

## OBSERVATION OF FERROELECTRIC DOMAINS IN $\text{LiTaO}_3$

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Periodic and partially reversed  $180^\circ$  domain patterns in  $\text{LiTaO}_3$  single crystals, engineered through pulse poling, can be directly observed by using environmental scanning electron microscopy (ESEM) in secondary electron emission mode. The ESEM technique does not require surface treatment and can be used to observe ferroelectric domains on a natural cracked surface in a bulk material. This is very important since the domain patterns obtained by this technique can truly represent the domain configurations in a bulk. The domain structures are confirmed by chemical etching and scanning electron microscopy. The ESEM gives stable and high resolution images.

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### INTRODUCTION

There has been a long debate regarding if the domain microstructures observed by using transmission electron microscopy (TEM) really reflect the true domain configurations in bulk materials. The reason is that the TEM samples must be thinned to a foil to allow the penetration of electron beam. Practically speaking, the samples become 2-dimensional and the boundary conditions are totally changed from that of the original 3-D bulk. If we assume that the system being observed is in thermodynamic equilibrium, then the domain patterns will change as the sample is being thinned down due to the release of constraints from one of the dimensions. In other words,

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the only way to preserve the bulk domain structure in the thin foil is to lock the system in a metastable state. This may be achieved for systems with a paraelectric-ferroelectric phase transition temperature much higher than the processing and observation temperatures, for example, the lead zirconate titanate which has the transition temperature of 375°C.<sup>[1]</sup> However, in general, it becomes questionable if the domain structures observed by TEM really reflect the pattern in a 3-D structure, particularly when the transition temperature is relatively close to the observation temperature. In many cases, the change of domain microstructures due to local electron beam heating is clearly visible under the microscope. As a result, the TEM observations can not convincingly prove or disapprove the theoretical prediction of the relationship,  $D \propto \sqrt{l}$ , between the domain size  $D$  and grain size  $l$ .

With the development of fine structure materials, the study of domain microstructures become increasingly important for materials engineering to produce materials of improved properties, such as high dielectric, piezoelectric and elastic properties. With the problem of low resolution of optical microscopy and the geometrical limitation of the TEM, there is an urgent need to develop better means for the observation of domain microstructures in a 3-D structure.

The traditional techniques used in domain pattern observation include optical microscopy, scanning electron microscopy and transmission electron microscopy. The first two techniques require the sample surface being etched so that a topographic pattern appear due to different etching rates in domains of different polarity or at the domain boundaries where are high stress concentrations. The acid etching not only leads to damaged surfaces but also could not distinguish the topographic pattern of defects, stress concentrations and polarization effects. The resolution of the etching technique is also too low to give subtle details of submicron domains and domain walls. While the TEM technique does not need surface etching and has high resolution, the samples need to be thinned down to a very thin foil of less than 1000 Å in order to allow the electron beam to penetrate through and to avoid the overlapping of layered domain images. Therefore, the domain structures obtained by TEM may not account for the domain patterns in a 3-D structure. The scanning force microscopy has opened up a new method to study the domain structures in ferroelectrics,<sup>[2]</sup> it has shown a great success for TGS which has atomically flat cleavage planes,<sup>[3]</sup> however, the interpretation of the images for a general ferroelectric system is still not satisfactory. The demand on the sample surface makes it difficult to be used for a general ferroelectric system.

In recent years, a new method began to evolve using low current scanning electron microscopy (SEM) to observe unetched ferroelectric materials.<sup>[4-10]</sup> The basic idea is to use low accelerating voltage and low current to reveal adjacent domains of opposite polarity in secondary electron emission mode. The technique does not require etching but the images only appear for certain length of time. The key to obtain the polarization domain images using the low field secondary electron SEM method is to avoid surface charge accumulation onto an insulating crystal from electron beam deposition. The choice of probe current and accelerating voltage are very critical, no contrast can be found if the parameters are not properly chosen. In addition, the contrast image is short-lived, it disappears under the illumination of electron beam after a few seconds to, at most, a few minutes. The observable time for the contrast image shortens with the increase of accelerating voltage. Consequently, it is not possible to obtain a contrast image with high resolution<sup>[4, 5]</sup> due to the insufficient number of electrons to brighten the contrast image.

Recently, we have tried to use the environmental scanning electron microscopy (ESEM) for the observation of ferroelectric domains in LiTaO<sub>3</sub> and achieved an amazing success.<sup>[11]</sup> Because the ESEM<sup>[12, 13]</sup> can operate at pressures ten thousand times higher than that of standard SEM, the free ions created by collisions between moving electrons and neutral gas molecules can provide a conductive path for beam-deposited surface charges. This allows us to observe unprepared, uncoated insulating samples with high resolution. More importantly, the domain contrast obtained from ESEM is very stable, the images are unchanged for several hours in the case of LiTaO<sub>3</sub> crystals.

## SAMPLE PREPARATION

The samples used in our experiments are LiTaO<sub>3</sub> with engineered periodic and triangular domain structures. Starting with a monodomain c-cut single crystal of 3m symmetry, the spontaneous polarization  $P_s$  is reversed in selected regions using a pulse electric field at room temperature.<sup>[14]</sup> Preliminary examination of the domain structures in a poled LiTaO<sub>3</sub> sample can be made by optical microscopy on an etched surface. The procedure described in Ref. [14] consists of making two kinds of aluminum electrodes: one is periodic, and the other is uniform plane. Through pulse poling, stripe and triangular shaped domains were produced by using these two kinds of electrodes mentioned above. Both the level of poling field and the duration

of the pulse can influence the final domain pattern in the system. More details of the fabrication technique has been discussed elsewhere in Refs. [14–15].

## DOMAIN OBSERVATION

The domain observations were performed using an ESEM (ElectroScan Model E-3, Wilmination, MA) in secondary electron emission mode. For comparison, we have performed the experiments in two stages:

First, a periodically poled sample was etched in a solution containing 2 parts  $\text{HNO}_3$  and 1 part HF for 15 hours at room temperature. The etched sample was attached to an aluminum sample mount using a double faced tape for observation. The aluminum sample mount was grounded. Figure 1 is a schematic diagram of the experimental arrangement and the crystal orientation of the sample.

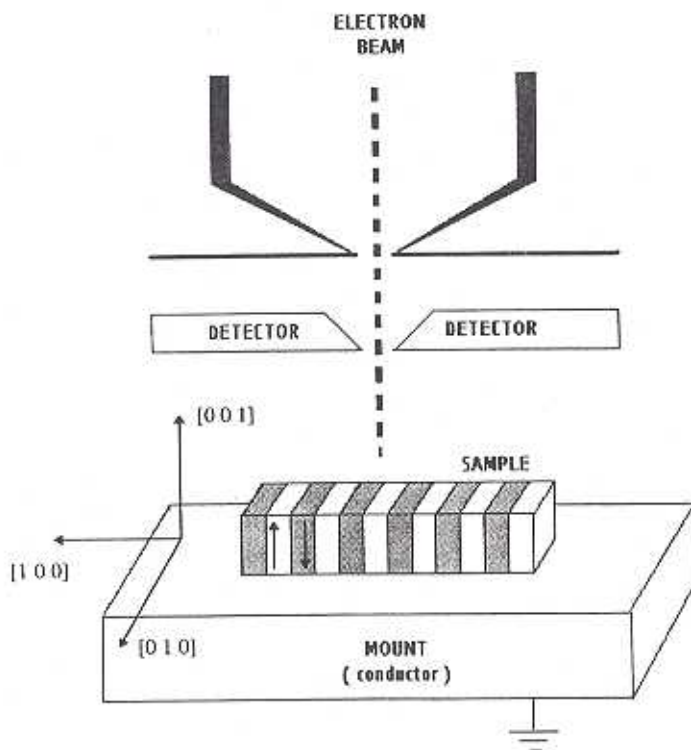


FIGURE 1 Schematic diagram of the experimental arrangement and sample orientation.

The unit vectors for the Cartesian coordinate system was chosen as the following:  $z$  is along the poling direction,  $y$  is in one of the mirror planes of the symmetry group in  $z = 0$  plane and perpendicular to  $z$ , and  $x$  is perpendicular to  $y$  and  $z$ .

Under normal observation conditions, *viz.*: Wet mode, Chamber pressure = 3–3.5 Torr, Accelerating voltage = 15 kV, Condenser = 40, Scan rate = 8–30 sec./frame and beam aperture size = 30  $\mu\text{m}$ , we got a topographic image of the periodic domain pattern on the original  $+c$  surface, as shown in Figure 2(a), which is in  $[001]$  of the orthogonal coordinate system described above. Water vapor was chosen as the imaging gas. In the image obtained, the surfaces of  $-P_s$  domains are lower than that of  $+P_s$  domains. The formation of the surface steps is due to different etching rate of positive and negative domains in the acid. A wider stripe and some island domains shown in the figure are attributed to imperfect poling or stress concentrations. One can see that the contrast image only outlines the domain boundaries which are brighter than the interior of domains, reflecting the fact that more secondary electrons are emitted at the edges of the etching steps. No contrast was revealed between the positive and negative domains due to the screening of the polarization  $P_s$  by the probing current. In other words, the positive and negative domains have nearly equal secondary electron emission rate if the depolarization field is screened by the charged ions and the beam deposition electrons.

In the second stage, the etched sample was taken out from the chamber and the  $[001]$  surface was polished. When the polished sample was re-examined using ESEM under the same condition, nothing interesting was seen except some topographic images of polishing scratches on the surface. We then changed the experimental conditions by decreasing the chamber pressure, decreasing the condenser setting and increasing the accelerating voltage, magically, contrast stripes began to appear (shown in Fig. 2(b)) and they stay stable. The locations and shapes of the contrast patterns in Figure 2(b) exactly match the etched patterns in Figure 2(a). This confirms that the contrast stripes are originated from the anti-parallel domains.

With a slight tilt of the sample, we could simultaneously observe the previously etched patterns of the periodic structure on  $[010]$  surface of the sample which was not polished (see the bottom of Fig. 2(b)). The image patterns on the two adjacent  $[001]$  and  $[010]$  faces are consistent. However, if we tilt the sample to the  $[0\bar{1}0]$  surface which was polished, no contrast stripes were found. This means that only the polar surfaces can show the domain contrast images, which indirectly telling us that the images are related to the unscreened portion of the depolarization field.

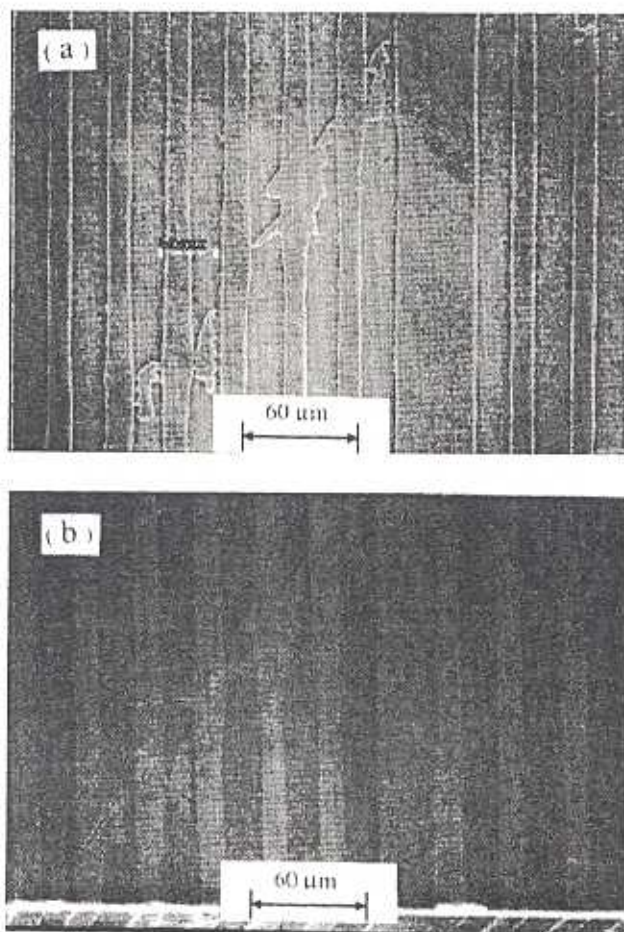


FIGURE 2 Comparison of ESEM images of a surface portion in a c-cut  $\text{LiTaO}_3$  with antiparallel domains: (a) Etched surface; (b) Polished surface.

In the ESEM technique, the visualization of domain contrast is also independent of surface roughness. We could clearly observe the contrast image of domains on a crack surface as shown in Figure 3 with appropriate experimental conditions. The sample in Figure 3 was partially poled under a pair of uniform plane aluminum electrodes. After poling, the electrodes were removed in NaOH solution which only resolves the aluminum but not the  $\text{LiTaO}_3$  crystal. In Figure 3 some triangular domains with positive polarity are shown as lighter regions on the dark background of negative polarity.

Such triangular domain pattern was produced by using a moderate field,  $E = 21 \text{ kV/mm}$ . The sides of the triangles corresponding to domain walls are parallel to crystallographic  $x$ -directions. The domains in Figure 3 have different sizes, which reveals that the polarization reversal in the  $\text{LiTaO}_3$  crystal is through nucleation and growth mechanism. At first, large number of inverted domains are nucleated at different sites, then they grow and coalesce to complete the domain reversal process in the single crystal system. Using a scanning electron microscope on a polished surface of a  $c$ -cut  $\text{LiTaO}_3$  crystal, we have confirmed our domain pattern observations shown in Figure 4. In comparison with Figure 3, one can see the difference between the two imaging methods. Here the image is formed through piezoelectric effect, *i.e.*, the surface charge accumulation expands the positive polar regions to give a topographic image on a negative polar background.<sup>[16]</sup> The density of the secondary electrons produced by the positive and negative polar regions are apparently the same in the SEM secondary electron method, since the image intensities are the same except at the domain boundaries.

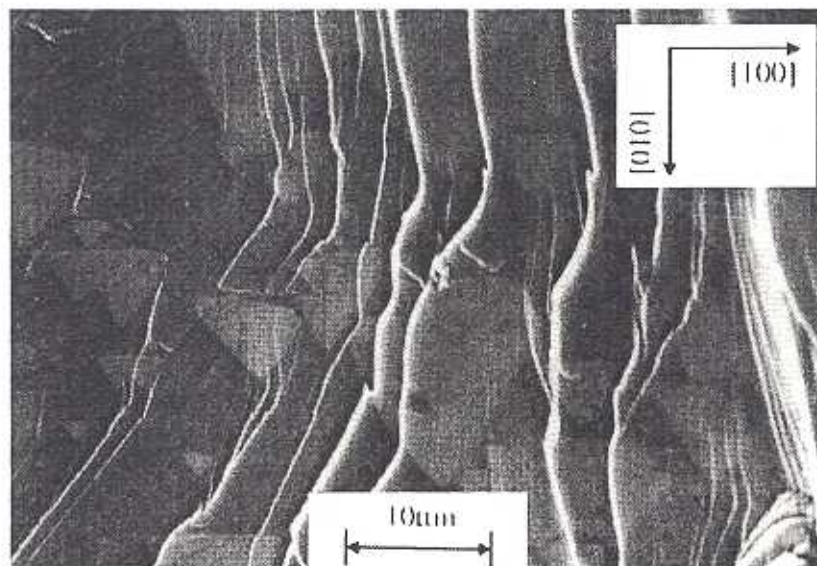


FIGURE 3 ESEM image of a crack surface of  $\text{LiTaO}_3$  crystal with nearly  $[001]$  orientation. The sample was partially poled by a poling field of  $E = 21 \text{ KV/cm}$ . The triangular anti-parallel domains with positive polarity are shown as brighter regions on the darker background.

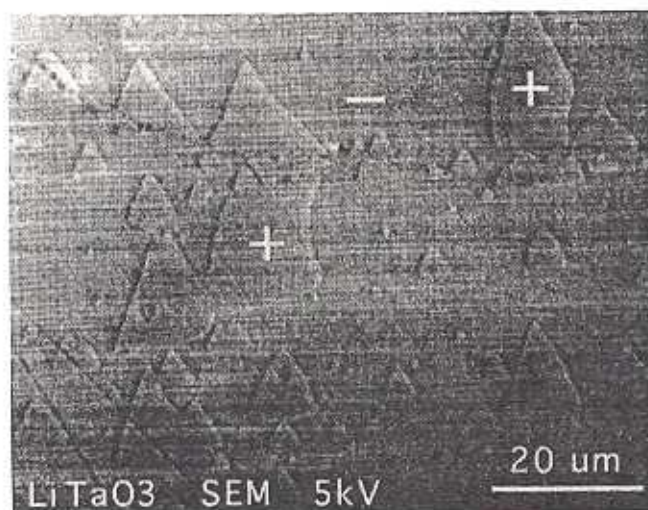


FIGURE 4 SEM secondary electron image of partially reversed domains in a  $\text{LiTaO}_3$  single crystal. The triangular domains are positive polar regions in a negative polar background.

## CONCLUSIONS

In conclusion, we have successfully observed stable contrast image of anti-parallel domains in poled  $\text{LiTaO}_3$  single crystals using ESEM technique. The images obtained from ESEM are further confirmed by chemical etching and the SEM secondary electron microscopy on polished surfaces.

The ESEM technique is very promising for the study of domain configurations in a 3-D bulk since it allows us to directly observe anti-parallel domains in an unprepared insulating sample surface. Because the technique allows the use of higher accelerating voltage with higher magnification, much better resolution than that of the low voltage low current SEM can be obtained. The technique also allows the measurement of rough surfaces, providing a reliable way to study the true 3-D domain configuration without the influence of polishing damages to the sample surface.

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