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Etch Patterns and Ferroelectric Domains in $BaTiO_3$ Single Crystals

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It has been found that ferroelectric $BaTiO_3$ single crystals show a differential etch rate when etched in hydrochloric acid. The positive end of the electric polarization etches much faster than the negative one. Thus this phenomenon affords a valuable new tool for the investigation of the ferroelectric domains in $BaTiO_3$. Some interesting pictures of domain arrangements are shown and discussed. The results obtained demonstrate the extremely strong electric dipole-dipole coupling in the forward direction and the weak coupling in the directions perpendicular to it. This electrostatic interaction governs the domain patterns in ferroelectric $BaTiO_3$ crystals.

I. INTRODUCTION

IT has been found that $BaTiO_3$ single crystals show a differential etch rate which can be related to the ferroelectric domains. The most important result of this observation is that we can easily and quickly distinguish between the positive and the negative ends of the electric dipoles. We find that the positive end (head) of the dipole etches quite rapidly in hydrochloric acid while the negative end (tail) of the dipole etches very slowly, if at all. The usual optical methods have been very useful for determining the domain arrangements and the direction of the electric polarization. However, the sense of the polarization could only be determined by applying external electric fields or stresses to the crystal.[1] Thus we find that the optical methods and the etching technique complement each other perfectly. In the following paragraphs we will report some interesting results obtained by this new method.

II. PROCESSING OF SAMPLES

The method of preparing the crystals for study is extremely simple. The crystals are placed in a test tube and etched for one to ten minutes, depending upon the desired degree of development of the patterns, in concentrated hydrochloric acid at room temperature. The acid is then poured off the crystal rinsed in water and washed in ethyl alcohol. The microscopic patterns are studied using reflected light. Magnifications in the 100× to 200× range are most satisfactory.

III. ETCH PATTERNS OF POLED CRYSTALS

At room temperature $BaTiO_3$ shows tetragonal symmetry which is associated with a spontaneous polarization which may be thought of as a shift of the Ti ions with respect to the oxygen octahedra. The polarization direction lies parallel to the tetragonal *c*-axis. Regions of the crystal in which all the dipoles are aligned perpendicular to the crystal flat are called *c*-domains because we look along the polar *c*-axis. Similarly, regions in which all the dipoles are aligned in a direction parallel to the crystal surface are called *a*-domains. Optically it is very easy to distinguish between an *a*- and a *c*-domain. However, it has been a problem to determine the sense of a given polarization direction because parallel and antiparallel domains have the same optical properties and thus look the same. By applying external electric fields or stresses it was possible to determine the sense of the polarization.[1]

Etching experiments on dc poled crystals show that the etchant (HCl) attacks very rapidly at the positive end (head) of the polarization and quite slowly at the negative end (tail), as can be seen in Fig. 1. The islands which are antiparallel regions go right through the crystal. Figure 1 represents a poorly poled crystal since it consists of almost as many domains polarized in one direction as domains polarized in the opposite direction. A well-poled crystal usually shows just very few scattered circular areas. Whether these areas resist the poling voltage or whether they are regions which invert after the field has been removed and before the crystal has been etched, has not been determined. Figure 1 shows beyond any doubt the differential etch rate for the two ends of the electric dipoles.

The etch rate perpendicular to the dipole direction, that is for an *a*-domain, is intermediate between the rapid rate for the titanium end of the dipoles and the slow rate for the oxygen end of the dipoles. The different etch rates are shown in Fig. 2.

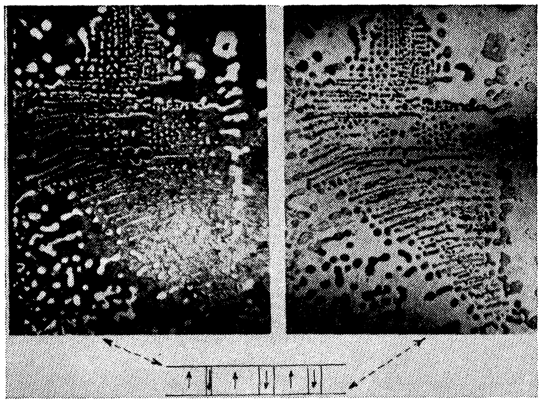

FIG. 1. Photograph of top and bottom of a poorly poled $BaTiO_3$ crystal showing many antiparallel polarized domains. Notice the perfect mirror image. (One print is reversed.)

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[1] Walter J. Merz, Phys. Rev. 95, 690 (1954).

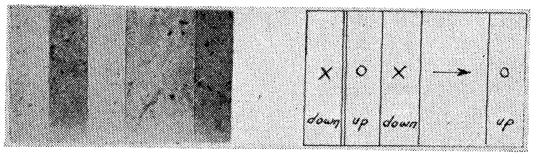

FIG. 2. Surface appearance of etch response of differently polarized regions.

IV. DOMAIN REFLECTIONS

Earlier investigations[1] have shown that the ferroelectric domains in $BaTiO_3$ crystals are always so arranged that there is no build-up of a space charge on the domain walls. This implies a very strong coupling between dipoles in the dipole direction whereas the coupling perpendicular to the dipole direction is weak. For example, we could show that the 90° walls between two *a*-domains are always along [011] directions and the subdomains in the two *a*-domains are arranged in such a way that the head of one dipole always joins the tail of the neighboring dipole as shown in Figs. 3 and 4.

We have etched some *c*-domain crystals containing a few *a*-domains which were so arranged as to illustrate clearly this strong linear coupling in the forward direction (head to tail coupling). This is shown in Fig. 5, where the dark areas are the regions where the positive ends of the dipoles are at the surface, the bright areas where the negative ends of the dipoles are at the surface and the grey areas are *a*-domains as explained before in Fig. 2. To the extreme left of Fig. 5 we see a distinctively shaped region (a) of inverted polarization. On the right side of the two very narrowly spaced sharp lines (two 90° walls) we see the mirror image (b) of this region. The inverted regions are oppositely poled with respect to each other and also to their background region. The two sharp lines represent the boundaries of the wedge-shaped *a*-domain through which the reflection of the oppositely polarized region takes place. Figure 5 thus shows in a striking way the strong coupling of the dipoles in the forward direction. The center part of Fig. 5 shows a second odd-shaped antiparallel polarized region (c) which is reflected through a wide *a*-domain to the right side of the picture (d). This reflection is the same type as the first one except that the path through the *a*-domain is large. The *a*-domain can easily be recognized by its intermediate shade.

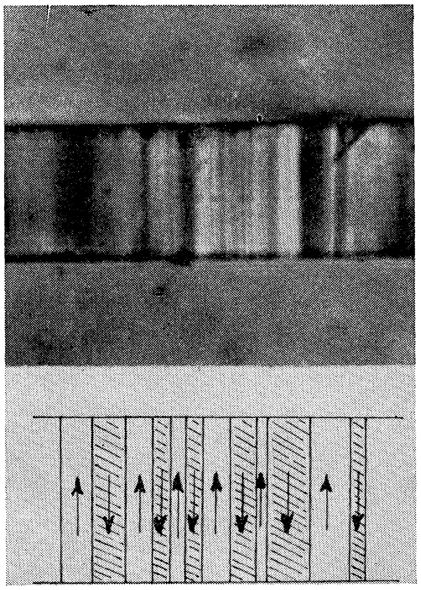

FIG. 3. Edge of a *c*-domain crystal of $BaTiO_3$ showing antiparallel domains obtained by stressing.

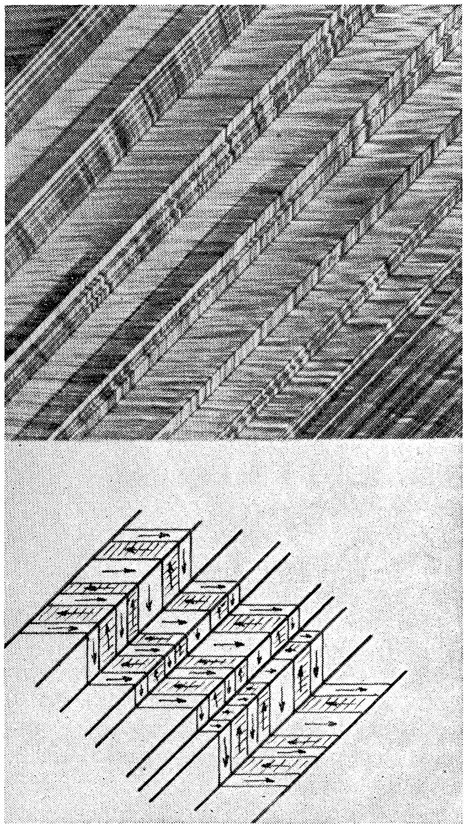

FIG. 4. Surface of an *a*-domain crystal showing 90° walls and antiparallel domains.

The same crystal was re-etched in HCl. We found that the 90° wall on the left had shifted to the left and that the broad *a*-domain region was subdivided into a number of *a*- and *c*-domains. The much more complicated results are shown and explained in Fig. 6. We can still observe the remanent images from the first etch (compare with Fig. 5), but we also observe changes produced by the new domains. We note that the dark image (a) (to the left) has shifted to the left because the 90° wall has shifted. At the point where we observed two sharp lines before we observe now three lines. We think this "triplet" is composed of the traces of the two original lines lying to the left and the new intersection of the same wall with the surface which has moved to the right down the 45° slope of the wall. This displacement to the right is equal to the amount of material etched away in the second etching. Thus the region between the single line to the extreme left and the third line of the triplet is now an *a*-domain.

The most striking results obtained are shown in the center of Fig. 6. Since two *c*-domains have been introduced into the *a*-domain the reflection of the bright odd-shaped region (*g*) on the extreme right through the *a*-domains cannot take place in one step. The reflection is accomplished in 3 steps and the sum of the 3 dark images (*d*, *e*, *f*) in the center of Fig. 6 is the mirror image of the bright spot (*g*) and is equivalent to the dark area (*c*) from the first etching. This multiple reflection again exhibits the strong forward coupling of the electric dipoles in a beautiful way.

In addition to the reflection through *a*-domains as shown and discussed above, there also is a coupling through *c*-domains. In Fig. 5 we can see that the two sets of reflections are not independent of each other because the four odd-looking regions (*a*, *b*, *c*, *d*) look very similar to each other and are nicely aligned. It seems that the first and second pair of reflections are coupled through a *c*-domain. This is substantiated by the fact that there are other regions in Figs. 5 and 6 which show similar behavior. For example, at the upper edge of the photographs we can see two sets of cigar-shaped reflections (though the last reflection on the right is not too clear). How can we have reflection through a *c*-domain perpendicular to the dipole direction? The only way we can explain it is by the very strong piezoeffect in $BaTiO_3$. The crystal shown in Fig. 5 was originally a *c*-domain crystal. The *a*-domains which were introduced are wedge-shaped. Thus the crystal is probably strained in a complicated way but mostly sheared as shown in Fig. 7. The shear stress T_5 around an axis perpendicular to the paper (y-axis) induces a polarization P_i in the horizontal direction (x-axis) through the piezoelectric strain constant $d_{15}(P_x = d_{15}T_5)$. The sense of this induced polarization P_i depends on the sense of the spontaneous polarization P_s. For the 90° wall at the left we find that P_i points to the right for the projection on the domain wall of the odd-shaped antiparallel region (*b*) and points to the left for the normal surrounding region. If we go through the same argument for the 90° wall to the right we find that P_i would have the opposite directions. However, since P_i has to be continuous (electrostatic coupling) we must have P_i pointing to the right for the odd-shaped region (*c*) and to the left for the surrounding region. This can only be obtained if the spontaneous polarization P_s reverses. Thus the *c*-domain has to reverse its polarization in the middle, there must be a 180° wall. This is exactly what we observe, the 180° wall is very easily visible because one side of it etches much faster than the other according to the arguments given in Sec. III. Thus the two sets of reflections are connected through the strong piezoeffect in $BaTiO_3$. This coupling, however, requires a 180° wall in the *c*-domain. It can be seen that it is not as strong as the direct head to tail coupling because the two sets of reflections do not quite look the same, whereas the direct coupling gives perfect mirror images. Even so, it seems very remarkable that such strong coupling can be obtained through a *c*-domain with the help of a strong piezoeffect and electrostatic forces.

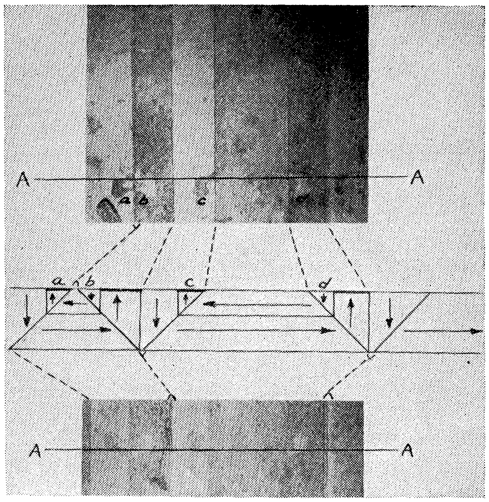

FIG. 5. Top and bottom view of a $BaTiO_3$ crystal showing domain reflections.

V. ETCH PATTERN OF TWINNED CRYSTALS

An interesting etch pattern of a twinned crystal is shown in Fig. 8. It shows a *c*-domain crystal containing

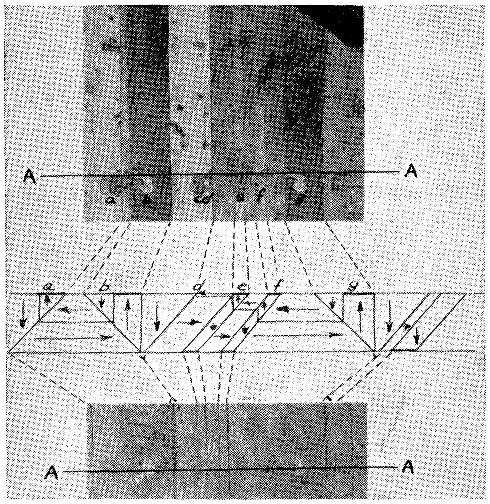

FIG. 6. Top and bottom view of a crystal showing a multiple domain reflection.

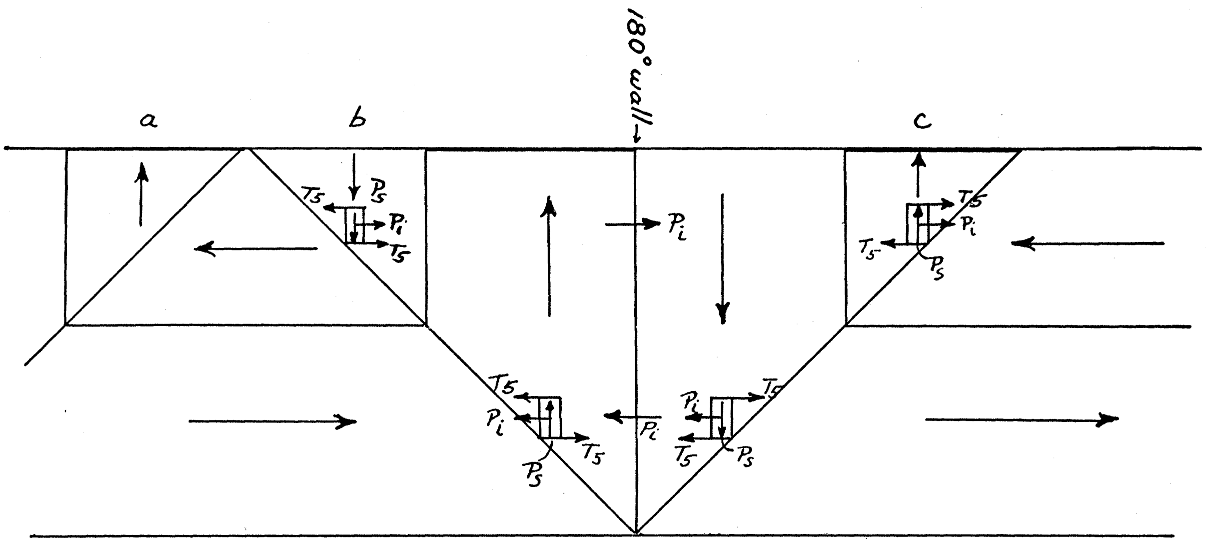

FIG. 7. Diagram illustrating the transverse coupling through a c-domain.

a few a-domains as can be seen very easily using transmitted polarized light [Fig. 8(b)]. The surface of the crystal, however, looks very different. It is shown in Fig. 8(a) using reflected light. The surface contains very many dark and bright lines which we call "channels." The picture looks very similar to Fig. 4 which was obtained optically by straining the crystal.[1] One is therefore tempted to believe that the etched crystal shown in Fig. 8 is a c-domain crystal with some a-domains, but covered with a layer of a-domain material at the surface. That is, it seems, that the polarization of the surface is parallel to the surface though the crystal is mostly a c-domain crystal. This surface polarization would be the electric analogue to the domains of closure in ferromagnetism.[2] However, we do not believe that the surface is polarized in a way different to the inside of the crystal because the mechanical strains would be very large and would increase the energy, though the electrostatic energy would be reduced. The etching experiment shows that the surface is not an a-domain because the etch is dark or bright and not greyish. Thus the surface is c-domain material and the dark and bright channels represent plate-like domains polarized upwards or downwards, respectively. Why are the antiparallel c-domains plate-like? The channels are the intersections of these plates with the surface. From Fig. 1 we know that in a poled c-domain crystal the antiparallel polarized islands are usually rounded and not long lines.

There are three interesting features in Fig. 8 which give us some insight into the domain pattern. First, there are a-domains present whereas in the case where we have rounded islands, as in Fig. 1, there are no a-domains. Actually there are more a-domains in this crystal than one observes in Fig. 8(b). All the sharp lines (actually they are double lines) on the surface [Fig. 8(a)] are the edges where a-domains intersect the surface. Only the thicker a-domains can be seen in transmitted light as the usual bright bands [Fig. 8(b)]. The thickness of the very thick a-domains can be measured directly by measuring the spacing of the double lines in Fig. 8(a) (center right, for example). The second feature is that the channels are always perpendicular to the aforementioned a-domain edges. If the channels coming from perpendicular sets of a-domains meet they try to join each other and form 45° lines. Third, the channels are more perfect (evenly spaced and parallel) the more a-domains we find in that particular region. Based on these 3 observations we propose that the channels, though they are c-domains, are caused by the a-domains. As a matter of fact, we have never observed channels on crystals where there were no a-domains and whenever we have a number of a-domains we can observe channels when the crystals are etched.

In order to understand the channels we assume a c-domain crystal with two widely-separated a-domains, as shown in Fig. 9(a). Since the two a-domains are far apart there will be no relation between their domain patterns. However, if the a-domains are closely spaced (overlap) as shown in Fig. 9(b) the following will happen. Let us assume that domain No. 1 consists of two parts, then only the lower part of domain No. 2 will be polarized to the left (head to tail coupling). But since the upper part of domain No. 1 is polarized to the left and since domain No. 2 is close to No. 1 we will find that also the upper part of No. 2 will be polarized to the left (heavy arrow) because of electrostatic forces. This is similar to the electrostatic coupling through a

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[2] Williams, Bozorth, and Shockley, Phys. Rev. 75, 155 (1949).

c-domain as explained in Fig. 7. Now, the whole *a*-domain No. 2 is polarized to the left and thus the region above and below it has to be polarized upwards (heavy arrows). The same argument can be made for domain No. 3. Thus the whole top surface is polarized upwards except the intercepts with the *a*-domains, which are polarized to the left. Figure 9(c) shows the crystal viewed from the top and shows the plate-like domain. The sign of polarization of these plates alternates. The dark and bright bands are planes polarized upwards or downwards, respectively. The width of these channels is of the order of 10^{-4} cm or smaller (near wavelength of light) which agrees very well with the values obtained in Figs. 3 and 4 before.[1] Following the arguments given in reference 1 [optimal width of nuclei and weak sidewise coupling] we conclude that the width of 10^{-4} cm is determined by the nucleation and growth of the new domains. Of course, if we use a dc-poled crystal we never find channels. We only find channels, as shown in Fig. 8, when the crystal is ac-poled in such a way that about half of the dipoles point in one direction and the other half in the opposite direction. In this case, the nucleation can determine the size. In order to find channel etch patterns, we have to use ac-poled crystals where there are *a*-domains which are closely spaced so that the electrostatic coupling through the *c*-domain is large. If the *a*-domains are widely spaced, the interaction is small and the channels lose their sharpness and spread out in a disordered way. If wedge-shaped *a*-domains are present, as in Fig. 5, the channel etch pattern cannot be obtained.

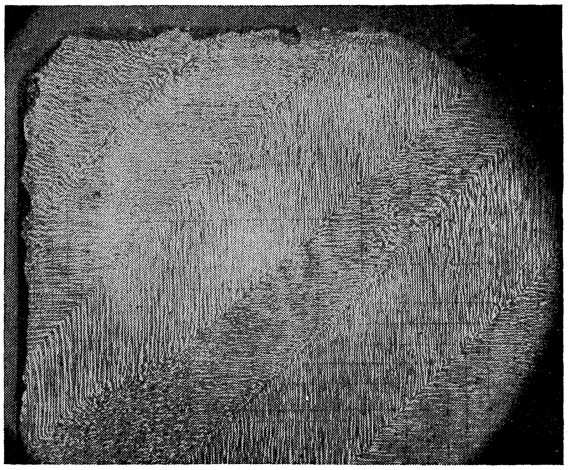

FIG. 8(a). Surface of a twinned BaTiO$_3$ crystal observed with reflected light.

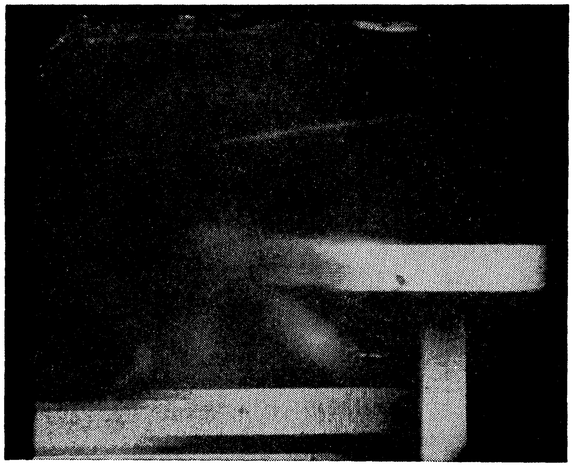

FIG. 8(b). Same crystal observed with transmitted polarized light.

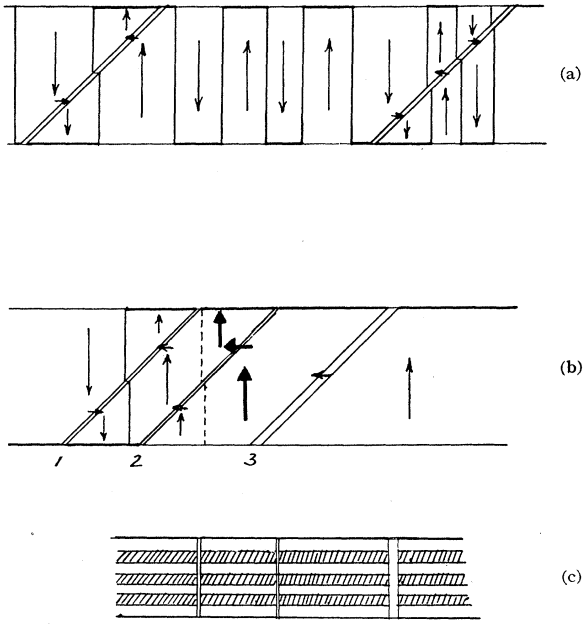

FIG. 9. Diagram illustrating the electrostatic coupling controlling the channel development.

VI. CONCLUSIONS AND ACKNOWLEDGMENTS

The etching technique, as described in the foregoing, is found to be a very useful tool for the investigation of the dipoles and domains in ferroelectric BaTiO$_3$ crystals. All the results obtained with optical methods can be verified and often clarified. The existence of the very strong forward coupling of the dipoles has been clearly demonstrated.

We would like to thank the following people who helped us on one or another stage of our work. Many problems were discussed with P. W. Anderson, S. S. Flaschen, and Mrs. E. A. Woods. E. M. Kelly, J. P. Remeika, and E. M. Walters helped us with the preparation of the samples.

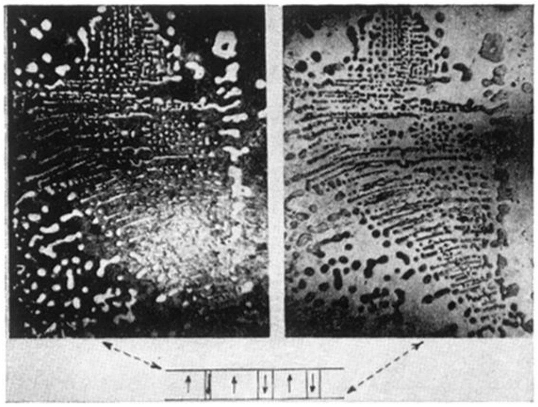

FIG. 1. Photograph of top and bottom of a poorly poled $BaTiO_3$ crystal showing many antiparallel polarized domains. Notice the perfect mirror image. (One print is reversed.)

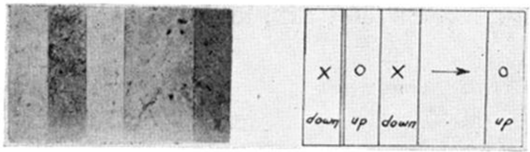

FIG. 2. Surface appearance of etch response of differently polarized regions.

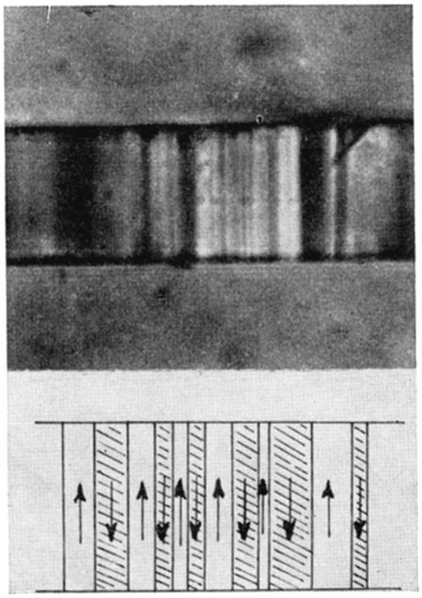

FIG. 3. Edge of a c-domain crystal of $BaTiO_3$ showing antiparallel domains obtained by stressing.

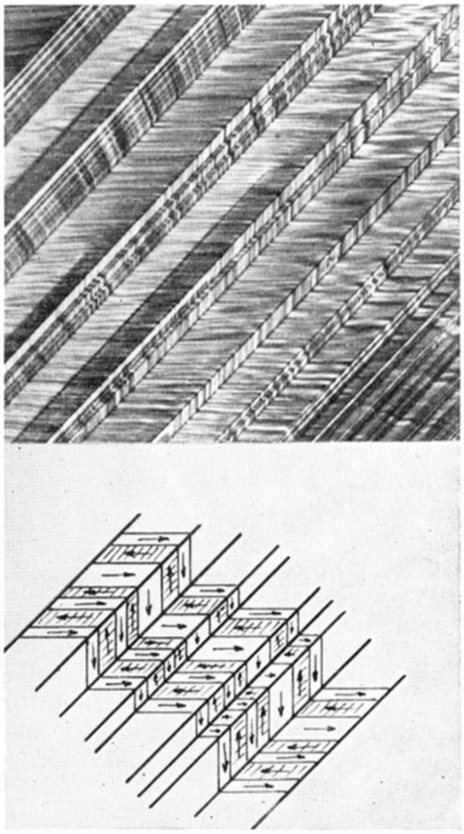

FIG. 4. Surface of an *a*-domain crystal showing 90° walls and antiparallel domains.

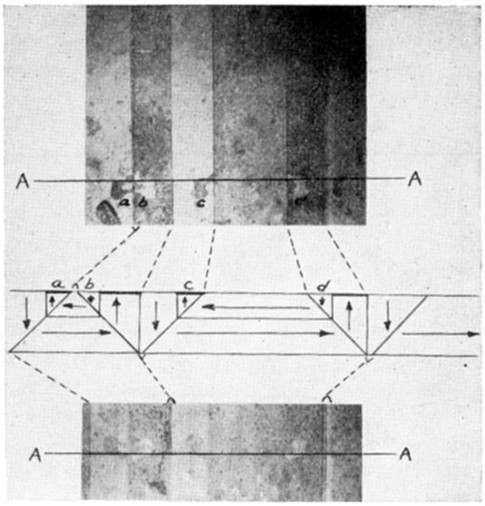

FIG. 5. Top and bottom view of a $BaTiO_3$ crystal showing domain reflections.

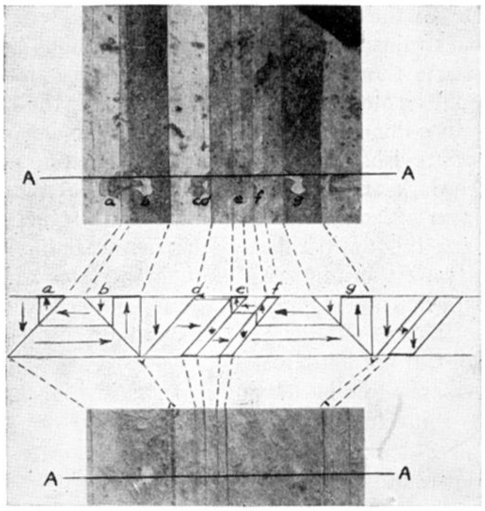

FIG. 6. Top and bottom view of a crystal showing a multiple domain reflection.

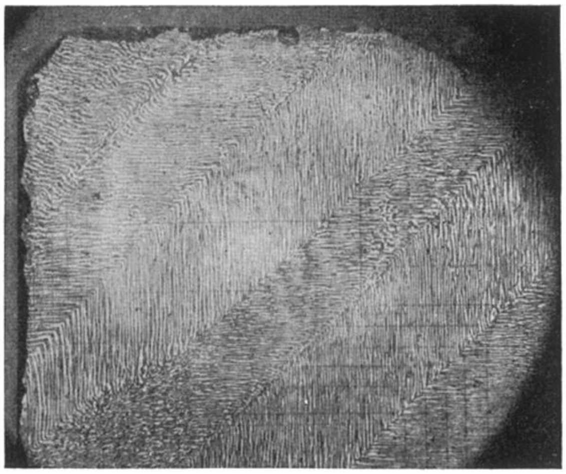

FIG. 8(a). Surface of a twinned $BaTiO_3$ crystal observed with reflected light.

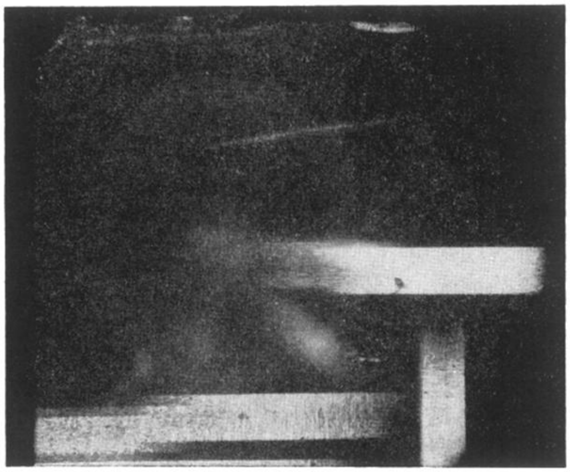

FIG. 8(b). Same crystal observed with transmitted polarized light.