Ferroelastic Multidomains in LaNbO_4 Crystals

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LaNbO_4 crystals show three lineal structures associated with domain formation under high-resolution polarizing optical microscope. One has a width of the order of 10 microns and the others are in order of 1 micron wide. The former is a large scale multidomain structure formed by twinning deformation due to monoclinic spontaneous strains below phase transition temperature and the latter is a small scale multidomain structure coming from discommensuration due to incommensurate-commensurate phase transition. Spacings of these multidomain structures are discussed on basis of experimental results and theoretical consideration.

Keywords: lanthanum orthoniobate, ferroelasticity, incommensurate-commensurate phase transition, discommensuration, multidomain, microdomain, spontaneous strain, twinning deformation, shuffle, W' wall, cleavage, atomic force microscopy, polarizing optical microscopy, transmission electron microscopy

I. Introduction

LaNbO_4 crystals exhibit structural transition from a normal phase ($I4_1/a$) to a ferroelastic commensurate phase ($I2/a$) at 773 K⁽¹⁾. This transition is considered to pass through an intermediate incommensurate phase in a very narrow temperature range between the two phases. After structural phase transition to $I2/a$, two kinds of ferroelastic domains occur according to the theory of ferroelasticity⁽²⁾. These domains are different only in their relative orientation by 90° forming twins of the third kind⁽³⁾. Their incommensurate (=irrational) twinning planes are called W' wall and induced by their spontaneous strains⁽⁴⁾.

LaNbO_4 crystals show three lineal structures of different sizes under high-resolution polarizing optical microscope (POM)⁽⁵⁾ as shown in Fig. 1. The first structure denoted by A and B consists of a series of large scale domains of 10 - 20 microns in width which are separated by the second structure C. These domains exhibit alternative dark (A) and bright (B) contrasts in Fig. 1. The contrasts can be inverted by every ~ 90° rotation of the sample in the crossed nicols configuration. The second structure C consists of broad stripes of 1 - 2 micron wide and its contrast does not change by the sample rotation. The third is fine stripes of width less than 1 micron in the domains A and B. The contrast of this structure changes in the same way as A and B, as found under a careful examination.

Fig. 1 High-resolution transmission POM image on the polished (0 1 0) plane of 0.2 mm thick. The line not parallel to the large scale domains is a giant cleavage-step.

The present paper describes the analysis of the second and third structures by atomic force microscope (AFM) and discusses the relationship between the three structures and the phase transition.

II. Experimental

LaNbO_4 crystals grown by Czochralski method were cleaved by a razor blade along the $\{0\ 1\ 0\}_m$ surfaces, where m denotes the monoclinic system; we describe them simply as $(0\ 1\ 0)$ plane. Microcrystals on the cleaved surfaces were removed in ethanol and pure

water by an ultrasonic cleaner. The cleaved surfaces on the both sides were examined by AFM with the same method as previously reported⁽⁵⁾, after finding the location of the lineal structures by high-resolution POM (BX50, Olympus).

III. Results

Figures 2 (a) and 3 (a) are AFM images, and Figs. 2 (b) and 3 (b) are POM images of a pair of the cleaved surfaces. The both figures show broad stripes (structure C) along the boundaries of the large scale

Fig. 2 (a) AFM image and (b) high-resolution POM image on one side of the cleaved $(0\ 1\ 0)$ plane of 2 mm thick. The area indicated by solid rectangle in the POM image corresponds to the area observed by AFM. All which intersect the stripes (= subbands) at near 60° in the AFM image are micro cleavage-steps. Irregular lines not parallel to the large scale domains in the POM image are giant cleavage-steps.

domains (structures A and B) in which regularly ordered fine stripes are observed, where the structures A and B belong to 90° domain of an exact angle 95.85° about the b -axis⁽⁶⁾. We call the broad stripes "bands". Although the difference in the domain patterns between the pair of the cleaved surfaces is not clear in POM images but is apparent in AFM images. Figures 4 (a) and 4 (b) show schematic illustrations of patterns denoted by solid rectangles in Figs. 2 (b) and

3 (b), respectively. The patterns of the AFM images in the bands reveal more detailed structure not observed in our previous investigation⁽⁵⁾. It is found that the minimum and maximum widths of sub-bands with different height in the bands denoted by C_1 , C_2 , etc. (see Figs. 2 and 3) are about 0.04 and 0.2 microns, respectively. A similar number is found in the other place in the same domains indicated by dotted rectangle in Fig. 2 (b) as shown schematically in Fig. 4 (c).

The above results reveal that the width of the large

scale domains is almost constant and the detailed sub-band patterns in the bands C are changed by our cleavage condition but the effect is slight. AFM images give less information than POM images for the fine stripes in the large scale domains.

In Fig. 1, the transmission POM images of the fine stripes are often weakly colored by interference of the light beam, but those of the broad stripes (=bands, C) are clearly white because the visible light beam passes without interference through the small domains found by AFM images.

Fig. 3 (a) AFM image and (b) high-resolution POM image on the other side of the cleaved (0 1 0) plane of 1 mm thick. The rectangle indicated in the POM image corresponds to the area observed by AFM. The top photo of the AFM image shows five large cleavage-steps in addition to the similar steps as shown in Fig. 2 (a). Irregular lines not parallel to the large scale domains in the POM image are giant cleavage-steps.

Our investigation may be summarized that the structures A and B are similar with the fine stripes in their microscopic structures and differ only in the order of magnitude of microdomains.

IV. Discussions

The followings are discussions on formations of the large scale domains and the microdomains in them.

If LaNbO_4 crystals have an incommensurate phase between normal and commensurate phases, the

Fig. 4 Schematics (a) and (b) correspond to the AFM images of Figs. 2 (a) and 3 (a), respectively. Schematic (c) corresponds to AFM image in the other place indicated in Fig. 2 (b) by dotted rectangle. The black sub-bands are lower than the white ones in the Z direction. Minimum width of the sub-bands shown here is 0.04 microns.

discommensuration is to lead to the width of ferroelastic domains comparable to that of the domain walls immediately above the phase transition temperature, T_C , according to the model of $2H\text{-TaSe}_2$ ^{(7),(8)}. The width of the domain walls of LaNbO_4 is about $3a_0$ as determined from the transmission electron microscope (TEM) lattice image shown in Fig. 5, where a_0 is a mean value between the monoclinic lattice parameters $a = 0.5570$ nm and $c = 0.5202$ nm, $a_0 = 0.5386$ nm⁽⁹⁾. The relationship between width and lattice parameters coincides with those of other reports^{(10),(11)}. Therefore, the crystals are covered with the microdomains separated by distance of about 1.6 nm at T_C . If the crystal is ideal (without defects and impurities),

Fig. 5 Lattice image around a W' wall under high-resolution TEM (JEM-1000, JEOL)⁽¹⁰⁾. A black band at the center area corresponds to the width of the wall.

microdomains grow up and down in two configurations parallel and perpendicular to each other under thermal fluctuation. They finally become wide domains oriented in only one configuration as the temperature decreases. This behavior has been demonstrated in molecular dynamics (MD) simulation at a quenched process from T_C to room temperature with a large scale model of $249 \times 249 \times 101$ elementary unit cells of LaNbO_4 ⁽¹²⁾.

We consider that the following macroscopic deformation exists independently of the microdomain annihilation in the actual process of slow cooling during crystal growth by Czochralski method. LaNbO_4 crystals deform by spontaneous strain due to variation of the monoclinic lattice parameters with the decreasing temperature, especially large change of the parameters in the temperature range from 773 K to 673 K⁽⁴⁾.

It is well known that multidomain with an equal width is produced in crystals by twinning deformation due to spontaneous strain. Relationship between single crystal size, s , and width of the multidomain, w , is given by the equation⁽¹³⁾

$$w = (\gamma s / k \lambda)^{1/2} / x_0, \quad (1)$$

where x_0 , λ and γ are spontaneous strain, elastic modulus and interface energy, respectively, and $k = 1 / 128 \pi$. Substituting the experimental values for x_0 , λ and s , respectively, $0.05^{(4)}$, $4.27 \times 10^{10} \text{ J / m}^3^{(14)}$ and $1 \times 10^{-2} \text{ m}^{(15)}$, and a typical value in solids for γ , $1 \times 10^{-2} \text{ J / m}^2$ into Eq. (1), we get $w = 20 \text{ }\mu\text{m}$.

Thus the multidomain formed by the spontaneous strain corresponds to the large scale domains A and B. The microdomains produced by incommensurate-commensurate phase transition do not coalesce abruptly but are growing up and down in these large scale domains as suggested in the MD simulation for $\text{LaNbO}_4^{(12)}$. Coalescence of the microdomains is promoted with the decreasing temperature. However, pinning effect near the large-scale-domain boundaries is larger than that between the bands, because the defect concentration along the boundaries is higher than that between the bands due to disorder of various atomic motions different from uniform twinning displacement called "shuffles"⁽³⁾. Hence we can get almost the same image for domain patterns in LaNbO_4 as shown in Fig. 1. This figure exhibits that there coexist the multidomains of 10 - 20 micron wide (= large scale multidomain), and the broad and fine stripes of about 1 - 2 micron wide in the large scale domains (= small scale multidomain).

V. Conclusions

We discussed the formation of the multidomains in LaNbO_4 crystals from the results obtained by AFM, POM and MD simulation, and concluded that the large scale multidomain is produced by the twinning deformation due to the monoclinic spontaneous strains below T_C and the small scale multi-domain comes from the microdomains introduced by a discommensuration due to incommensurate-commensurate phase transition.

We have estimated the spacings of the multidomains from our experimental results. A slight effect of cleavage on the spacings is found in the AFM and POM observations.

More AFM observations are necessary to understand the detailed structures of the fine stripes and the bands.

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