# 走査型プローブ顕微鏡による相転移時の結晶の分域構造の評価

SPM Observation of Domain Structures on Successive Phase Transitional Crystals

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Scanning probe microscopic observations were made for domain structures of crystals in $WO_3$ and $BaTiO_3$, both of which show successive phase transitions with alteration of crystal systems. The variety of ferroic twin (domain) structures due to the lattice distortion associated with the successive transitions was visualized. In $WO_3$, the crossings of two types of domains such as between the monoclinic and triclinic domains were observed. In $BaTiO_3$, the crossing of 90° domains in the tetragonal phase was observed.  As a result, the surface structure of crystals undergoing successive phase transitions is strongly dependent on the boundary conditions imposed by the previously appeared phases.

**Key words:**　ferroic crystal, domain, $WO_3$, $BaTiO_3$, twin, Scanning probe microscope, SPM

## 1. INTRODUCTION

The present work deals with the domain structures of two crystals $WO_3$ and $BaTiO_3$ undergoing successive phase transitions. The variety of ferroic twin (domain) structure associated with the phase transitions results in complex morphology of the crystal surface. For example, $WO_3$ shows tetragonal – orthorhombic – monoclinic – triclinic phase sequences with decreasing temperature. In the triclinic phase, three types of surface images due to the orthorhombic, monoclinic and triclinic domain structure can be seen.[1)] Sometimes, intersection of two types of domains occurs at the same crystal plate.[1-3)] In that case, the morphology of the crystal surface such as bending angles from the horizontal level shows a different value from the ideal crystallographic value determined by other methods such as X-ray diffraction. In the well-known $BaTiO_3$, which undergoes cubic – tetragonal – orthorhombic – rhombohedral phase transitions, various types of the intersection of 90° domains are observed in the tetragonal phase of the thin *c*-plate sample.

The purpose of the present work is to visualize such a complicated surface feature in $WO_3$ and $BaTiO_3$ and to obtain quantitative topographic information by scanning probe microscopy (SPM).

## 2. EXPERIMENTAL

For experiments, Digital Instruments NanoScope III and temperature-varying unit (Molecular Imaging, Inc., Nanopico-series) were used. The operation to obtain topographic images was made in the contact mode with a scan range of 40×40 [μm$^2$]. The scan time of 40×40[μm$^2$] area at the fixed temperature is about 512[sec]. Samples of $WO_3$ are as-grown *c*- and *a*-plates with thickness of 0.1~0.3[mm] prepared by the sublimation method. Those of $BaTiO_3$ are as-grown *c*-plates with thickness of 0.05~0.1[mm] prepared by KF flux method.

## 3. RESULTS AND DISCUSSION

### 3. 1 $WO_3$

The crystal undergoes the successive transitions from the tetragonal symmetry phase(*P4/nmm*) to the orthorhombic phase (*Pnmb*) at 740[°C], the orthorhombic to the monoclinic phase(*P21/n*) at 330[°C], and then from the monoclinic to the triclinic phase(*P1*) at 17[°C], respectively.[4,5)]

The surface topography associated with the above transition is illustrated in Fig.1(a)~(d). When the crystal is cooled from the tetragonal phase with a flat surface (Fig.1(a)), the orthorhombic domain occurs below 740[°C](Fig.1(b)), where the surface bends due to interchange of *a*-and *b*-axes at the boundary. Next, below 330[°C] due to the monoclinic distortion,

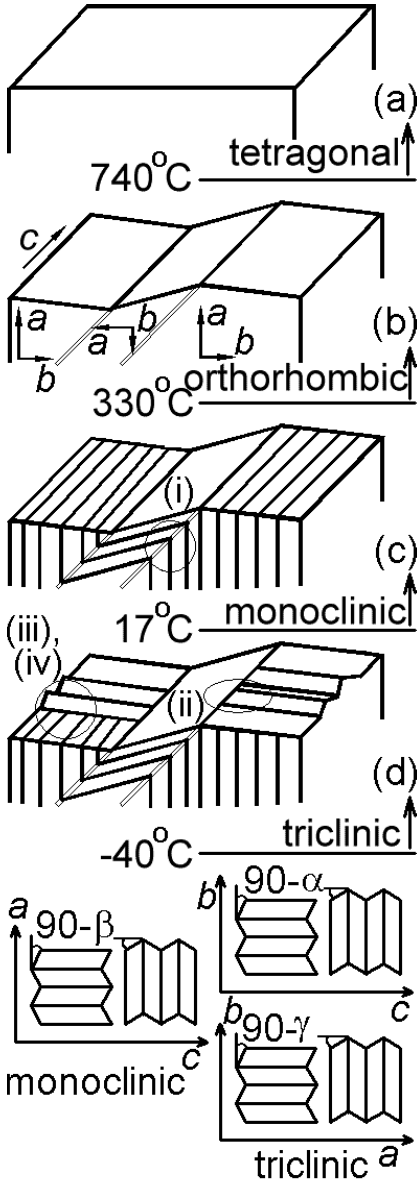


**Fig.1** Schematic illustration for occurrence of the twin structures in $WO_3$.

the angle between a- and c-axes deviates from 90° (monoclinic angle β, see also bottom left in Fig.1). As the result, the *a*-(or *c*-)plane is undulated by the angle ±(90-β) along the *b*-axis, as shown in Fig.1(c). On further cooling, the triclinic distortion occurs below 17[°C]. In this case, as shown in Fig.1(d), the *b*-(or *c*-)plane is undulated by the angle ±(90-α) along the *a*-axis, or the *a*-(or *b*-)plane is undulated by the angle ±(90-γ) along *c*-axis, where α and γ are triclinic angles(see also bottom right in Fig.1).

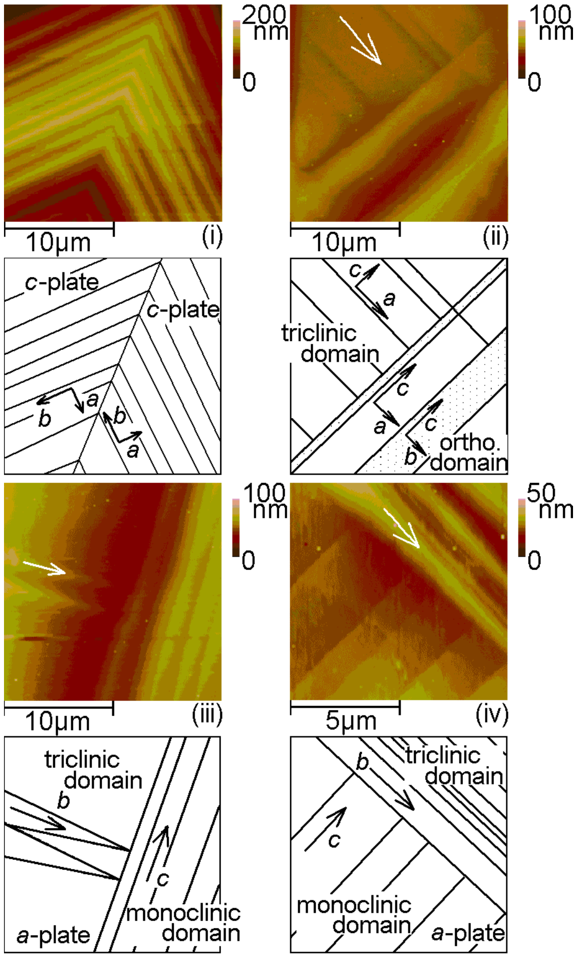


**Fig.2** Four types of domain intersection in $WO_3$. Observed areas correspond to those shown in Fig.1.

Figures 2(i) ~(iv) show examples of the four types of crossed domains observed. The corresponding areas for these images are shown also by (i)~(iv) in Fig. 1. Among them, (i) and (ii) have already been reported in refs.1-3. (iii) and (iv) were newly taken in this study. For (i), the monoclinic angle β shows almost the same value (0.8°) as reported by X-ray method,[5)] whereas in other three cases, β and triclinic angles α and γ are fairly smaller than those by X-ray method. For (iii), the cross sectional profiles of the wedge-shape triclinic domain are shown in Fig.3. The angle observed here is smaller than the triclinic γ-angle 0.93° reported by X ray method.[5)]

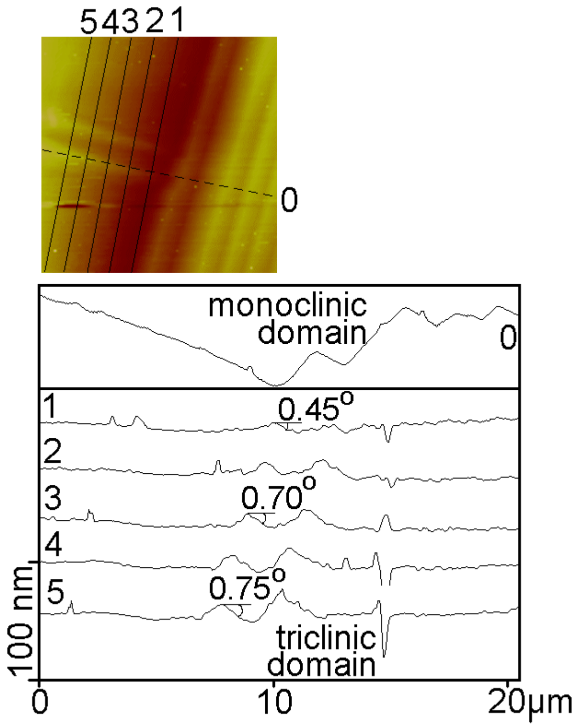


**Fig.3** Cross sectional profiles of the wedge-type triclinic domain.

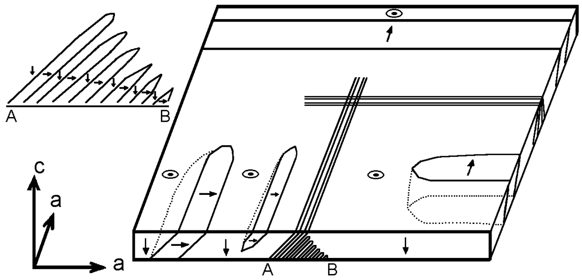


**Fig.5** Schematic illustration for occurrence of various types of twin structures in $BaTiO_3$.

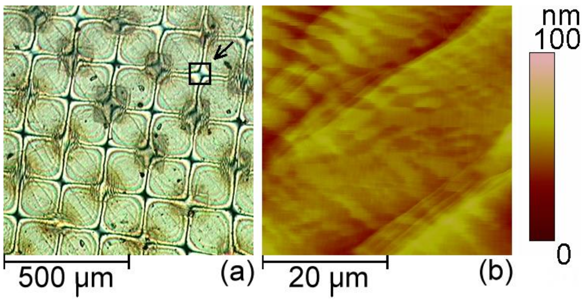


**Fig.6** Square net domain pattern in $BaTiO_3$. (a)polarizing micrograph, (b)SPM topographic image for the area marked in (a).

3. 2 $BaTIO_3$

SPM topographic image of the tetragonal 90° domain was first reported by our research group in 1995[6]. Usually, at the 90° domain boundaries, the surface bends with the angle $\theta$=(2tan-1$c/a$ – 90)°, where $c$ and $a$ are lattice parameters. $\theta$ about 0.6° at room temperature and in fact the approximate value is observed as shown in Fig.4. However, real crystals contain various types of domain configuration, as shown schematically in Fig.5, where the intersection of laminar group and wedge-type domains are depicted. It is easily supposed that the surface topographies for such cases are different from the normal $a$-$c$ domain boundaries in Fig.4.

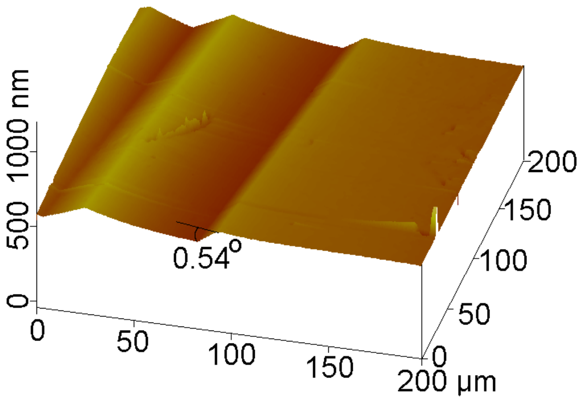


**Fig.4** Normal-type 90° domain boundaries in $BaTiO_3$.

Concerning SPM topographic images of the intersection of laminar groups, there is a work by Balakumar et al.[7], indicating much suppression of the bending angle(~0.17°) near the intersection point. In the present work, we observed a $c$-plate sample with the square net domain pattern[8], which is also a sort of laminar group having layered structure. Figure 6(a) is the polarizing micrograph of the square net domain taken at room temperature. Figure 6(b) is the topographic image for the marked area in Fig.6(a), where almost no significant bending of the surface is observed. Probably, this means that the crystal structure is much deformed due to strong stress exerted near the intersectional part.

## 4. SUMMARY

In the present work, we demonstrated several non-standard domain structures in $WO_3$ and $BaTiO_3$. The reason for the formation of domains in single crystals is that it is energetically difficult for crystals to be ordered over long distances in a single direction. For example, if the symmetry is orthorhombic with three orthogonal axes, it is possible to have a 90° domain in addition to a 180° domain, which is shown in the surface structure in this paper.

However, if the first-order transition from that state to a lower symmetry, the 90° domain can no longer exist, and all of its 90° intersecting quadrants must be converted to a unique 180° domain. In other words, in this paper, the process is viewed as a change in surface structure, and it is clearly shown that the history of the original 90° domain is responsible for the construction of the next domain structure. In the strain-free crystal, the surface topography by domain boundaries depends only on the microscopic crystallographic data, however, in the crystal undergoing successive phase transitions, a domain structure strongly depends on the boundary conditions made by the phase appeared before. Therefore, the surface topography sometimes becomes very complicated. Such observations will be a good subject for future studies on surface irregularities, such as SPM and the recent laser microscope.

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