

## Imaging of Ferroelectric Domains in LiTaO<sub>3</sub> by Environmental Scanning Electron Microscopy

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Antiparallel ferroelectric domains in LiTaO<sub>3</sub> single crystal can be directly imaged by using environmental scanning electron microscopy in secondary electron emission mode. Because the observation was performed at a water vapor atmosphere (wet mode), the sample surface was free from charging, therefore, no surface treatment was required. The image of domains can be seen for several hours. The technique may be extended to study domain structures in other ferroelectric crystals and ceramics.

**Keywords:** LiTaO<sub>3</sub>; ferroelectric domain; environmental scanning electron microscopy; secondary electron emission

### INTRODUCTION

The study of domain microstructures becomes increasingly important for materials engineering<sup>[1-2]</sup>. Therefore, visualization of domains has gained broad interests in both physics and materials science communities. Since 1980's, scanning electron microscopy has found applications in the study of ferroelectric domain structures<sup>[3-4]</sup>. Using low accelerating voltage and low beam current, a contrast image of anti-parallel ferroelectric domains could be obtained from the polar surface of ferroelectric crystal in secondary electron emission mode<sup>[5-6]</sup>. However, if the observed sample is an insulator crystal

with very small conductivity, such as  $\text{LiTaO}_3$  crystal, it is very difficult to avoid charge accumulation on the sample surface. The contrast image, if can be observed, may only appear in a few seconds<sup>[7]</sup>. In this paper, we report a new imaging method of using environment scanning electron microscopy (ESEM). Being different from conventional scanning electron microscopy (CSEM), the ESEM can be used to observe samples at a relatively high pressure from 1 to 20 Torr. The positive ions produced by the collision between moving electrons and gas molecules can neutralize the surface charges of the irradiated sample<sup>[8]</sup>, avoiding the charge screening effect. Using ESEM, stable domain contrast images have been obtained from the polished but un-coated polar surfaces of  $\text{LiTaO}_3$  crystal with engineered domains<sup>[9]</sup>.

#### SAMPLE PREPARATION

The samples used in our experiments are  $\text{LiTaO}_3$  single crystals with engineered periodic domain structures. Starting with a mono-domain c-cut single crystal plate, the spontaneous polarization  $P_s$  is selectively reversed under patterned electrode using an electric pulse at room temperature. Preliminary examination of domain structure in the poled  $\text{LiTaO}_3$  sample had been made by optical microscopy on its etched surfaces. The procedure was described in Ref.[10].

#### ESEM OBSERVATION

The domain observations were performed using an ESEM (ElectroScan Model E-3, Wilmington, MA) in secondary electron mode, and water vapor was chosen as imaging atmosphere. For comparison, we performed the experiments in two steps: First, the sample was etched and observed under normal observation condition, viz., chamber pressure  $p=3.5$  Torr, accelerating voltage  $V=15\text{ kV}$ , condenser  $C=40$ , scan rate  $v=8\text{--}30$  sec./frame and beam aperture size  $d=30\ \mu\text{m}$ . A topographic image of the periodic domain on

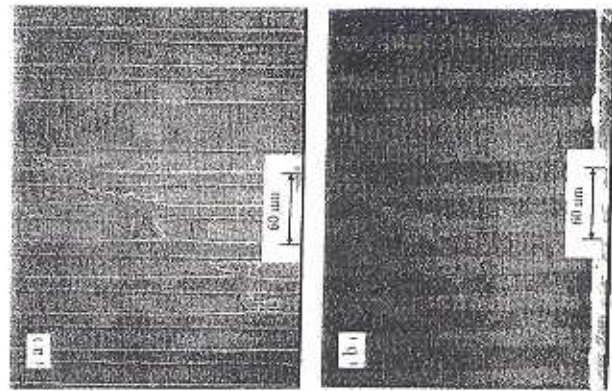


FIGURE 1 ESEM images of a +c surface of  $\text{LiTaO}_3$  with antiparallel engineering domains. (a) The topographic image on the etched surface. (b) The contrast image on the sequentially polished surface. (Experiment conditions: see the text)

etched + c surface was obtained at these conditions as shown in Fig.1(a). The formation of the topographic pattern is due to different etching rates of positive and negative domains in acid.

In the second step, the etched sample was taken out of the chamber and both surfaces of the sample were re-polished to eliminate these etching patterns. When the polished sample was re-examined under the same conditions using ESEM, topographic image of domains disappeared as expected. No domain pattern can be seen except some topographic images of polishing scratches on the surface. However, when the experimental



conditions were changed by decreasing the chamber pressure and the condenser setting, and increasing the accelerating voltage, a contrast stripe pattern began to appear, as shown in Fig. 1(b). The locations and shapes of the contrast pattern in Fig. 1(b) exactly match the etched pattern in Fig. 1(a). This confirms that the contrast stripes are originated from the anti-parallel domains. Optimum contrast was obtained under the following conditions; accelerating voltage = 30 kV; chamber pressure = 2 Torr; aperture size = 50  $\mu\text{m}$  (maximum for the E-3 system); condenser setting = 10 (lowest of the E-3 system); and scan rate = 17-30 scc/frame. The positive domains were brighter than the negative domains, indicating that the positive domains have higher secondary electron emission rate.

We also observed the -c surface of the sample (Fig. 2). On -c surface, the background was the negative polarity, therefore, darker, and the inverted domains were the positive polarity, therefore, brighter. The observation result is consistent with that of the +c surface.



FIGURE 2 The contrast image of antiparallel domains on -c surface of  $\text{LiTaO}_3$ . The regularity of domain structure on -c surface is worse than on +c surface since the electrode stripes for domain reversal is on the +c face.

## DISCUSSION

The imaging of ferroelectric domain may be based on different physical principles, such as the depolarization field, the pyroelectric or piezoelectric effects, etc. Which effect plays the dominant role depends on the particular observation conditions and the physical properties of the observed material. In the ESEM, the sample is detected under a certain vapor pressure. The free ions, which are created by collision between secondary electrons and gas molecules, can neutralize the beam-deposited surface charges, thus high surface potential can not be built up on the irradiated sample surface, which mean that the piezoelectric effect should be very weak.

On the other hand, the neutralization action is not instantaneous, the positive ions move slower than electrons due to their larger mass. There are positive and negative charges absorbed on the ends of negative and positive domains, respectively, before the probe electrons arrive. The beam deposited charges on the surface of negative domain will first neutralize the absorbed positive charges. The neutralization action does not occur on the surface of positive domains. The depolarization field in negative domains may not be shielded effectively due to this neutralization action, which makes the emission of secondary electron from the surface of the negative domain more difficult. Therefore, the negative domains appear darker.

Another factor contributes to the contrast is the pyroelectric effect. The probe beam accelerated under 30 kV voltage, has quite high energy density when they bombard the sample, they will no doubt cause heating effect in the irradiated volume of the sample. For a pyroelectric crystal with large pyroelectric coefficient, like  $\text{LiTaO}_3$ , a pyroelectric potential can be produced. The sign of the pyroelectric potential is defined by the direction of the polarization. It is opposite for the positive and negative domains. Because secondary electrons are low in energy, a small pyroelectric potential can lead

to big difference on the their emission rates. This difference will also produce the contrast image for antiparallel ferroelectric domains. According to pyroelectric analysis, the positive domain should have higher emission rate of secondary electron, therefore will be brighter.

## CONCLUSION

The contrast image of antiparallel ferroelectric domains in  $\text{LiTaO}_3$  can be shown by using ESEM. The image of domains is stable. The advantage of the ESEM, which can be operated at low vacuum, allows the observation of domain structure of ferroelectric crystal without surface etching and coating. The non-destructive method may be very useful to examine the engineering domain structures of ferroelectric crystals used widely in nonlinear optics and acoustic devices.

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