

# Domain Orientation in Barium Titanate Single Crystals

## Introduction

The relationship between etch patterns and domain orientation in barium titanate crystals in the tetragonal state has been shown by Hooton and Merz<sup>1</sup> and illustrated with low-power photomicrographs. In hydrochloric acid the positive ends of the electric dipoles etch rapidly, forming a rough surface, the negative ends etch slowly, forming a smooth surface, and the "sides" (dipoles parallel to the surface) etch at an intermediate rate, forming a semi-rough surface. This paper will discuss results obtained by this technique on partially switched crystals in the tetragonal state and results of studies of domain structure in the orthorhombic state. The crystals, which averaged 0.010 inch in thickness, were examined by transmitted light at magnifications up to 1000X in a light microscope and at higher magnifications in an electron microscope.

## Tetragonal crystal structure

BaTiO<sub>3</sub> is tetragonal from about 5°C to about 120°C. The *c* axis is 1% longer than the *a* axis (Fig. 1) because

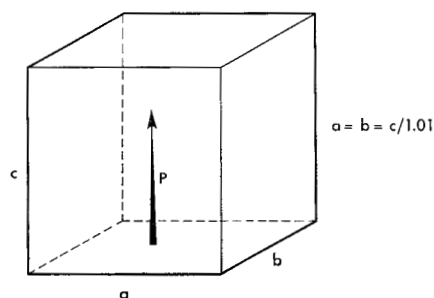


Figure 1  
Barium titanate unit cell in tetragonal state.

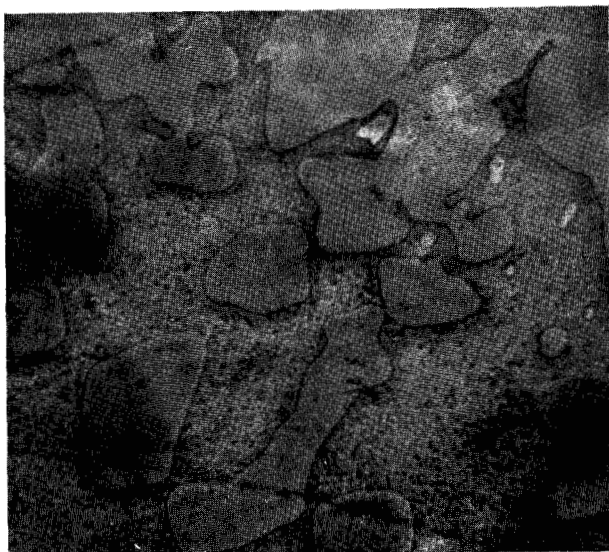
the unit cell is spontaneously polarized in a direction parallel to the *c* axis. A *c* region is a volume in which all the dipoles are perpendicular to the large plane crystal surface. Opposite this volume may happen to be a single domain (region in which all dipoles are polarized in one direction) but it is more likely to consist of many domains polarized in opposite directions. These domains, regardless of direction of polarization, have the same optical properties, and therefore one sees in the light

**Abstract:** An acid etching technique makes visible the domain structure of barium titanate crystals as reported by Hooton and Merz. Earlier observations by Merz of the mechanism of switching are confirmed by experiments using this technique. A discussion of domain wall formation in the orthorhombic state leads to the explanation of observed domain patterns. Photomicrographs are shown and discussed.



Figure 2  
Domain with positive ends of dipoles at surface, surrounded by oppositely polarized domain, 7,000X.

microscope the whole *c* region but not the domains in that *c* region. But when a *c* region is etched, the resulting pattern shows the location of oppositely polarized domains; Fig. 2 is an electron micrograph of a BaTiO<sub>3</sub> crystal with one domain surrounded by another. Exami-



(a)



(b)

Figure 3

**Domains in  $c$  region, 330X. (a) top of crystal, (b) bottom of crystal photographed through the crystal.**

nation of top and bottom surfaces [Figs. 3(a), (b)] shows that the domains go straight through the crystal. If, before etching, the entire crystal is made a single domain by application of a dc field, one surface is almost completely smooth and the other surface almost completely rough.

### Study of switching

The etching technique seemed ideal for getting a better idea of how the polarization of a crystal is reversed. By discharging a capacitor into an electroded BaTiO<sub>3</sub> crystal, it is possible to switch the crystal partially or completely, depending on the amount of charge. Complete switching of a poled crystal requires a charge equal to twice the

value of the remanent polarization ( $P_r$ ) and a voltage greater than the coercive voltage of the crystal. Partial switching requires a charge of  $2P_r X/100$  to achieve  $X\%$  of complete switching. It should be pointed out that this method of switching is somewhat different from switching by pulses, and therefore the results of this experiment may not be valid for a pulsed crystal.

A freshly grown crystal is poled at  $10^6$  v/m dc for 5 seconds and is switched by discharging into it a previously charged capacitor. The electrodes are dissolved and the crystal is etched in concentrated HCl at room temperature for four minutes. Typical results are shown in Fig. 4. Part

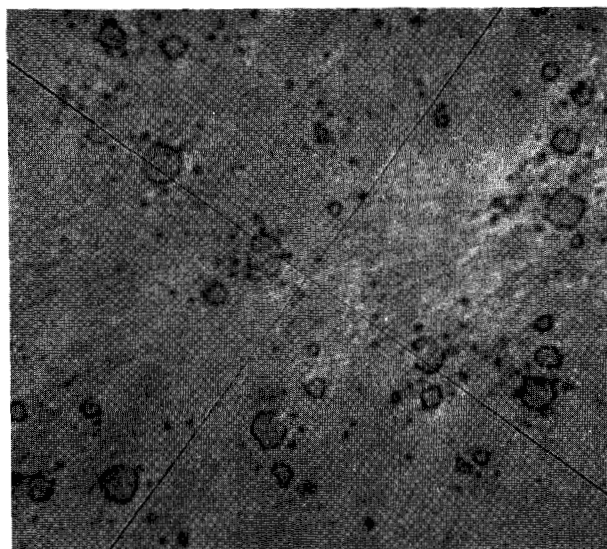


Figure 4

**Corner of electrode area of crystal switched 20%, 940X.**

of the electroded area is shown for a crystal that was switched approximately 20%. Inspection under the microscope showed that almost all of the domains go through the crystal but that there are a few which start on either side and do not go through. On a crystal that was switched 45%, detailed inspection shows that, by comparison with the previous crystal, the domains appear to be larger (or to have "agglomerated"), and the top and bottom are mirror images to a lesser degree, i.e., domains seem to change size and shape as they go through the crystal, and more domains do not go through. A crystal that was switched 100% did not show any domain structure and looked just like a crystal which had been poled but *not* switched.

These observations agree with the present concept of the mechanism of switching<sup>2</sup> — the domain being switched is a small cone starting at one surface and pointing toward the opposite surface. It progresses through the crystal like a single wave front, reaches the opposite surface, and continues to grow like a truncated cone.

It appears from this study of partially switched crystals that the first domains to switch are the ones near the edge of the electrode area and the one around inclusions and other crystal imperfections.

## Orthorhombic crystal structure

In the following discussion reference will be made, for the sake of convenience, to the original cube axes (Fig. 5) rather than to the crystallographer's orthorhombic axes, and the term "domain wall" will be used instead of "twin surfaces."

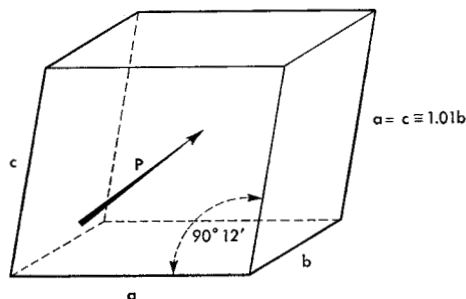


Figure 5  
Barium titanate unit cell in orthorhombic state.

The orthorhombic state in  $\text{BaTiO}_3$  lies approximately between  $-70^\circ$  and  $+5^\circ\text{C}$ . The  $a$  and  $c$  axes are equal and longer than the  $b$  axis by about 1%, there is a shear of about 12 minutes in the  $a$ - $c$  plane, and the polarization is along the face diagonal in the  $a$ - $c$  plane.<sup>3</sup>

In order to try to explain the etch patterns obtained in the orthorhombic state it is necessary to determine the possible domain wall orientations, and the angle between the crystal axes and the intersection of the domain wall with the crystal surface.

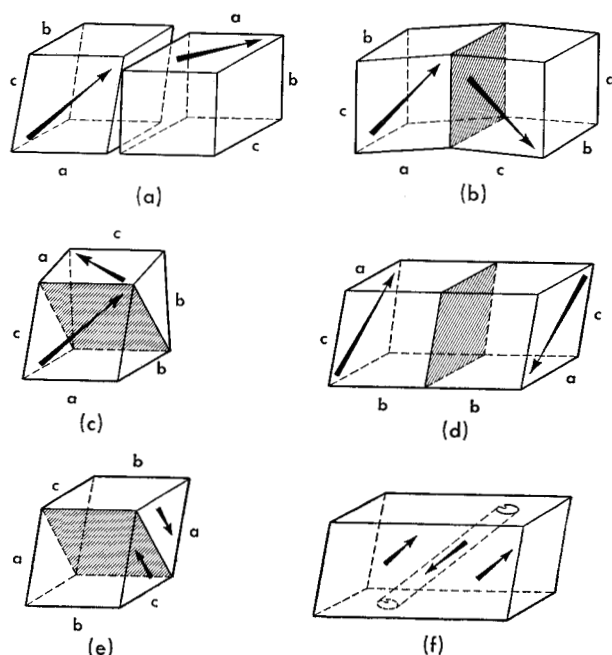


Figure 6  
Domain wall orientations in orthorhombic state; wall impossible in (a).

The obvious restriction is that there can be no discontinuity in the normal component of polarization at the domain wall. In addition, the wall must have dimensions such as to fit simultaneously the two adjacent domains in order to minimize strains. In discussions of the tetragonal state, the second restriction is seldom mentioned because it is automatically satisfied if the first is satisfied, but in considerations of the orthorhombic state, both restrictions must be satisfied separately.

Fig. 6 (a) shows a case where a domain wall cannot exist because the cell dimensions and angles do not match. Figs. 6 (b), (c), (d), (e) and (f) show domain wall orientations which satisfy the above restrictions. These cases show domain walls whose intersection with the crystal surface can make only angles of  $90^\circ$  and  $45^\circ$  with each other and with the primitive crystal axes, and these intersections create the long straight lines on the etched crystal surface. Fig. 6 (f) shows the case which allows the "lakes" or any other irregular pattern to exist; the only restriction is that the domain wall must be parallel to the direction of polarization. The intersection of the wall with the crystal surface can describe figures such as straight lines, irregular lines, and closed irregular figures ("lakes"); if the domain goes through the crystal, the pattern will appear on both sides of the crystal, but displaced on one side in the direction of polarization by a distance equal to the thickness of the crystal. Figs. 6 (d) and (e) are special cases of Fig. 6 (f), in which the domain wall is a plane parallel to the direction of polarization.

## Crystals etched in orthorhombic state

Several  $\text{BaTiO}_3$  crystals were etched in concentrated HCl at  $0^\circ\text{C}$  for four hours. These crystals had no electrical treatment; they were used as grown.

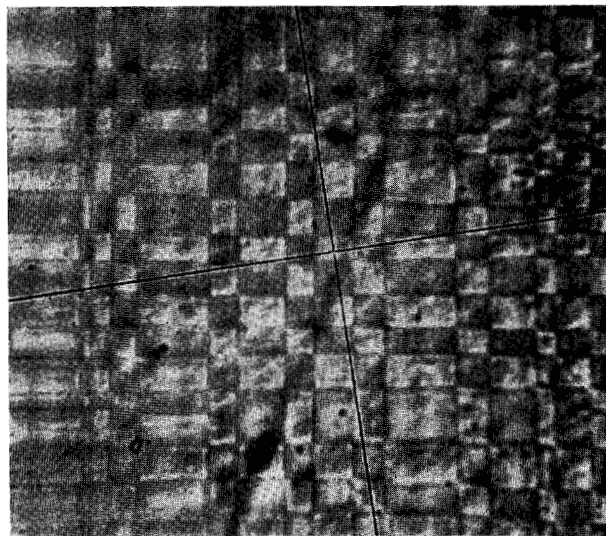
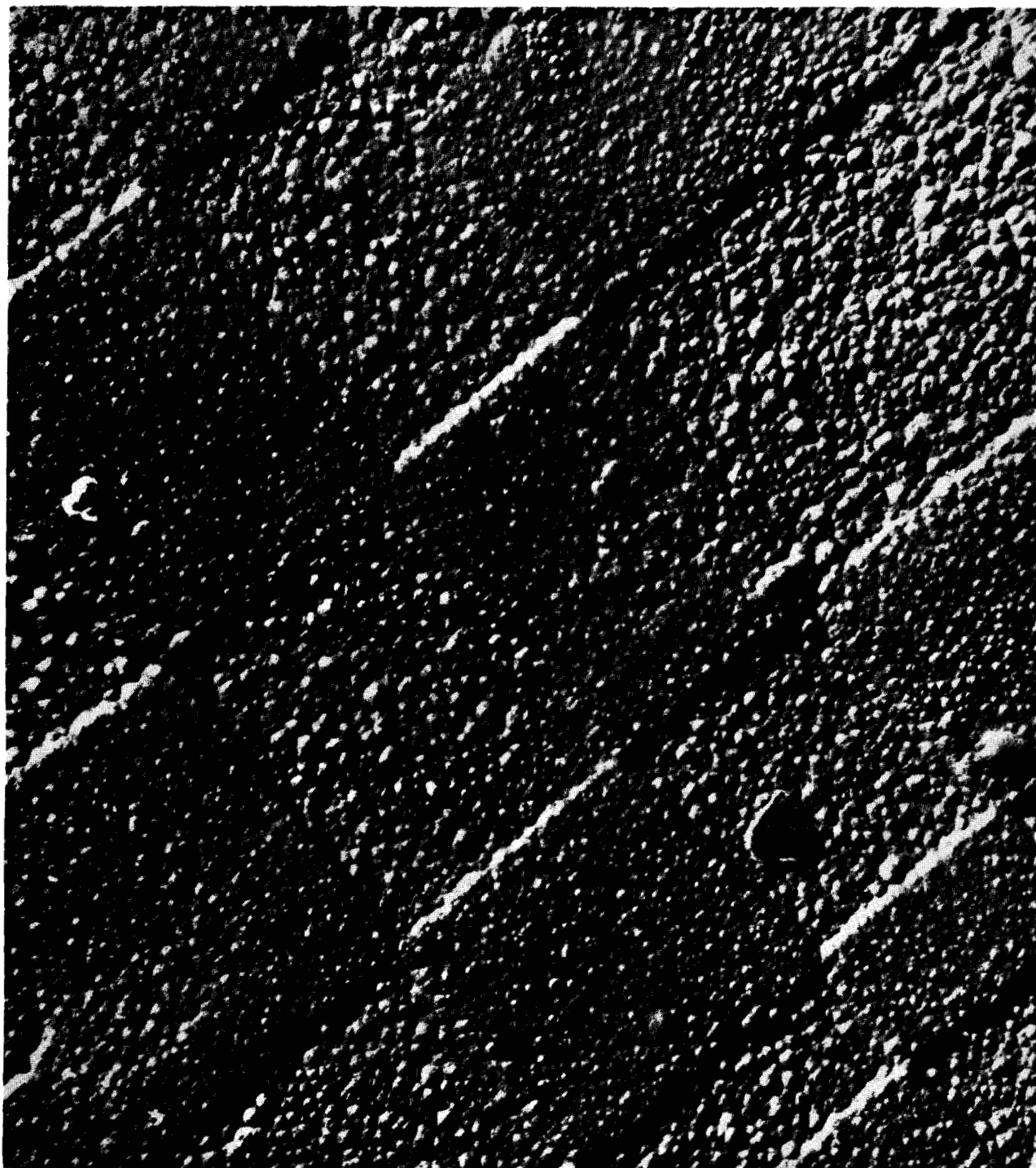


Figure 7  
"Checkerboard" domain pattern obtained by etching in orthorhombic state, 940X.



**Figure 8**  
Electron micrograph of "checkerboard" domain pattern, 18,000X.

The "checkerboard" pattern of Figs. 7 and 8 indicates domains which go through the crystal making a similar pattern on the opposite side. Observations show that the pattern on the opposite side is displaced as expected in the direction of one of the primitive crystal axes, the displacement being equal to the thickness of the crystal.

Fig. 9 shows how the domain walls form the pattern of Figs. 7 and 8. Domain walls  $e, e, e, e \dots$  go through the crystal at  $90^\circ$  to the surface [Fig. 6 (d)], while domain walls  $f, f, f, f \dots$  go through the crystal at  $45^\circ$  to the surface [Fig. 6 (e)].

"Lakes" in the orthorhombic state look similar on the

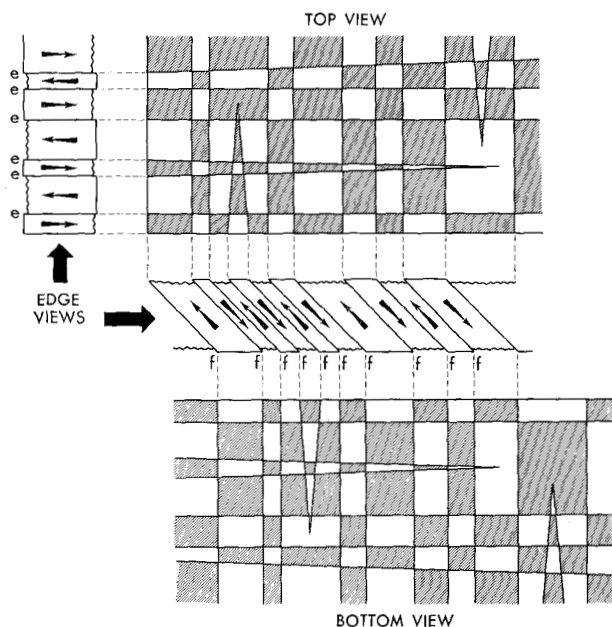


Figure 9  
Domain structure of "checkerboard" pattern.

surface to those in the tetragonal state which are shown in Figs. 1 and 3. The dipoles causing the rougher area are parallel to those causing the smoother areas but polarized in the opposite direction. The walls are of the type shown in Fig. 6 (f). Fig. 10 shows three directions of polarization. In the smoothest area, the negative ends of the dipoles are at the surface, and in the roughest areas the positive ends of the dipoles are at the surface. In the areas of intermediate roughness, the dipoles are parallel to the surface.

Up to the present it has not been possible to diagram the domain walls and the exact directions of polarization, as was done for the "checkerboard" pattern (Fig. 9).

## Conclusion

The etching technique is shown to be valuable in the study of the behavior of barium titanate crystals in different crystalline states and in partially switched conditions. Physical evidence supports the hypothesis that switching is accomplished by cone-shaped domains originating at one surface and growing through the crystal to the opposite surface. It is possible to explain simple domain patterns formed in the orthorhombic state by examining several possible domain wall orientations.

## Acknowledgment

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## References

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2. W. J. Merz, *Phys. Rev.* **95**, 690 (1954).
3. R. G. Rhodes, *Rep. Brit. Elect. Res. Assn., Ref. L/T* 244 (1950).

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Figure 10  
Three directions of polarization, 45,000X.

