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Banded domain structures and polarization arrangements in $PbTiO_3$ single crystals

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Abstract

Banded ferroelectric domain structures and the corresponding polarization arrangements of flux-grown $PbTiO_3$ single crystals have been studied using optical and electron microscopy. Most of the specimens show banded domain arrangements, which correspond to surface relief characteristics of as-grown crystals. Using crystals with different etching conditions, the three-dimensional arrangements of the domains can be constructed. It is found that banded domain boundaries show relatively high energy, which enhances the etching of these boundaries. Drawing schematic polarization configurations, one finds that head-to-head, tail-to-tail, and other unconventional polarization configurations exist constantly in $PbTiO_3$ crystals, indicating that the high electrical energy configurations are quite common in lead titanate crystals. © 2000 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Lead titanate has a ferroelectric phase transition temperature, T_c, near 500°C [1,2]. $PbTiO_3$ is cubic above T_c and exhibits a strong tetragonal distortion at 20°C: $c/a=1.06$ which persists up to T_c ($c/a=1.01$) [3,4]. PbTiO3 single crystals present a highly polar structure with very high spontaneous polarization in the perovskite family [1,2,5].

Since the tetragonal phase is ferroelectric, two types of domain boundaries can be observed. One is 90° and the other is 180° domain boundaries. The structure of ferroelectric domains is of practical interest since the motion of domain walls, particularly 90° domain walls, has been shown to have a great influence on the dielectric and electromechanical properties in polycrystalline ferroelectrics [6,7]. 90° domain boundaries run parallel to {110} and exhibit almost straight lines [8–11]. On the other hand, 180° domains show no crystallographic features and they often meander around the whole crystal [12–15]. In most cases, researchers believe that polarization arrangements in 90° domain should follow "head to tail" or "tail to head" rules in order to achieve lower electrical energy [16]. However, some peculiar domain arrangements have been reported [17–20]. For instance, Hu et al. [17] have implied that unconventional domain wall which is not stable exists in $BaTiO_3$ crystals. The unstable domain structure was replaced by conventional domains after a period of investigation under electron beam radiation. Yakunin et al. reported a "head to head" 90° domain boundary which shows zigzag morphology in a $BaTiO_3$ film in order to form a low energy polarization configuration [18]. Shakmanou and Spivak [19] showed a complex *a–c* domain structure in $BaTiO_3$ crystals. In their interpretation, *a–c* domain wedges were located in an *a* domain of a big *a–a* arrangement. Arlt and Sasko reported that the domain structures formed under a clamped condition in ceramics are a little different from those in $BaTiO_3$ single crystals, and two types of band-forming boundaries were proposed in their paper [20]. It is more convenient to study a static domain structure using a $PbTiO_3$ rather than a $BaTiO_3$ because of the immobility of domain boundaries during investigation in $PbTiO_3$ [12–15,21]. Moreover it has also been suggested that domain arrangements and domain dynamics may be greatly

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influenced by different growing conditions which also determine the properties of a crystal. Here, we grow $PbTiO_3$ single crystals using different fluxes, study the domain structures in crystals from each flux, and show some high-energy domain structures in the present work.

2. Experimental procedures

$PbTiO_3$ crystals were grown by slow cooling from flux methods [15,22]. A flux containing KF, Pb_3O_4, PbF_2, KBF_4, and TiO_2 was cooled at a temperature around 475 to 300°C with a well protected atmosphere (group A) [22] and the other containing PbO and TiO_2 was cooled from 1150 to 900°C with a rough-protected atmosphere (group B) [15] in a 50 cc platinum crucible. Crystal growth proceeds in an oxygen atmosphere with a vertical tube furnace, which was programmed to give a very slow cooling rate. The as-grown crystals were cubic in shape or elongated cubic and orthogonal forms and were ground by hand to a thickness about 150 μm. Some were etched using two different solutions: hot 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 μm and an ion miller was employed at 6 kV, 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 Jeol 2000FXII microscope with a double-tilt specimen holder operated at 200 kV.

3. Results and discussion

The domain structures in the crystals were investigated using optical microscopy and electron microscopy. Typical etched patterns and some interesting features have been observed in the crystals. Fig. 1 shows 90° domain structures observed in as-grown $PbTiO_3$ single crystals. Fig. 1(a) is an SEM micrograph showing several bands of regions with different etched rates in a crystal grown using a multi-flux method. The etched bands are corresponding to *a–c* domains, and the unetched regions are *a–a* type domains. The widths of the domain bands are not all the same and later we may find that this can be correlated with stress conditions. Fig. 1(b) is an optical micrograph showing herring-bone structure in a crystal of a self-flux growing condition. An interesting feature is that there are three regions in the micrograph and two of them showing two different sets of herring-bone structure with different $\langle 110 \rangle$ orientations. Along these two $\langle 110 \rangle$ directions, bands of hill-and-valley or surface-tilting were observed. The third region is a simple *a–c* area with large domain width. In many cases, two adjacent domain bands are believed to have mirror relations. However, many images show two adjacent regions having different density of domains. The interfaces of band boundaries are not so straight and smooth as that seen in 90° domain boundaries. This implies that band boundaries are basically different from the 90° domain boundaries and the polarization relationship in two adjacent domains may be different from the ideal arrangements proposed before, as discussed later [17–20]. In many cases, materials show intersecting bands with etched and unetched regions. Ordinary the etched regions are corresponding

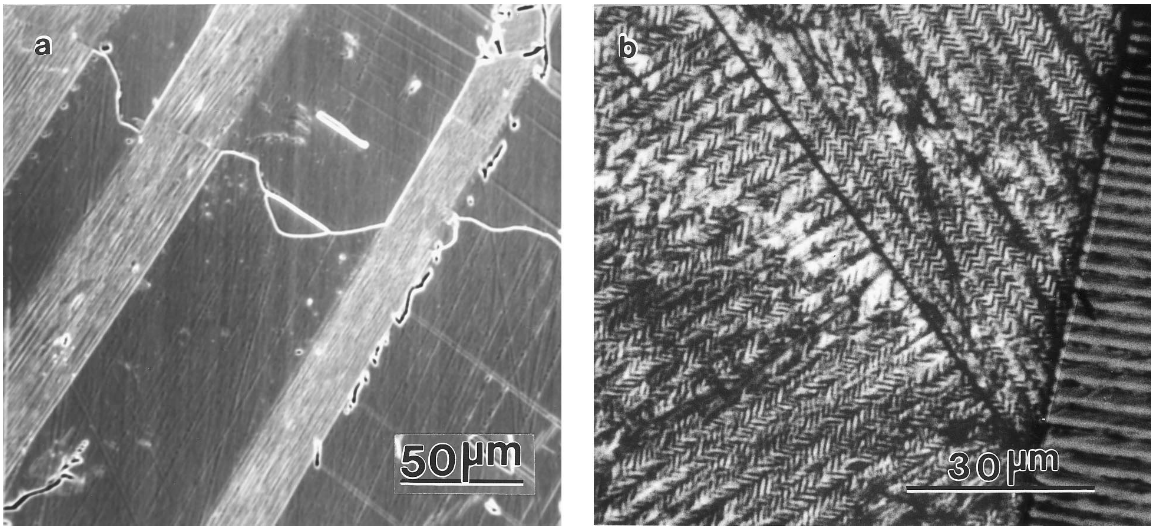

Fig. 1. 90° domain structures observed in lead titanate single crystals. (a): typical 90° domain bands with 90° domain arrangements of *a–a* or *a–c* type; (b) herringbone 90° domain structures.

to the *a–c* domain configurations which shows different etching rate in *a* and *c* domains and therefore domain arrangements can be revealed. On the other hand, the etched regions can be ascribed to the *a–a* domain arrangement, which shows no etching difference in each domain. In case the specimen plane under investigation was ground tilting to the {100} plane intentionally, the unetched regions will become etched. In most etched intersection regions finer structures have been observed, indicating complicated domain configurations between these intersecting regions.

Fig. 2(a) is a TEM micrograph showing two sets of adjacent *a–a* domain bands. Fig. 2(b) is a corresponding diffraction pattern showing typical *a–a* domains with a twin relationship. The highly separated diffraction spots imply a large tetragonality of the ferroelectric phase. An intriguing feature is the boundary of the two sets of *a–a* 90° domains, as indicated. It is clear that the boundary does not lie on a well defined {110} plane as a conventional domain boundary does. The domain boundaries from each side intersect to form a boundary lying on an irrational plane, which is rather like a "variant" boundary in a martensite of an alloy or metal. This micrograph shows a detail boundary structure of a herring-bone structure in Fig. 1(b), which is very different from the straight lines as observed in 90° domain boundaries. The *a–a* 90° domain boundaries appear to conserve higher energy than the matrix, because the boundaries show radiation damage that appears as dark spots after a short period of investigations.

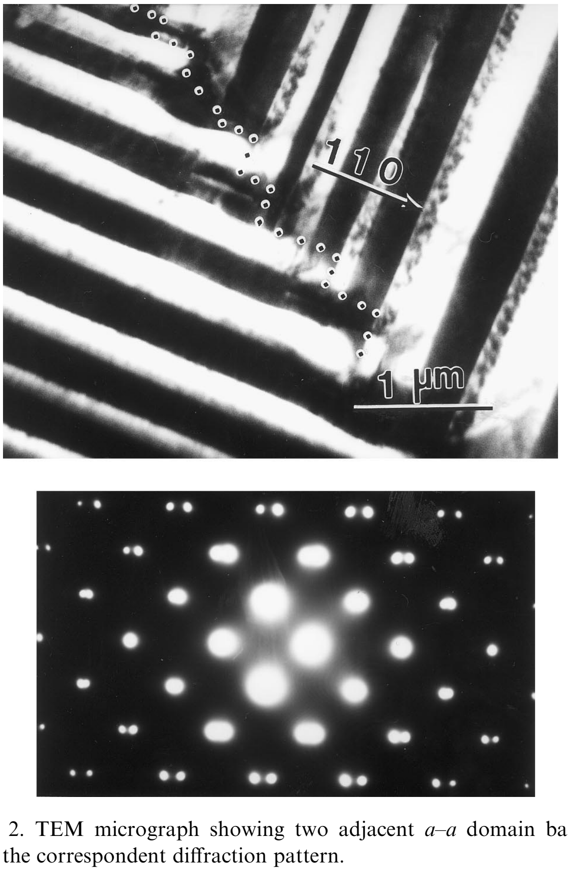

Fig. 2. TEM micrograph showing two adjacent *a–a* domain bands and the correspondent diffraction pattern.

Fig. 3 is an optical micrograph showing surface relieves of an as-grown crystal. The surface relief phenomenon has been discussed intensively in metals and it is often attributed to a diffusionless structure transformation [23,24]. It is seen that the relief traces are roughly parallel to [100] directions in this case, but many of them are not exact straight, indicating that the relief traces are not twin boundaries, but identical to

Fig. 3. Surface relief showing close relation with band structures.

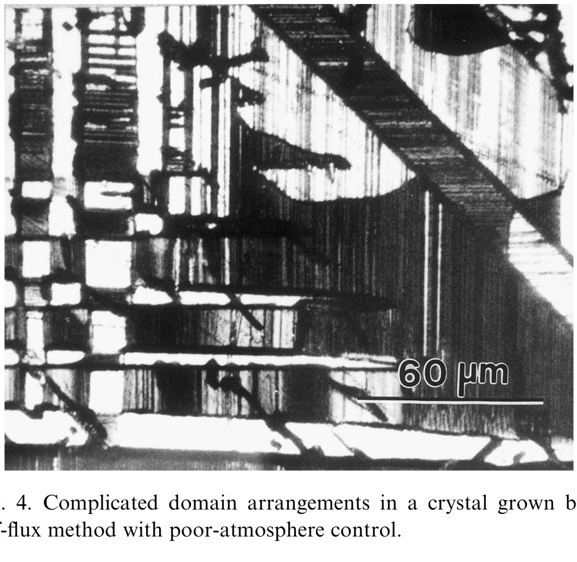

Fig. 4. Complicated domain arrangements in a crystal grown by a self-flux method with poor-atmosphere control.

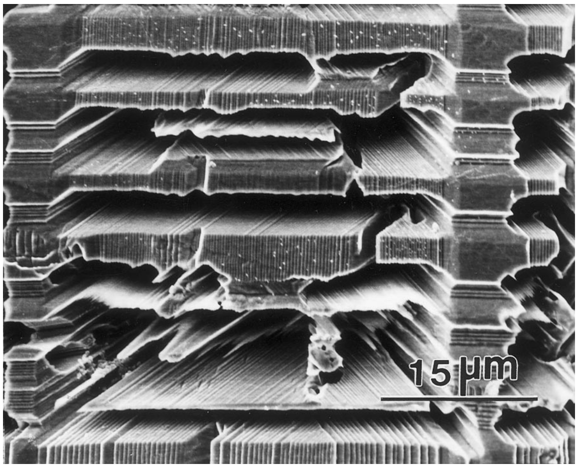

Fig. 5. An electron micrograph showing heavily etched regions enlarged from Fig. 4, which are corresponding to high-energy configurations.

band boundaries if the specimens were etched to show the interior structures, which have been shown in Figs. 1 and 2.

Crystals grown by the self-flux method with a rough atmosphere control (group B) are often defective, and show much more complicated 90° domain arrangements, such as the one in Fig. 4. In this crystal, 90° domain bands along {100} and {110}, band intersections, deeply etched and unetched regions are all observed. These microstructure characteristics may be correlated to the cubic to tetragonal transformation during crystal growing. On the other hand, much fewer 180° domain were seen and their, if any, scale is larger.

Several structure characteristics are shown in the following with larger magnifications. Fig. 5 is two heavily etched regions showing complicated domain arrangements. Three dimensional information has been revealed in deep-etched regions which may correspond to high energy configurations. If one notices, some 90° domain walls in each band may incline to one direction and some incline to the other, even though the surface etched pattern looks similar, Fig. 5(b). A high electrical energy domain arrangement with two possible polarization configurations, enlarged from Fig. 5(b), are shown in Fig. 6. Drawing the possible polarization arrangements, one sees that the head-to-head and/or tail-to-tail arrangements are inevitable, indicating the existence of a high electrical energy configuration.

From the experimental results, one sees polarization arrangements which do not follow head-to-tail configurations and heavily chemical-etched band boundaries. The etched pattern may be attributed to being with high electrical or elastic energies, as shown in Figs. 4–6. It was quite often that previous researchers drew perfect head-to-tail polarization arrangements based upon two-dimensional domain structures derived from a slightly etched crystal [3–5,16,17]. The three dimensional information derived from deeply etched specimens in the present experiment has demonstrated that the geometry of domain arrangements may introduce head-to-head,

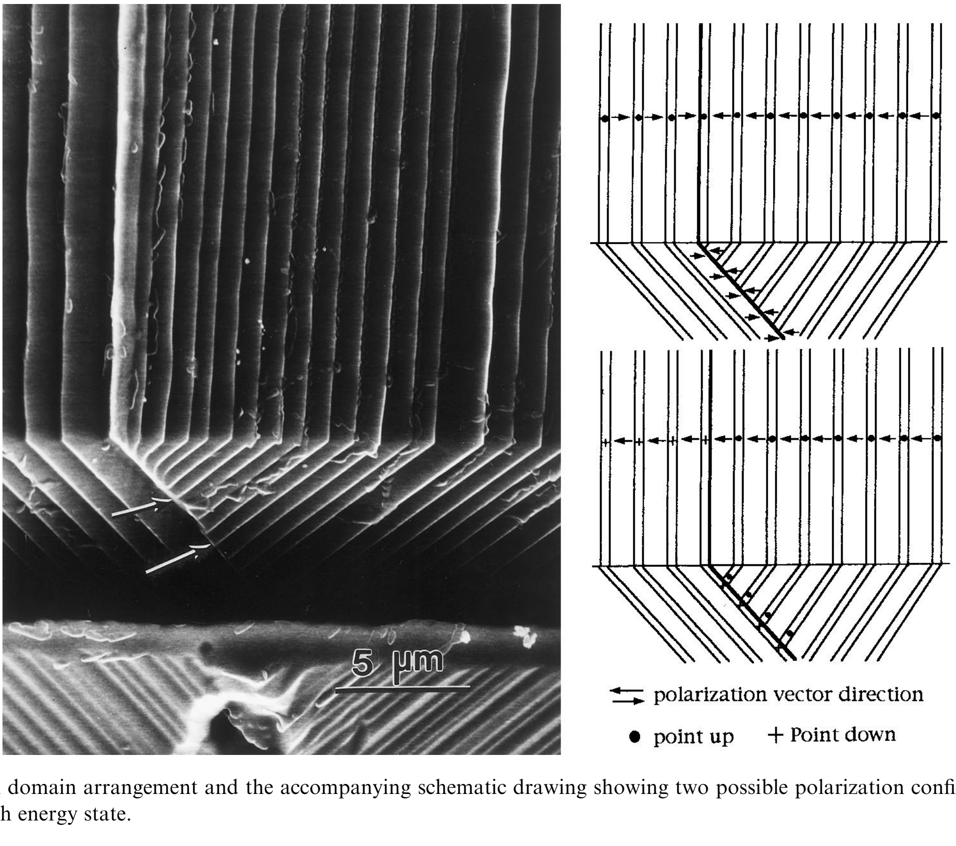

Fig. 6. An abnormal domain arrangement and the accompanying schematic drawing showing two possible polarization configurations, suggesting the existence of a high energy state.

tail-to-tail or other unconventional polarization configurations.

In some cases, the polarization arrangements of two adjacent bands with *a–c* domains nearly perpendicular to each other (herring-bone structure) were also schematically drawn as perfect head-to-tail arrangements. However, if the thickness of the domains in each band is not the same, the polarization arrangements will not be the case as discussed above. This is shown in Figs. 1(b) and 2. One sees the domains in each side are not necessary to be symmetrically distributed. One more feature is that the boundary of two sets of bands is not necessary to be a well-defined plane, as observed in Fig. 2. Some irregular intersections of two sets of domain bands are clearly observed in a micrograph with higher magnification, which show no clear-cut boundary at the intersections.

Moreover, the etched patterns show that the regions with unconventional polarization arrangements are not always etched away, as shown in Fig. 6. But regions show possible high strains are constantly deep etched, implying that strain energy appears to be higher than electrical energy which may appear as head-to-head, tail-to-tail or unconventional polarization vector arrangements.

If one notices, several microstructural characteristics have been observed in the crystals. For instance, (i) the 90° domain bands, which corresponds to the surface relieves in an as-grown crystal, are analog to the “variants” in an alloy martensite; (ii) 90° domains were identified as twin-related, Fig. 2(b), in each band, and the domain boundaries are twin planes which correspond to invariant plane shear in a variant of a martensite; (iii) the domain arrangements, as shown in Fig. 4, are closely related to the variant intersections and self-accommodation which has been observed in many ferrous and non-ferrous alloy systems, and these may be produced when high strain energies exist. These are the major characteristics of a martensitic transformation as suggested by Khachaturyan [25] and Chou et al. [26,27]. Therefore, it may be more appropriate to interpret the microstructural characteristics of a lead titanate crystal in terms of a structure of a martensitic transformation which applies to alloys, metals and some ceramics fairly well.

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.
2. Most of the specimens show band arrangements which may be corresponding to surface relief characteristics of as-grown crystals. The interfaces of band boundaries are not so straight and smooth as that seen in 90° domain boundaries. This implies that band boundaries are basically different from the 90° domain boundaries.
3. High energy domain arrangements have been observed constantly in crystals grown under both crystal-growing conditions, indicating that the high electrical energy configuration appears to be quite common in lead titanate crystals.
4. As-grown lead titanate crystals show very similar structure characteristics to martensite of various alloys and ceramics, implying that the transformation behavior may be predicted by the phenomenological martensitic crystallographic theory.

Acknowledgements

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