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Ferroelectric Domain Structures in Flux-Grown $PbTiO_3$ Single Crystals

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The domain structures of poly-domain lead titanate single crystals grown by the flux method have been studied using optical and electron microscopy. Etched crystals using optical and scanning electron microscopic investigation indicate that crystals grown at different conditions show very different domain arrangements. Crystals using well protected atmosphere show relatively simple and well-defined domains, and, on the other hand, complicated and intriguing domain arrangements are observed for crystals grown at poor-controlled environment. High energy domain arrangements have been observed constantly in crystals grown under both conditions, indicating that the high energy configuration appear to be quite common in lead titanate crystals. As-grown lead titanate crystals show very similar structure characteristics to martensites of various alloys and ceramics, implying that the transformation behavior may be predicted by the martensitic phenomenological crystallographic theory.

1. INTRODUCTION

Ferroelectric materials with perovskite structure have been widely used in many fields. However the exploration on the domain boundary structures which are closely related to the properties are relatively limited compared with properties of the materials.

Two types of domain boundaries can be seen in perovskite materials with tetragonal structure. One is 90° and the other is 180° domain boundaries. Although many works have been done on the domain boundaries in $BaTiO_3$ crystals, relatively few have been performed on those in $PbTiO_3$ because of the difficulty of growing crystals as well as the similarity of the two materials [1]. However, there are still differences between $BaTiO_3$ and $PbTiO_3$. Such as, $PbTiO_3$ possesses the highest polarization in the similar series of materials and higher ionization polarity [2,3]. Moreover, the tetragonality during the cubic to tetragonal transformation is much higher in $PbTiO_3$ which may introduce different effect on the microstructure in the material [4].

In the present work, we grow $PbTiO_3$ single crystals using different fluxes and study the domain structures in crystals from each flux and try to correlate the domain structures and crystal growing conditions.

2. EXPERIMENTAL PROCEDURE

The crystal growing procedure and specimen preparation method please refer to our previous work [4-6]. Two groups of crystals are investigated. Group A are crystals grown using a multi-flux method [7] and group B are crystals using self-flux method in a poor-controlled atmosphere [8]. As-grown crystals were ground by hand to a thickness about 150 um. Some were etched using two different solutions: phosphoric acid and (95% HCl + 5% HF) for optical and scanning electron microscopy (SEM) investigations. Some crystals were then ground by a commercial dimple machine down to 10 um and an ion miller was employed at 6kV, 0.5 mA, each gun with tilting angle 18° for further thinning. After perforation, the specimens were bombarded by the ion beam with reduced voltage and tilting angle for several minutes. Transmission electron microscopy (TEM) investigation was conducted using a Hitachi H800 and a Jeol 2000FXII microscope with a double-tilt specimen holder operated at 200kV.

3. RESULTS AND DISCUSSION

The domain structures in the crystals were investigated using optical microscopy and scanning electron microscopy. Typical etched patterns and some interesting features have been seen in the crystals. Figure 1 shows domain structures in the crystals grown using a multi-flux method (group A). The 90° domain arrangements appear to be relatively simple but the 180° domain boundaries show various morphologies. Figure 1(a) shows some 180° domain boundaries meandering around the crystal and some attached to 90° domain bands. Some 180° domain boundaries appear to nucleate from the 90° domain bands and therefore pikes of 180° domains accumulate at these regions. Note that the 180° domain boundaries are oriented to two different directions, as indicated. This may suggest an interesting domain formation sequence or a crystallographic feature, but we are unable to say much here. Figure 1(b) is a typical image of 180° domain boundaries passing through 90° domains. One sees that the etched pattern show opposite contrast across a 180° domain boundary, implying different etched rates at two adjacent domains.

Figure 2 are optical and electron micrographs showing an etched pattern revealed in a crystal of group A. The etched pits look like separated or line-up hills observed in optical microscopy, whereas SEM micrographs, with much higher depth of field, show that each hill is corresponding to an etched groove which is produced by different etching rates of domains of different polarization vectors. In fact, this is produced by 180° domain boundaries passing through 90° domains. More interestingly, the contrast of 180° domain boundaries is not all the same in a specimen with the same **g** vector, if investigated using a TEM. For instance, some show bright EFC and some show dark EFC in the BFI, and sometimes domain walls with D-D and B-B EFC show up alternatively. A 90° and 180° domain intersecting configuration shown in figures in our previous works [5,6,8] is an example. An intriguing fringe contrast behavior in this 180° domain configuration is present; that is, the 180° domain walls symmetrically distribute around a center line and the EFC varies alternatively at each side, as schematically shown in figure 3(c) in Ref.6. We tilted the specimen through different zone axes, and the three dimensional construction of this domain arrangement was revealed. The morphology of the center domain is shown in figure 4 in Ref.6. This very common arrangement of domain boundaries is schematically drawn in Figure 2(c). Layers of 180° domain boundaries across 90° domains form shell-like arrangement which is seen in Figure 2(b) and is evident in TEM picture shown in Figure 2(d), which demonstrates a 180° domain forming sequence.

Crystals grown by a self-flux method with poor-atmosphere control (group B) are often defective, and show much more complicated 90° domain arrangements, Figure 3. In this crystal, 90° domain bands along {100} and {110}, band intersections, deeply etched and unetched regions are all observed. These features are corresponding to microstructure characteristics correlated to the cubic to tetragonal transformation during crystal growing. On the other hand, much fewer 180° domain were seen and, if any, the scale is larger. Several structure characteristics are shown in the following. Figure 4(a) is a heavily etched region showing complicated domain arrangements. Three dimensional information has been revealed in deep-etched regions which may correspond to high energy configurations. A high energy domain arrangement and two possible polarization configurations are shown in Figure 4(b). One sees that the head-to-head and/or tail-to-tail arrangements are inevitable, indicating the existence of a high energy configuration. Not only this arrangement was observed, some other high energy configurations are also frequently observed. For instance, Figure 5 is a region showing 90° domain bands in which a-a or a-c 90° domains are distributed.

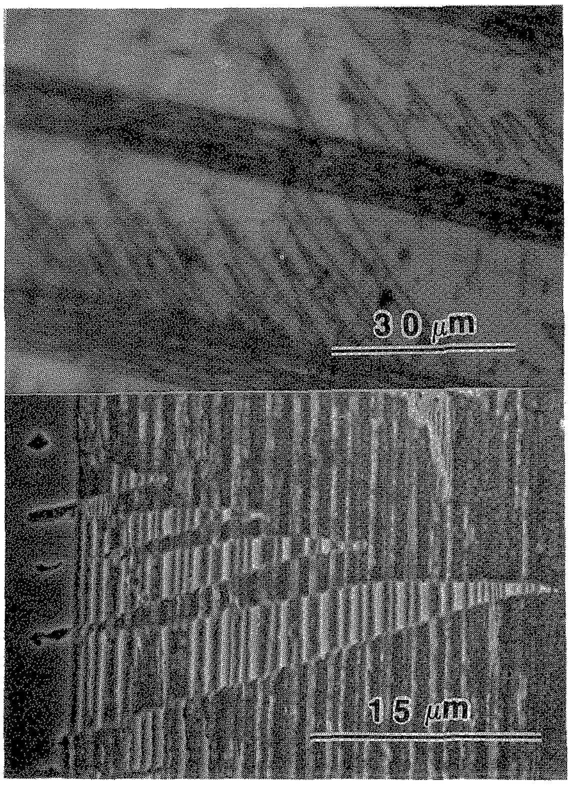

Figure 1 Domain structures in an as-grown $PbTiO_3$ crystal using a multi-flux method (group A).

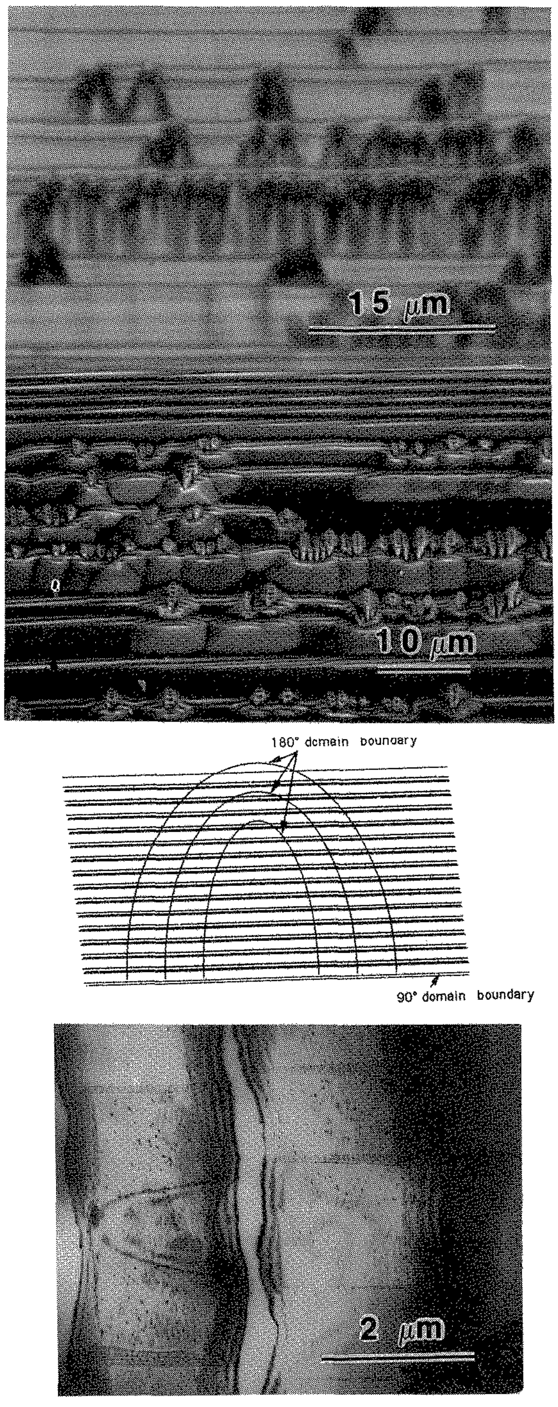

Figure 2 Optical and electron micrographs showing a 180° and 90° domain intersection configuration. (a) Optical micrograph; (b) SEM micrograph showing layered 180° domain structure; (c) schematic drawing of the 180° domain arrangement; (d) TEM micrograph showing layered 180° domain structure.

The unetched regions are a-a type domains because the adjacent domains have equivalent etched rate and the others are a-c type. If the specimen was etched longer, one find that deep etched grooves are generated at the interfaces of domain bands, as pointed, indicating a high energy configuration. Considering polarization arrangements and real geometry of domains, one find that high energy polarization configurations are also inevitable. More importantly, the high energy configurations are observed in both crystal groups, suggesting a common phenomenon in lead titanate crystals.

Crystals under different growing conditions possess different domain arrangements. This may be due to the impurity and/or tetragonality as a result of growing conditions. For crystals contain large amount of impurities may reduce the tetragonality of cubic /tetragonal transformation and therefore reduce the transformation strain in the crystal. The consequence of reduction of strain energy is a simpler domain arrangement. Similarly, the lower the tetragonality is, the smaller the domain boundary energy is. Besides, the general domain arrangements observed in many crystals show variant-like bands which contains twin-related domains; reliefs on crystal surfaces were also observed [4], indicating basic martensitic transformation characteristics. This may suggest the applicability of the martensitic phenomenological crystallographic theory to the transformation behavior of this material system.

4. CONCLUSIONS

(1) Crystals grown by means of multi-flux method show simpler 90° domain arrangements and more 180° domain boundaries; crystals using self-flux and grown under poor-controlled atmosphere show complicated 90° domain arrangements.

Figure 3 Complicated domain arrangements in a crystal grown by a self-flux method with poor-atmosphere control (group B).

(2) Several high energy domain arrangements have been observed constantly in crystals grown under both conditions, indicating that the high energy configuration appear to be quite common in lead titanate crystals.
(3) As-grown lead titanate crystals show very similar structure characteristics to martensites of various alloys and ceramics, implying that the transformation

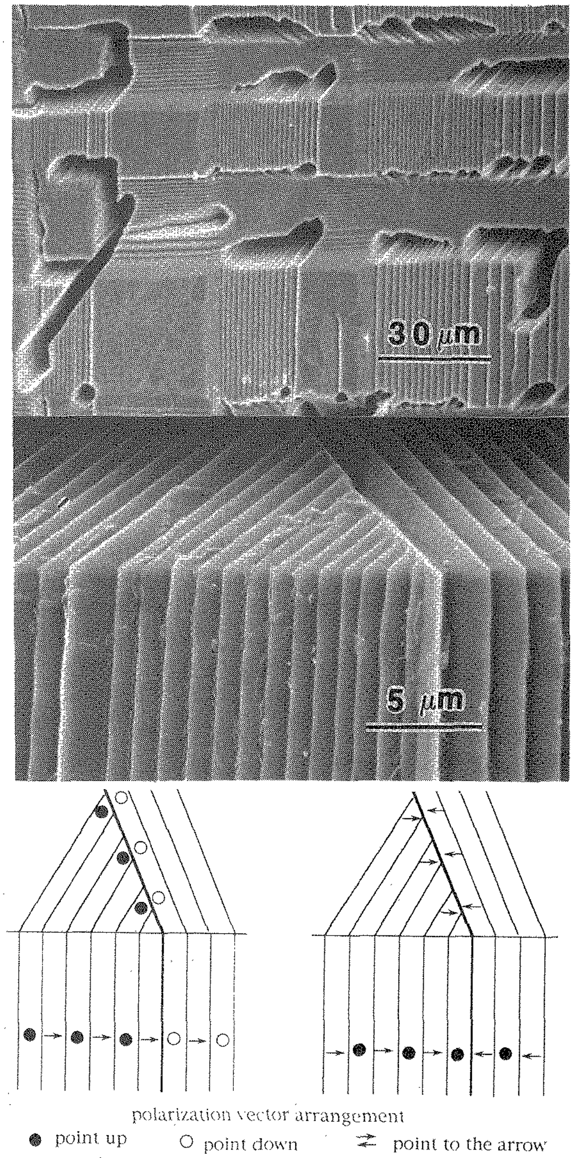

Figure 4 (a) An enlarged region in figure 3 showing heavily etched regions which are corresponding to high energy configurations. (b) An abnormal domain arrangement and the accompanying schematic drawing showing two possible polarization configurations, suggesting the existence of a high energy state.

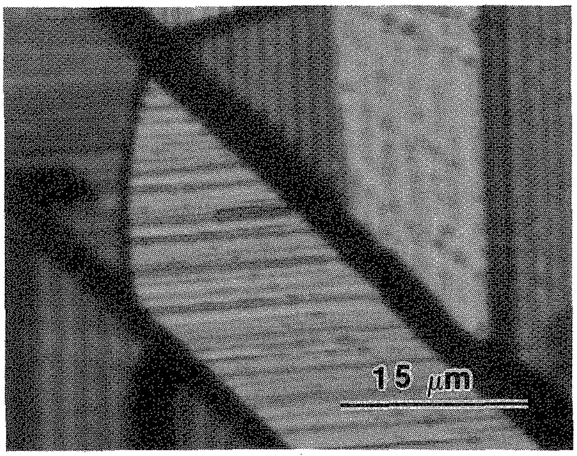

Figure 5 A micrograph showing the arrangements of 90° domain bands. The deeply etched intersecting region are corresponding to high energy polarization arrangements.

behavior may be predicted by the martensitic phenomenological crystallographic theory.

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