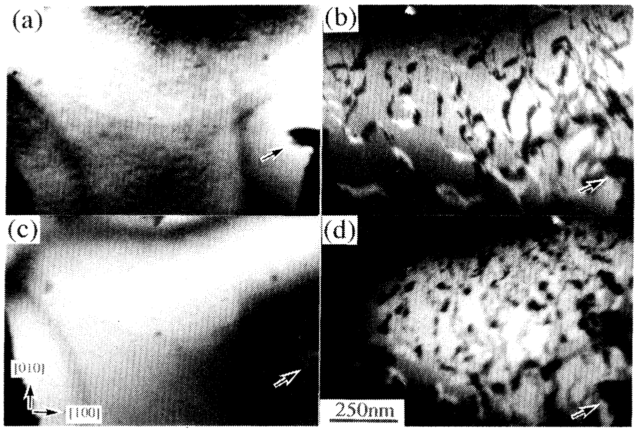

FIG. 3. Changes in microstructure in the ferroelectric transition on heating. (a) and (c) are dark field images taken by using a fundamental reflection spot at room temperature and at 393 K, respectively. On the other hand, (b) and (d) are dark field images taken by using a satellite reflection spot characterizing the incommensurate structure at room temperature and at 393 K, respectively. In each figure, an arrow indicates the same position of the sample.

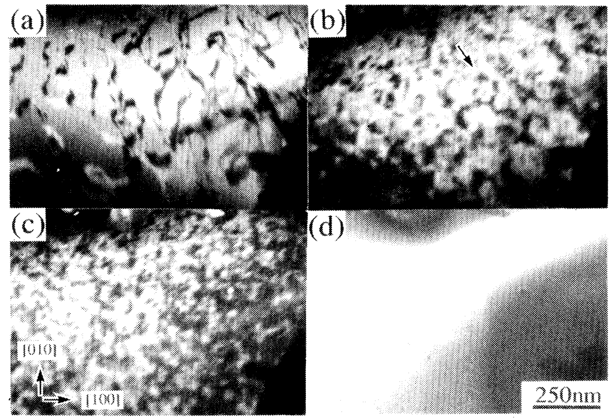

FIG. 4. Changes in microstructure in the incommensurate transition during the heating process. The images were taken by using a satellite reflection spot at (a) room temperature, (b) 423 K, and (c) 493 K, respectively. Only image (d) is a dark field image taken by using a fundamental reflection spot at 573 K, where a phase of the sample is the high-temperature one.

transition. This indicates that the ferroelectric transition basically has no influence on the microstructures of the incommensurate phase.

In the previous work,[1–8,14–19] features of the incommensurate phase in BSN have been investigated sufficiently, while a change in microstructures during the incommensurate transition of BSNT has not been examined so far. Thus, we made an *in situ* observation of the incommensurate transition on heating in BSNT. Figure 4 shows a series of satellite dark field images showing a change in microstructures during the incommensurate transition of BSNT with $x = 0.57$ in the heating process from room temperature. Figures 4(a)–4(c) are images taken by using the (α)-type satellite reflection spot at room temperature, 423 K, and 493 K, respectively. In Fig. 4(a), the wavy black line contrasts due to the discommensurations are observed in the ferroelastic domain, as shown in Figs. 2(a) and 3(b). When the temperature is raised from room temperature, dark dot-shaped contrasts marked by an arrow in Fig. 4(b) appear around 423 K in the ferroelastic domain, in addition to the contrast due to the discommensurations. In other words, there exists only a gradual change in the contrast due to the discommensuration in a temperature range below 423 K. On further heating in the incommensurate phase, the number of the dark dot-shaped contrasts is increasing while the contrasts due to the discommensurations become invisible. As is seen in Fig. 4(c), the image taken at 493 K shows both bright and dark dot-shaped contrasts but no black line ones. Note that the similar dot-shaped contrasts are observed in the $2q$ incommensurate phase of BSN during the heating process and are understood to be due to two types of the ferroelastic microdomains with the modulation along the [100] direction, respectively.[16] Although the image taken at 493 K by the (β)-type spot is not shown here, the region giving rise to a dark dot-shaped contrast in the image [Fig. 4(c)] taken by the (α)-type spot was found to correspond to a bright contrast region in the image taken by the (β)-type spot. This means that the dot-shaped contrast in BSNT is also due to two types of ferroelastic microdomains, as in the case of the $2q$ incommensurate phase of BSN.[7,16,19] Eventually, BSNT with $x = 0.57$ around 493 K is concluded to be regarded as a $2q$ incommensurate state in an average structure, which consists of two types of the ferroelastic microdomains. In other words, a change from the $1q$ state to the $2q$ one occurs around 493 K. On further heating to the high-temperature tetragonal phase, around 543 K satellite reflection spots become invisible and no characteristic contrast is observed in the satellite dark field image. A dark field image at 573 K, Fig. 4(d) was then taken by a fundamental reflection spot. Since no contrast is seen in the image, BSNT undergoes the incommensurate transition around 543 K on heating. That is, a change in the microstructures of BSNT is entirely the same as that in BSN, except that the incommensurate transition in BSN takes place in the ferroelectric phase. A difference is that the transition temperature in BSNT with $x = 0.57$ is lower by only 30 K than that in BSN.

In the present work, it is revealed that BSNT undergoes two successive phase transitions, that is, the ferroelectric transition around 373 K and the incommensurate transition around 543 K in $x = 0.57$ on heating. Because BSN exhibits the incommensurate transition around 573 K and the ferroelectric transition around 833 K, respectively,[1,2] the substitution of Nb by Ta mainly affects the ferroelectric transition. As a result of the remarkable lowering of the transition temperature of the ferroelectric transition, the ferroelectric transition takes place in the incommensurate phase in BSNT. In addition, although there is the gradual change in the wavy line contrast due to the discommensuration below 493 K in the incommensurate phase on heating, a sudden change in the discommensuration cannot be detected in the ferroelectric transition. This clearly means that the ferroelectric transition does not play any role for the incommensurate transition. Actually, the behavior of the incommensurate transition in BSNT was found to be exactly the same as that in BSN.

Takashige *et al.* reported from the polarizing microscopic observation that a transition from the biaxial to the uniaxial state occurs around 488 K.[13] Such an optical experiment provides information of a change in a macroscopic distribution of ferroelastic domains, that is, the appearance of the macroscopic twin structure due to the ferroelastic domains with the orthorhombic symmetry. From the present work, however, the transition toward the tetragonal state was found to occur around 543 K. Actually there exists the $2q$-to-$1q$ transition around 493 K. Since the $2q$ state is an average tetragonal structure consisting of two types of ferroelastic microdomains with orthorhombic symmetry, there is a possibility that the optical experiment regards the $2q$ state as a macroscopically uniaxial state. Eventually, a discrepancy between the transmission electron microscopy and the optical experiment is due to be different in the resolution power between these two experiments.

The ferroelectric and incommensurate transitions take place by the atomic displacements of the Nb (Ta) and apex O atoms involved in the NbO_6 octahedra, respectively. Concretely, the former is the displacement of the Nb atom along the [001] direction, while the incommensurate structure is produced by the collective shearing of the apex O atoms along the [100] direction. Recently, Cohen and Krakauer pointed out on the basis of first-principles band calculation that a physical origin of the ferroelectric transitions in perovskite oxides such as $BaTiO_3$ is due to a decrease in the repulsive force, which is induced by a hybridization between the $3d$ orbital of a transition metal and the $2p$ one of the O atom.[20,21] On the basis of their calculation, the hybridization between the d orbitals of the Nb and Ta atoms and the $2p$ orbital of the apex O atom should be important in the ferroelectric transition of BSN and BSNT. This suggests the possibility that there is an interaction between the ferroelectric and incommensurate transitions in these oxides. In the present work, however, it was found that the ferroelectric transition never affects the microstructures due to both the ferroelastic orthorhombic domains and the discommensuration in the incommensurate phase. In addition, in the case of BSN, the incommensurate transition does not induce any change in ferroelectric properties.[22] These facts suggest that the displacement of the apex O atom along the [100] direction does not affect the hybridization between the d orbital of the transition metal and the $2p$ orbital of the apex O atom. Because a maximum magnitude of the displacement of the apex O atom was reported to be about 0.02 nm,[23,24] the magnitude of 0.02 nm is understood to be small enough to produce no change in the hybridization.

In summary, the *in situ* observation of the ferroelectric and incommensurate transitions in $Ba_2NaNb_{5(1-x)}Ta_{5x}O_{15}$ during the healing process was carried out in order to examine the interaction between these transitions. The observation clearly revealed that the ferroelectric and incommensurate transitions take place without any interaction. That is, the ferroelectric transition does not affect the microstructures in the incommensurate phase.

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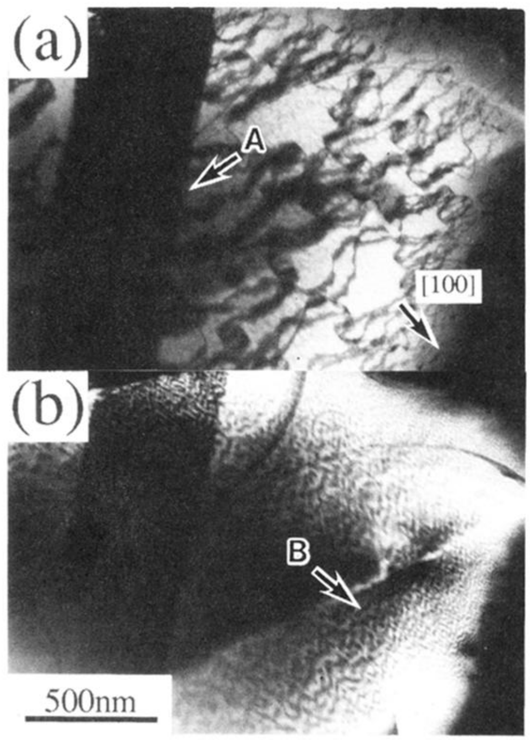


FIG. 2. Microstructures of BSNT with $x = 0.57$ obtained at room temperature. The images (a) and (b) were taken by using a satellite reflection spot characterizing the incommensurate structure and a fundamental reflection spot due to the orthorhombic structure, respectively.

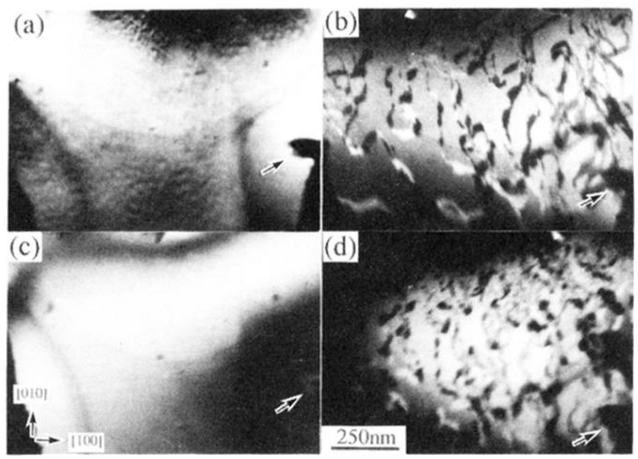
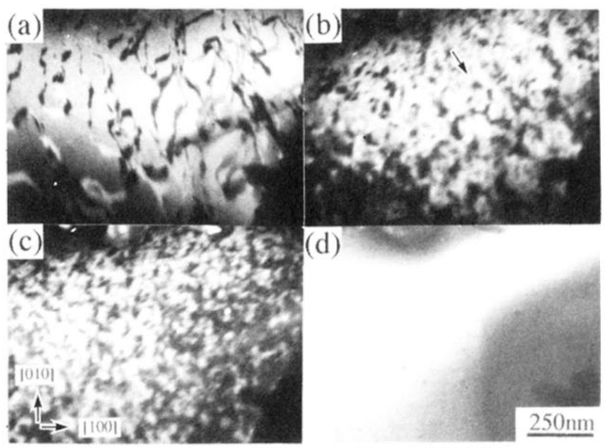


FIG. 3. Changes in microstructure in the ferroelectric transition on heating. (a) and (c) are dark field images taken by using a fundamental reflection spot at room temperature and at 393 K, respectively. On the other hand, (b) and (d) are dark field images taken by using a satellite reflection spot characterizing the incommensurate structure at room temperature and at 393 K, respectively. In each figure, an arrow indicates the same position of the sample.



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