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Observation of three-dimensional domain configurations in $0.92\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.08\text{PbTiO}_3$ crystal by environmental scanning electron microscopy

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Abstract

The images of three-dimensional 180° and non- 180° (90°) domain configurations on the unpolished and unpoled (111) face of $0.92\text{PZN-}0.08\text{PT}$ rhombohedral relaxor-ferroelectric crystal have been obtained by environmental scanning electron microscopy for the first time. The size of the 180° domains ranges from 10 to $50\ \mu\text{m}$, and that of the non- 180° domains from 1 to $10\ \mu\text{m}$. The boundaries of the crossed three-dimensional non- 180° domain bands are nonparallel and have a triangular shape. This unique non- 180° domain architecture is different from the 109° or 71° domain structure in normal rhombohedral ferroelectric materials, and is helpful for completely relaxing the additional stresses due to domain deformation in $0.92\text{PZN-}0.08\text{PT}$ crystals.

1. Introduction

In recent years the relaxor-ferroelectric single crystal $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}x\text{PbTiO}_3$ (PZN-PT) has become more and more attractive due to its excellent piezoelectric and electrostrictive properties which are superior to those of conventional ceramic materials such as PZT systems [1–4]. It is well known that these properties can be influenced by their domain states, which has triggered a new wave of research to reveal the formation and structure of domains in these crystals [5, 6]. Although, as a typical relaxor ferroelectric, the $0.92\text{PZN-}0.08\text{PT}$ rhombohedral crystal poled along the [001] direction has a very high electromechanical coupling coefficient and piezoelectric coefficient [7, 8], its spontaneous polarizations are

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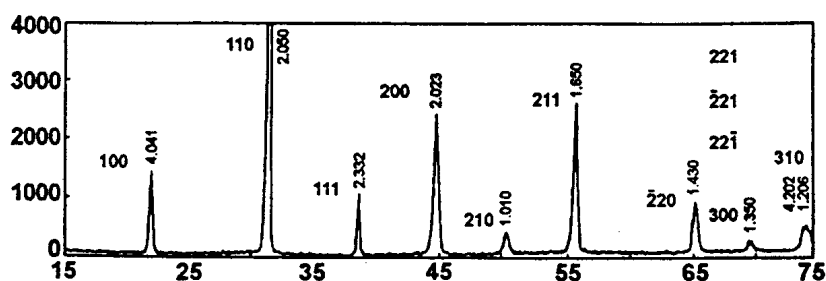


Figure 1. Powder x-ray diffraction pattern of 0.92PZN-0.08PT crystals, indicating the R3m space group.

along the [111] orientation. Therefore, different methods [9–12] have been used to study the domain structures along these two directions. Because any process of machining or poling can damage the original domain structures, it is necessary to investigate the domain configurations in unprepared and unpoled samples. Environmental scanning electron microscopy (ESEM) [8, 13], which appeared in recent years, is a valuable technique for attaining this aim. It can provide high spatial resolution and three-dimensional images when observing the natural surfaces of samples. Because ESEM can operate under vacuum conditions which do not have to be so strict as in standard SEM, the free ions which are generated by collisions between moving electrons and neutral gas molecules can be used to neutralize the beam-deposited surface charge. This makes it possible to examine unprepared and uncoated insulating samples, at the same time obtaining stable and clear domain contrast images. By contrast, conventional SEM cannot produce stable contrast images due to the surface charge accumulation on an insulating crystal.

In this paper we applied ESEM to study the domain structures of unpolished and unpoled 0.92PZN-0.08PT single crystals along the [111] direction for the first time, and obtained images of three-dimensional 180° and non-180° domain configurations that are difficult to observe on the polished and poled surfaces by other methods.

2. Experimental procedure

The 0.92PZN-0.08PT crystal used in this work was grown by the PbO flux method in our laboratory [14]. In order to separate the as-grown crystals from the flux, after the growth stage, the crucible and materials were immersed in hot HNO₃ solution for 10 h. From powder x-ray diffraction the crystal was determined to be of rhombohedral structure and to belong to the R3m space group (see figure 1). The composition of the crystal with a slight deviation from the starting ratio was characterized by chemical analysis. From x-ray orientation measurements it was determined that the large faces were nearly normal to the [111] direction.

The domain observation was performed by an environmental scanning electron microscope (KYKY1500 ESEM) (see figure 2). In this experiment, an unpolished, uncoated and unpoled crystal surface perpendicular to the [111] direction was characterized. After the crystal was loaded into the ESEM sample stage, the chamber was evacuated and then filled with neutral N₂ gas. For a chamber pressure of about 400–600 Pa, the accelerating voltage was 25 kV and the scan rate 10–30 sec/frame. Under these conditions we obtained stable topographic images of both 180° and non-180° three-dimensional ferroelectric domain structures on the (111) surface.

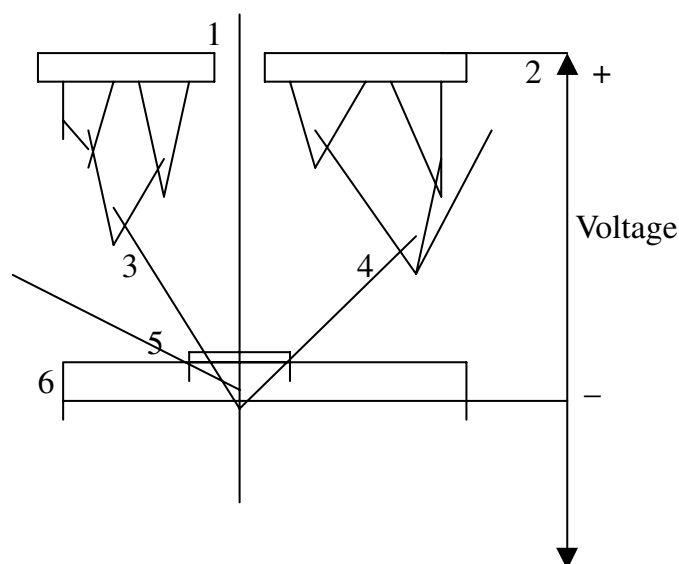


Figure 2. Schematic diagram of the ESEM experiments: 1. incident electrons; 2. electrode and detector; 3. back scattering electrons; 4. second electrons; 5. sample; 6. loading stage.

3. Results and discussion

The antiparallel 180° domain pattern is shown in figure 3(a), where we can see some stripes of different contrast and size. The bright and dark stripes represent the positive and negative domains, respectively, which indicates that the secondary electrons emitted from the positive domains exceed those emitted from the negative domains. Both domains are between 5 and $50 \mu\text{m}$ in size.

In figure 3(b), stereoscopic surface undulations consisting of many small hillocks and grooves can be observed. These are nearly arranged in the same direction with a width of $10\text{--}50 \mu\text{m}$, which can also be considered to be due to formation of 180° ferroelectric domains along the $[111]$ direction. During the process of crystal growth, the domains form when the phase transition from the paraelectric to the ferroelectric phase takes place. After the growth stage, the crystals must be separated from the flux by using a hot solution of HNO_3 acid. Since the etching rate of the positive domains in the acid is different from that of the negative domains, it is reasonable to deduce that the surface is full of small corrugations.

Furthermore, figure 4 shows an image of the unique three-dimensional structure along the $[111]$ direction of the rhombohedral 0.92PZN-0.08PT single crystals. From the special fine domain structures in the three-dimensional image, it does not seem to be an edge dislocation etching pit produced by the hot HNO_3 solution. On the other hand, it is also not a very small incongruent phase, because the phase that is different from the perovskite PZN-PT is a pyrochlore phase. Although these two kinds of compounds cannot be dissolved or etched by hot HNO_3 solution, the tiny pyrochlore phase crystal grains can be moved away from the perovskite crystal surface by the hot HNO_3 solution, because the phase boundaries between them can be easily etched by this solution. Therefore, the unique structure shown in figure 4 can be determined to be a new domain configuration, i.e. a three-dimensional non- 180° domain configuration. In the figure, two stereoscopic triangular bright domain bands and a series of parallel lamellar domains are observed. It is estimated that the parallel lamellar

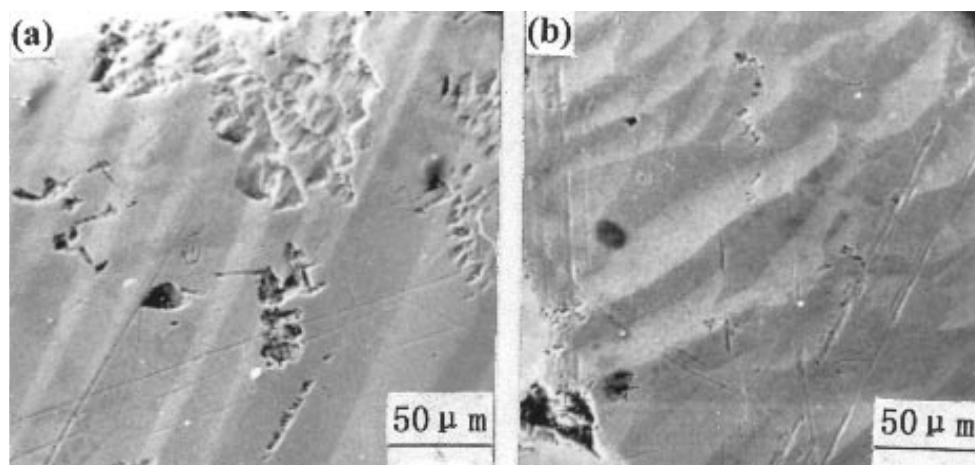


Figure 3. ESEM images of antiparallel 180° domain configurations in 0.92PZN-0.08PT crystal along the [111] orientation. (a) a usual domain structure, in which the bright and dark parallel stripes represent the positive and negative domains, respectively; (b) stereoscopic image of the 180° domain configuration.

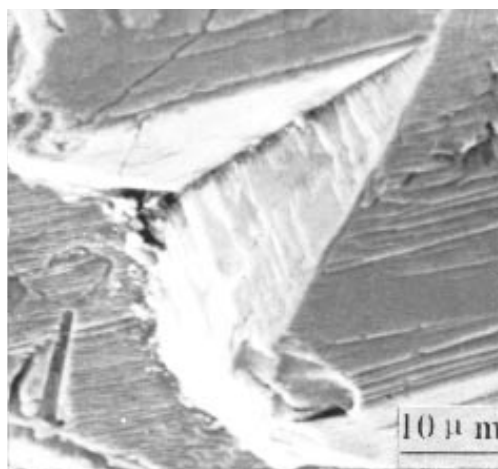


Figure 4. ESEM image of three-dimensional non- 180° domain configuration.

domains in the dark bands and bright triangular bands are between 1 and $10\ \mu\text{m}$ in size, which is smaller than the antiparallel 180° domains observed in figures 3(a) and (b). From figure 4 it is not difficult to see that the angle between the non- 180° domain walls is nearly 90° , while the boundaries of the two bright domain bands are nonparallel and triangular in shape. This unique three-dimensional domain structure is different from that of ordinary non- 180° domains of normal rhombohedral ferroelectric materials, in which the angle between domain walls is about 109° or 71° . Figure 5 is a schematic diagram illustrating the possible state or orientation of this unique three-dimensional non- 180° domain based on the crystallographic symmetry. Since the observed unpolished and unpoled surface is a (111) face, the faces of the two bright triangular domain bands may be perpendicular to the [100] and [010] directions, respectively.

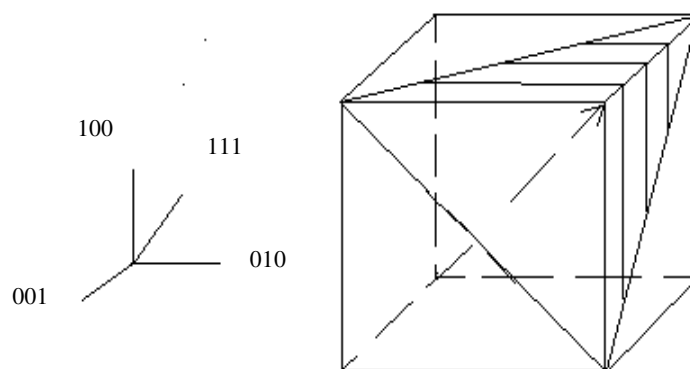


Figure 5. Schematic diagram illustrating the state or orientation of the three-dimensional non-180° domain configuration shown in figure 4.

Although the formation mechanism of the observed three-dimensional domain configuration shown in figure 4 is not clear, we hypothesize that it may be the result of the domain deformation [15, 16] induced by crystal defects. Large numbers of defects such as dislocations and stacks are produced during the process of crystal growth due to fluctuations of the growth conditions, which can increase the surface energies and strains. During the transition from the paraelectric to the ferroelectric phase, the 180° and non-180° domains will form to minimize the electric and elastic energy. Since the spatial strains resulting from defects are nonuniform and domain deformation is likely to occur, the additional stresses satisfying the conditions of mechanical compatibility cannot be simply relaxed by planar domain structures. Therefore, in order to completely relax the stresses, the particular type of three-dimensional domain architecture shown in figure 4 appears. Since the sample has not been polished and poled, the original surface structure will be preserved, and can be observed by ESEM.

4. Conclusion

In summary, we have successfully observed for the first time using ESEM the stereoscopic or three-dimensional configurations of antiparallel 180° and non-180° domains in rhombohedral 0.92PZN-0.08PT crystals along the [111] direction, without surface coating and poling. The 180° domains are between 10 and 50 μm in size, while that of non-180° domains ranges from 1 to 10 μm . This indicates that the formation of spontaneous polarization is not spatially uniform and the domains are irregular. The boundaries of the stereoscopic non-180° domains bands are nonparallel and triangular in shape. The unique configuration of the three-dimensional non-180° domains obtained in this work is different from the non-180° (109° or 71°) domain structure of normal rhombohedral ferroelectric materials, and may be the result of domain deformations induced by crystal defects, in which the additional internal stresses in this crystal can be completely relaxed.

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