Symmetry of the Low-Temperature Phase of Barium Titanate*

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In order to find the crystal symmetry of $BaTiO_3$ below $-80°C$, the domain patterns and optical properties were examined using thin (111) plates specially prepared for this purpose. Four kinds of domains have been differentiated; these domains are optically uniaxial. The crystal symmetry proved to be rhombohedral. The effect of a dc field on the domain configuration was studied. Explanations were given for the strange dielectric and optical behavior which had been thought paradoxical.

INTRODUCTION

BARIUM titanate exhibits three well-known phase transitions[1,2] when the temperature is changed. Above 120°C the crystal is cubic without a spontaneous polarization. Below 120°C, the symmetry changes to tetragonal and a spontaneous polarization appears along the *c*-axis direction. Below 0°C, the symmetry is orthorhombic with the spontaneous polarization along one of the face diagonal directions, [110], of the original cubic perovskite lattice.

Below $-80°C$ a fourth phase appears. The symmetry seemed to be rhombohedral; however, previously no conclusive evidence was found. There are several experimental facts which suggest rhombohedral symmetry, while some experimental results suggest a lower symmetry. X-ray studies of the low-temperature phase by Kay and Vousden,[1] and Jona and Pepinsky[3] show that the lattice spacings along the original cubic axes are equal and the cubic faces are sheared through a small angle. This result strongly suggests that the symmetry is rhombohedral with $a=4.001$ A and $\alpha=89°51'$. Furthermore, optical studies of extinction positions support this suggestion. Devonshire's phenomenological theory of ferroelectricity[4] also predicts that the symmetry of the low-temperature phase should be rhombohedral.

On the other hand, as pointed out by Jona and Pepinsky,[3] there are several experimental facts which question the existence of rhombohedral symmetry in barium titanate. For example, the dielectric constants observed by Merz[5] on two (100) plates of $BaTiO_3$ were remarkably different below $-80°C$. The dielectric constant observed by Jona and Pepinsky[3] below $-80°C$, before and after annealing at 250°C, showed a considerable variance. It is difficult to explain this observed fact if one assumes the crystal symmetry is rhombohedral; because, if the crystal has rhombohedral symmetry and the domain interactions are very small, the dielectric constant observed in any (100) plate should not vary. The effect of a dc electric field on the optical properties of a (100) plate was examined by Jona and Pepinsky.[3] Again, the suggestion was that rhombohedral symmetry is unlikely below $-80°C$. By taking into account the many experimental results, Jona and Pepinsky suggest that the crystal below $-80°C$ has possibly monoclinic or triclinic symmetry.

The symmetry of $BaTiO_3$ can be determined by several methods. (1) A very precise analysis of the crystal structure by neutron diffraction below $-80°C$ could be used to find the crystal symmetry, as pointed out by Jona and Pepinsky. (2) Using single crystals, the direction of spontaneous polarization could be found by observing the hysteresis loop in various crystallographic directions. The direction showing maximum polarization is the direction of spontaneous polarization. From this the symmetry of the crystal could be determined. (3) If the optical properties of single crystals are precisely examined below $-80°C$, the crystal symmetry can be determined. Further, the symmetry may be confirmed by an examination of the effect of an electric field on the domain configuration.

One must use specially prepared single crystals to perform these experiments. Consider the first method. In order to obtain neutron diffraction data which can be used for precise structural analysis, one must use a large single domain crystal below $-80°C$. It is very difficult to prepare such a single domain crystal and keep it below $-80°C$ for the long times required for neutron diffraction experiments.

The second method preferably requires a large single crystal. At present, it seems impossible to prepare large plates of single crystals whose major surfaces are specific crystallographic planes. The only exception is the (100) surface. This is because the (100) surface grows naturally from the KF melt.[6] If small single crystals are used it is impossible to obtain reliable data because of the large experimental errors.

Fortunately very small crystals are satisfactory for the third method. This method was employed and was successful in determining the crystal symmetry below $-80°C$. The symmetry was found to be rhombohedral.

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[1] H. F. Kay and P. Vousden, Phil. Mag. **40**, 1019 (1949).
[2] For the phase transitions of $BaTiO_3$, see for example; Shirane, Jona, and Pepinsky, Proc. Inst. Radio Engrs. **43**, 1738–1793 (1955).
[3] F. Jona and R. Pepinsky, Phys. Rev. **105**, 861 (1957).
[4] A. F. Devenshire, Phil. Mag. **40**, 1040 (1949).
[5] W. J. Merz, Phys. Rev. **76**, 1221 (1949).
[6] J. P. Remeika, J. Am. Chem. Soc. **76**, 940 (1954).

PREPARATION OF (111) PLATE

Very small thin sections having (111) major surfaces were prepared for the low-temperature optical studies. Usually $BaTiO_3$ single crystals grown from KF or $BaCl_2$ melt are thin plates or small cubes with (100) exposed surfaces. To prepare a (111) plate, a thin single crystal grown from a KF melt was first sealed between two glass microscope slides with glycol pthalate. It was then ground and polished so that a (111) face became the exposed surface. Next the crystal was removed from the glass plates and resealed between new plates. The second (111) face, which is the reverse side of the former (111) face, was prepared in the same manner. During the grinding and polishing operations the crystal was frequently examined under the microscope, to verify that the polished surface did not deviate from (111) or the crystal did not become too thin. The specimen thus obtained was $3.7 \times 0.20 \times 0.029\ mm^3$, with the longitudinal edge parallel to the $[\bar{1}10]$ direction. The reference is the cubic perovskite lattice and all indices given are referred to it.

DOMAIN OBSERVATION ON (111) PLATE

The specimen was placed in a low-temperature optical stage so that the longitudinal direction, $[\bar{1}10]$, is parallel to the polarization direction of the incident light. The low-temperature stage is similar to that originally designed by Pepinsky *et al.*[7] A major difference is that the lower window, through which incident light comes, is made large enough so that by tilting the stage the specimen can be inclined with respect to the microscope axis from zero to approximately 30 degrees. Figure 1(a) is the tetragonal phase observed with crossed nicols. The direction of the tetragonal *c*-axis in each domain is inclined to the surface of the specimen (111) by 35.3 degrees. Two kinds of domains are seen running to the edge of the specimen at an angle of 30 or 60 degrees. Several specimens showed another type of domain boundaries which were either perpendicular or parallel to the edge of the specimen. All of these boundaries are the so-called 90 degree domain walls commonly observed in the (100) single crystal. In the orthorhombic phase, Fig. 1(b), or in the third ferroelectric phase which exists below −80°C, Fig. 1(c), the crystal consisted of many small complex domains. Analysis of these domain configurations could not be performed. It is very probable that some mechanical stress, induced in the surface during polishing, still remains. The residual stress is probably what makes the domain configuration so complex.

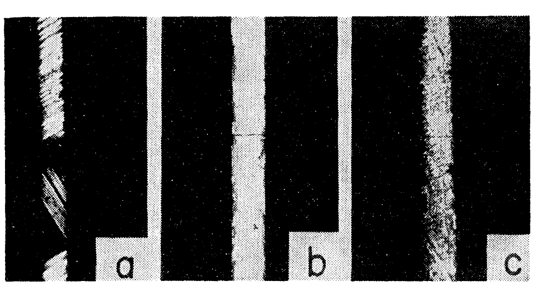

FIG. 1. Domain structure of $BaTiO_3$ observed in (111) plate. (a) Tetragonal phase; (b) orthorhombic phase; (c) below −80°C. The directions of the crossed nicol are horizontal and vertical in the photograph.

[7] R. Pepinsky *et al.* (private communication).

The specimen was etched in H_3PO_4 at about 150°C for three minutes to remove any residual surface stresses. After etching, the surface of the crystal appeared rather rough under natural light; however, the domain configuration turned out to be much simpler. The domain patterns observed below −80°C are shown in Fig. 2. When the edge of the specimen was parallel to one of the crossed nicol directions, several areas of the specimen showed extinction; $[\bar{1}\bar{1}1]$ domains of Fig. 2(a). When the crystal was rotated 30° about the microscope axis, other parts were in the extinction position; $[1\bar{1}\bar{1}]$ domains of Fig. 2(b). A further rotation of 30° made the remaining domains dark; $[\bar{1}1\bar{1}]$ domains of Fig. 2(c). An important fact is that one region, which is designated as a [111] domain, *always remains dark even though it is rotated about* $c-c'$.

If it is assumed that each domain has rhombohedral crystal symmetry, these observations can be easily explained. The threefold symmetry axis in each domain should be in one of the ⟨111⟩ directions. This axis should also be an uniaxial optical axis. Now, it is desirable to examine if the above assumption is correct. This can be done if the optical symmetry of the crystal is determined.

If the direction of the spontaneous polarization deviates from the [111], then the [111] direction could never be an axis of uniaxial symmetry. Tegragonal symmetry is impossible because the crystal lattice deforms[1,3] in the [111] direction. Therefore, if it can be proved that the crystal is optically uniaxial, then

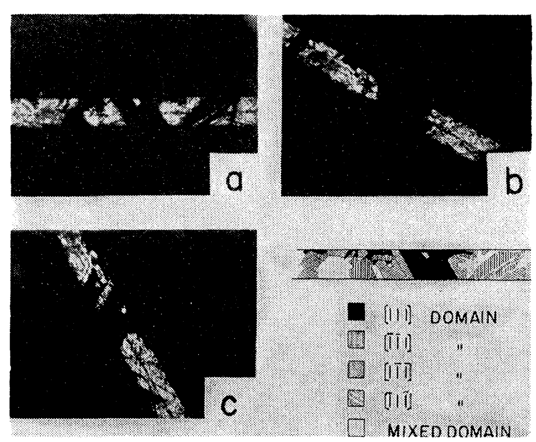

FIG. 2. The domain pattern of (111) plate observed below −80°C. Crossed nicol directions are horizontal and vertical in the photograph. Notice that the [111] domain is always dark.

the only possibility is rhombohedral symmetry, with the spontaneous polarization in the [111] direction.

Examination of the birefringence figure is one of the best methods of discriminating between uniaxial and biaxial symmetry. However, it was impossible to observe because the specimen was very small and the low-temperature stage did not permit strongly convergent light to enter the specimen. An alternate method, schematically shown in Fig. 3, was attempted. The low-temperature stage, including the specimen, was tilted, by an angle θ ($\theta = 5° \sim 30°$), with respect to the microscope axis. The stage can be rotated about its axis, $c-c'$, while the $c-c'$ axis remains fixed relative to the microscope axis. A gypsum test plate was used with the polarizing microscope to increase the sensitivity. If the c-domain has uniaxial symmetry, its interference colors must not change as the specimen is rotated about the axis $c-c'$. If the color does change, the crystal must be biaxial. At several fixed positions of θ, namely 5°, 10°, and 20°, the specimen was rotated about the stage axis, $c-c'$, while the interference colors were observed. No appreciable change was detected in the interference colors. Therefore, the crystal is undoubtedly uniaxial and should be rhombohedral. The interference color also shows that the crystal is optically negative, the same as the tetragonal phase at room temperature.

EFFECT OF dc FIELD ON THE DOMAIN STRUCTURE

The (111) plate was placed between two thin platinum electrodes. The small air gaps between the specimen and the electrodes were filled with ethyl alcohol so that the voltage drop would be across the specimen and not the air gap. As shown in Fig. 4(b), the specimen consisted of various kinds of domains before the application of a dc field. After applying a dc field of 5 kv/cm [Fig. 4(c)], nearly all the domains were converted to a single domain. When the field was further increased to 10 kv/cm, the entire specimen became a single domain. This corresponds to the $[\bar{1}\bar{1}1]$ domain of Fig. 2. These observations support the assumption that the spontaneous polarization lies in one of the ⟨111⟩ directions.

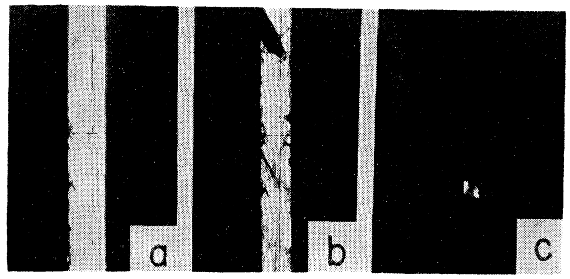

FIG. 4. Effect of an electric field on the domain structure of $(11\underline{1})$ plate below $-80°C$. The direction of the electric field is $[11\bar{2}]$. (a) Observed with natural light; (b) with crossed nicols and no electric field; (c) with crossed nicols and dc field of 5 kv/cm.

Next the effects of a dc field on a (100) plate were examined below $-80°C$. The applied field and the optical observations were both in the [001] direction. Transparent electrodes were thus needed to apply the field. A conducting liquid of ethyl alcohol containing a little H_3PO_4 was used for this purpose.

First the specimen is placed at a maximum extinction. This occurs when the [110] direction is parallel to one of the crossed nicol prisms. Though most areas show complete extinction, some do not, see Fig. 5(a). When a dc field of about 10 kv/cm was applied some areas became brighter and some became darker [Fig. 5(b)]. Jona and Pepinsky,[3] in a similar experiment, also found that the microscope field became brighter when an electric field was applied. It seemed difficult to explain such behavior in the light of the previous experimental evidence; for if the crystal symmetry is rhombohedral, then, in the experimental arrangement mentioned above, the crystal ought to show complete extinction whether or not an electric field is applied. The strange behavior was explained by assuming that light is reflected or refracted at the domain boundaries. If a specimen consists of many minute domains, then

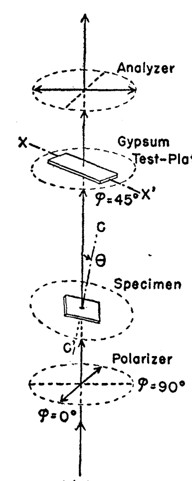

FIG. 3. A method for discriminating between uniaxial and biaxial symmetry. The specimen can be rotated around $c-c'$ which is one of the optical axes of the specimen. Any inclination of the axis, $c-c'$, ($30° > \theta > 0°$ and $360° > \varphi > 0°$) with respect to the microscope axis may be used, but the direction of the $c-c'$ should not be changed when the specimen is rotated. The optical symmetry can be discriminated by examining whether or not the birefringence colors are changed by such rotation.

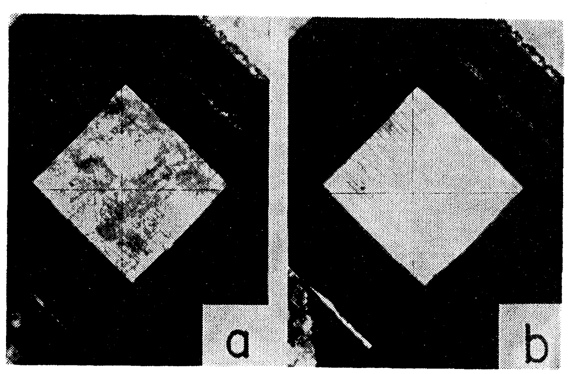

FIG. 5. Effect of dc field on a (100) plate of $BaTiO_3$ below $-80°C$. (a) Without field; (b) with a field of 10 kv/cm. For the optical observation, a square hole is made on the silver electrode, and is filled with a transparent conductive liquid.

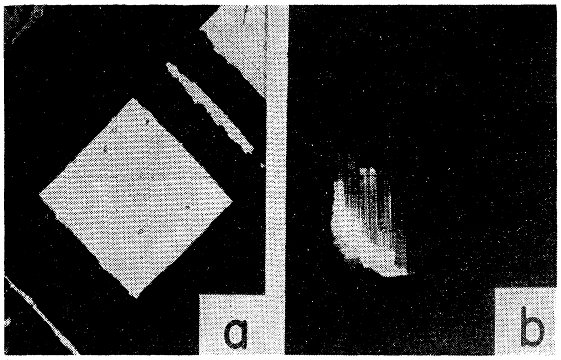

FIG. 6. Influence of complex domain boundaries in the tetragonal phase on the extinction of polarized light. (a) [110] is parallel to a crossed nicol direction; (b) [100] is parallel to a crossed nicol direction (extinction position).

incident light should be reflected or refracted at the various boundaries. This effect should disturb the ideal interference of polarized light and ideal extinction would not occur. The observed result shown in Fig. 5 is now quite reasonable if one remembers that the specimen contained many minute domains and a dc field should move the domain boundaries. A similar experiment was performed at room temperature, where the crystal is tetragonal, to verify the previously mentioned hypothesis. One part of the specimen contained many small domains, this region was very bright [see Fig. 6(b)]. When a dc field of 1 kv/cm was applied, the specimen was converted entirely to a c-domain. All the domain boundaries and the bright areas suddenly disappeared, no figure is given since the entire area was black.

DIELECTRIC CONSTANT OF THE RHOMBOHEDRAL PHASE

It has long been pointed out that the dielectric constant observed below $-80°C$ does not remain constant from observation to observation. Merz[5] measured the dielectric constant as a function of temperature using two (100) plates of the single crystal. One was an a-domain plate and the other was a c-domain plate at room temperature (tetragonal phase). He found that the two dielectric constants were quite different below $-80°C$. Jona and Pepinsky[3] found that the dielectric constant of a multidomain (100) plate below $-80°C$ was changed considerably after the crystal was annealed at 250°C. These facts do not seem to be consistent with rhombohedral symmetry. The dielectric constant of any rhombohedral crystal should be the same when observed in any one of the [100], [010], or [001] directions. It is possible to show that the observed facts are not inconsistent with rhombohedral symmetry if one considers the effect of the domain configuration in the crystal.

In Devonshire's theory of barium titanate,[4] he obtained the susceptibility, η', piezoelectric coefficient d, and elastic compliance coefficient, s^E, as a function of temperature. These quantities are defined by the following equations:

$$\Delta x_h = -\sum_{i=1}^{6} s_{hi}{}^E X_i + \sum_{m=1}^{3} d_{mh} E_m, \qquad h=1,2,3,\cdots 6,$$
$$\Delta P_m = -\sum_{h=1}^{6} d_{mh} X_h + \sum_{k=1}^{3} \eta_{km}' E_k, \qquad m=1,2,3. \tag{1}$$

where Δx's are changes in strain and ΔP's are changes in polarization; Voigt's notation is used for the tensor matrices. Suppose a weak ac field, E_3 $(=E_z)$, is applied in the [001] direction. In the rhombohedral crystal, not only a polarization ΔP_z but also x and y components of the polarization, ΔP_x and ΔP_y will be induced by E_3. For an audio or radio frequency field, which is commonly used for the measurement of the dielectric constant, very little electric charge flows through the crystal by conduction during one cycle. Therefore the change of the dielectric displacement, ΔD_x and ΔD_y, can be negligibly small,

$$\Delta D_x = E_1 + 4\pi \Delta P_1 = 0,$$
$$\Delta D_y = E_2 + 4\pi \Delta P_2 = 0. \tag{2}$$

The dielectric constant is defined by,

$$\epsilon = \partial D_3 / \partial E_3. \tag{3}$$

The following three cases are considered in calculating ϵ from Eqs. (1) and (3).

1. $X_1 = X_2 = X_3 \cdots X_6 = 0$; this is the ideal case where no external stress exists. Under this condition, the free dielectric constant is obtained. If the (100) plate is a single domain crystal and the frequency of the ac field is much lower than the resonant frequency of the plate, then this condition is physically realizable.

2. $x_1 = x_2 = x_3 = \cdots x_6 = 0$; when the ac field frequency is very much higher than the resonant frequency of the plate, then almost no piezoelectric strain can occur. Under these circumstances the above condition should hold. Even when the field frequency is less than the resonant frequency, the above condition may hold approximately if the crystal plate contains a large number of 180° domain boundaries. Since the sense of the piezoelectric strain due to the applied voltage in one domain is quite opposite to that of the neighboring domain, nearly no strains could occur in either domain. A clamped dielectric constant is obtained in this case.

3. $X_1 = X_2 = X_3 = 0$ and $x_4 = x_5 = x_6 = 0$; suppose all the domains have their spontaneous polarization in either of the [111], [$\bar{1}\bar{1}$1], [$\bar{1}$11], or [1$\bar{1}$1] directions. For these domains, the strain components x_1, x_2, and x_3 induced by E_3 are the same. Approximately speaking, even if the four kinds of domains are distributed at random, the strains x_1, x_2, and x_3, produced by E_3 are not impeded. We may approximate this condition by $X_1 = X_2 = X_3 = 0$ with fair accuracy. The strain components x_4, x_5, and x_6 have opposite tendencies (that is, the shears in adjacent domains tend to move

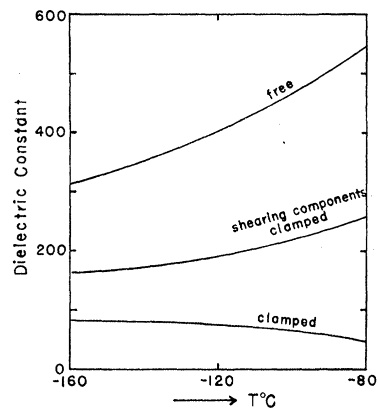

FIG. 7. Calculated dielectric constant of $BaTiO_3$ single crystal below $-80°C$.

in opposite directions) for certain combinations of the four domains. In this case the shearing strain must be very small since the domain cannot shear freely. Let us approximate this by the condition $x_4=x_5=x_6=0$. Roughly speaking, this condition may be realized after an intense dc field is applied to a (100) plate in order to rearrange the domain configuration. A partially clamped dielectric constant is obtained in this case.

The calculated results are shown in Fig. 7. η', d, and s^E were estimated from Figs. 1, 2, and 3 of Devonshire's paper.[8] As seen in Fig. 7, the three dielectric constants are quite different. This clearly indicates that the observed dielectric constant depends very much on the domain configuration in the crystal. There is no wonder that the dielectric constant varies from case to case, since the domain configuration may not be the same every time.

[8] A. F. Devonshire, Phil. Mag. **42**, 1065 (1951). The d_{33} value of Fig. 1, of Devonshire's paper, should be about doubled if the η', d, and s^E values appearing in his paper are to be consistent. The corrected value of d_{33} was used.

CONCLUSION

1. Four kinds of domains, shown in Fig. 2, were differentiated below $-80°C$ in a (111) barium titanate plate. This is consistent with the assumed rhombohedral symmetry of barium titanate.

2. Optical observations made on the [111] domains proved that the crystal is uniaxial. This result gives conclusive evidence that the symmetry is rhombohedral.

3. The effects of an electric field on the domain structure were examined. A puzzling optical behavior, which has been known for several years, was explained by a disturbance of the incident light at various domain boundaries.

4. It was shown that the observed dielectric constant could be very dependent on the domain configuration in the crystal. This explained the fact that the dielectric constant was not the same from observation to observation.

ACKNOWLEDGMENTS

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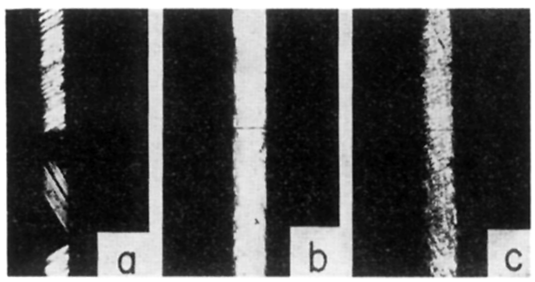


FIG. 1. Domain structure of $BaTiO_3$ observed in (111) plate. (a) Tetragonal phase; (b) orthorhombic phase; (c) below $-80°C$. The directions of the crossed nicol are horizontal and vertical in the photograph.

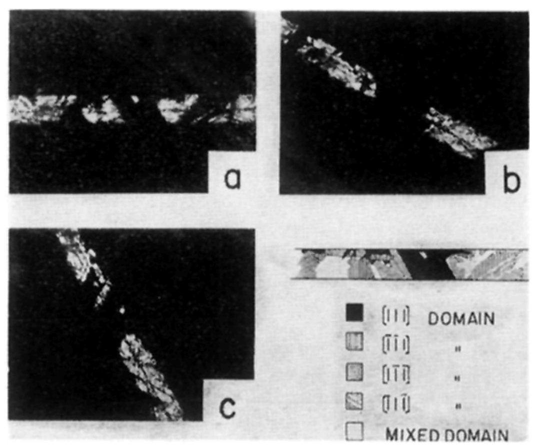


FIG. 2. The domain pattern of (111) plate observed below −80°C. Crossed nicol directions are horizontal and vertical in the photograph. Notice that the [111] domain is always dark.

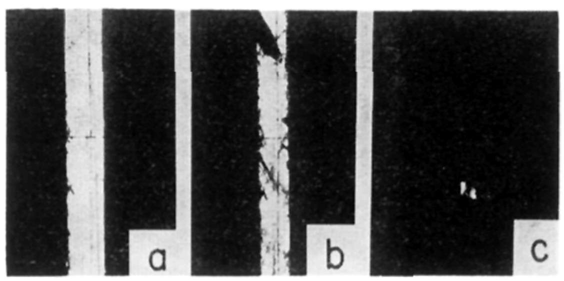


FIG. 4. Effect of an electric field on the domain structure of (11$\bar{1}$) plate below $-80°C$. The direction of the electric field is [11$\bar{2}$]. (a) Observed with natural light; (b) with crossed nicols and no electric field; (c) with crossed nicols and dc field of 5 kv/cm.

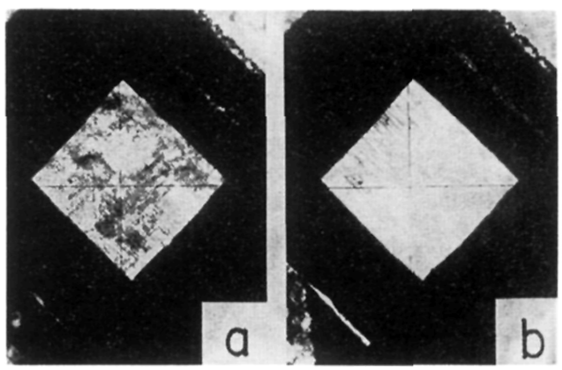
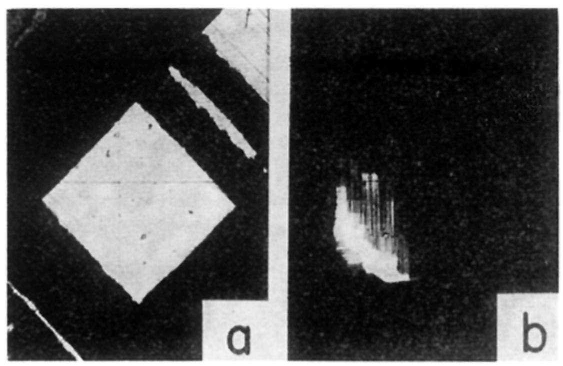


FIG. 5. Effect of dc field on a (100) plate of $BaTiO_3$ below $-80°C$. (a) Without field; (b) with a field of 10 kv/cm. For the optical observation, a square hole is made on the silver electrode, and is filled with a transparent conductive liquid.



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