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Domain Structure and Dielectric Response of Barium Titanate Single Crystals*

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Single crystals of $BaTiO_3$ have been grown and investigated by means of the polarization microscope, x-ray diffraction, and their dielectric and piezoelectric response. It has become possible to see the domains in the ferroelectric state and to change their number, size, and orientation. Wall displacements and the alignment of such domains, for which well-known indirect evidence exists in the case of ferromagnetics, have been observed in both polarized and unpolarized light, and the influence of temperature and electric fields on the domain structure and orientation of the polar axis have been investigated. In addition to the Curie point near 120°C, there exist two polymorphic transitions near 5°C and −70°C. A tentative explanation for the development of the ferroelectric state is given which brings the new ferroelectric group of the titanates into close relation to those of the tartrates and phosphates.

1. INTRODUCTION

INVESTIGATIONS on titania ceramics have made it seem probable that $BaTiO_3$ and solid solutions of barium-strontium and barium-lead titanates represent a new class of ferroelectric materials.[1–3] Ferroelectrics, the electric analogs of ferromagnetics, were previously discovered among the tartrates and the dihydrogenphosphates.[4] An accurate study of the titanates necessitated proceeding from multicrystalline materials to studies on single crystals.

A first attempt to grow single crystals of $BaTiO_3$ in an arc furnace proved unsuccessful.[1] Crystals of hexagonal, cubic, and monoclinic symmetry, however, were obtained in Switzerland by Blattner, Matthias, Merz, and Scherrer from ternary melts.[5, 6] Their method was taken up in this laboratory and further improved. An accurate chemical analysis of the hexagonal modification in Zürich[5] and of the cubic one here[7] established that both correspond to the composition $BaTiO_3$. Only the latter type is ferroelectric and is identical with the cubic modification identified previously in ceramics.[1, 8]

Since then these cubic crystals have been investigated in detail. Dielectric constant and


FIG. 1. Cubic $BaTiO_3$ crystal.


FIG. 2. Crystal type 1 (45° stripes).

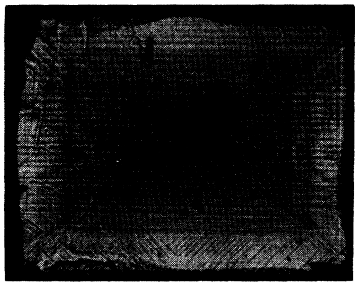
FIG. 3. Crystal type 2 (stripes parallel to one cube edge).

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[1] A. von Hippel and coworkers, NDRC Reports 14–300 (1944), 14–540 (1945); A. von Hippel, R. G. Breckenridge, F. G. Chesley, and L. Tisza, J. Ind. Eng. Chem. **38**, 1097 (1946).

[2] B. M. Wul, J. Phys. USSR. **10**, 95 (1946); *ibid.*, Nature **157**, 808 (1946).

[3] S. Roberts, Phys. Rev. **71**, 890 (1947).

[4] G. Busch, Helv. Phys. Acta **11**, 269 (1938).

[5] H. Blattner, B. Matthias and W. Merz, Helv. Phys. Acta **20**, 225 (1947).

[6] H. Blattner, B. Matthias, W. Merz, and P. Scherrer, Experientia **3**, 4 (1947).

[7] B. Matthias, R. B. Breckenridge, and D. W. Beaumont Phys. Rev. **72**, 532 (1947).

[8] H. D. Megaw, Proc. Roy. Soc. London **A189**, 261 (1947).

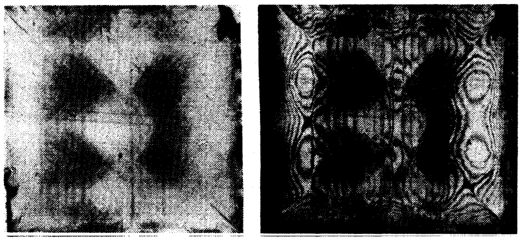
A B

FIG. 4. Crystal type 3. (A) Natural light. (B) Polarized light.

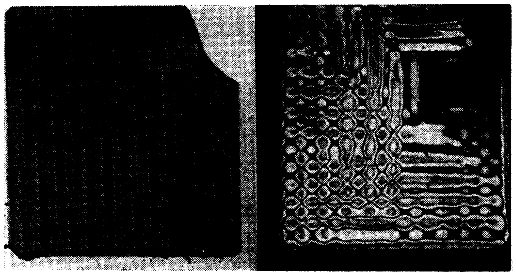
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FIG. 5. Crystal type 4. (A) Natural light. (B) Polarized light.

loss, and piezoelectric effect have been measured as a function of temperature, crystallographic orientation, and biasing voltage. It has also become possible to follow the formation of ferroelectric domains and to observe their orientation, growth, and decay under various field and temperature conditions.[9] The present paper summarizes our experiments and draws qualitative conclusions as to the mechanism of ferroelectric polarization and its action in ceramic materials.

2. APPEARANCE OF THE BARIUM TITANATE CRYSTALS

Figure 1 shows a crystal of the cubic modification. The hexagonal and monoclinic ones have not yet been studied in detail. The crystals are usually obtained in the form of flat plates. Growing conditions and discoloration have been discussed previously.[7, 9]

A microscopic inspection reveals that the plates exhibit a great variety of structures. To describe them, it will be convenient to refer to four groups of patterns which either alone or combined have been found in all crystals observed thus far.

(1) The crystal may be divided into regions shaded by fine parallel lines, oriented at an angle of 45° to the cube edges (Fig. 2). The lines are sometimes so closely spaced as to blur the transparency of the crystal. Observed between crossed Nicols, the crystal shows parallel extinction except in regions of great strain.

(2) The crystal may have stripes of varying widths parallel to one cube edge. Between crossed Nicols such a crystal shows parallel extinction and is, in intermediate positions, white or faintly colored (Fig. 3).

(3) The crystal appears transparent with a very slight indication of faint lines parallel to the cube edges, spaced rather widely from each other. Between crossed Nicols, strong colors are seen which give the appearance of birefringent or of photo-elastic strain patterns. They are divided by black lines and regions which show a centered uniaxial interference figure. These black regions are free from striation and strains (Fig. 4).

(4) The crystal is transparent in natural light. Between crossed Nicols, however, it shows an extremely regular square net pattern (Fig. 5).

3. EFFECT OF TEMPERATURE

Measurements on the barium titanate ceramics have established that $BaTiO_3$ goes through three transitions between approximately 120°C and liquid-air temperature.[1, 2] With decreasing temperature the lattice changes near 120°C from cubic to pseudo-cubic; this is the "Curie point" of the material at which temperature the dipoles seem to line up spontaneously and thus ferroelectricity develops. In addition, there exist

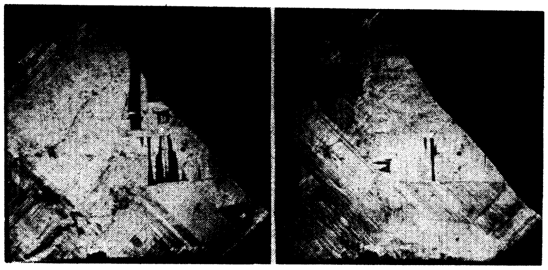
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FIG. 6. (A) Initial pattern at 25°C. (B) The same crystal at 25°C after heating above Curie point.

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[9] B. Matthias and A. von Hippel, Phys. Rev. **73**, 268 (1948).

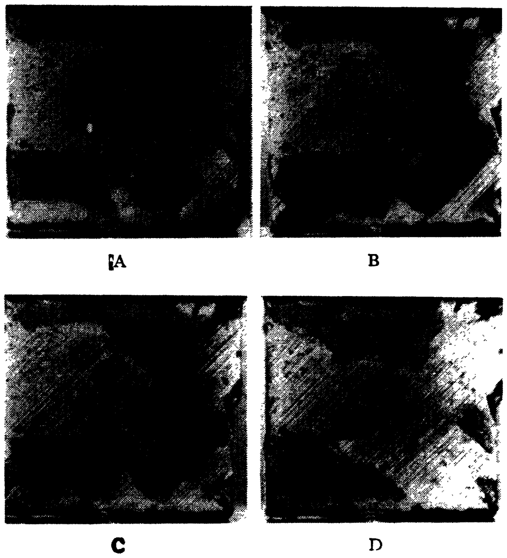
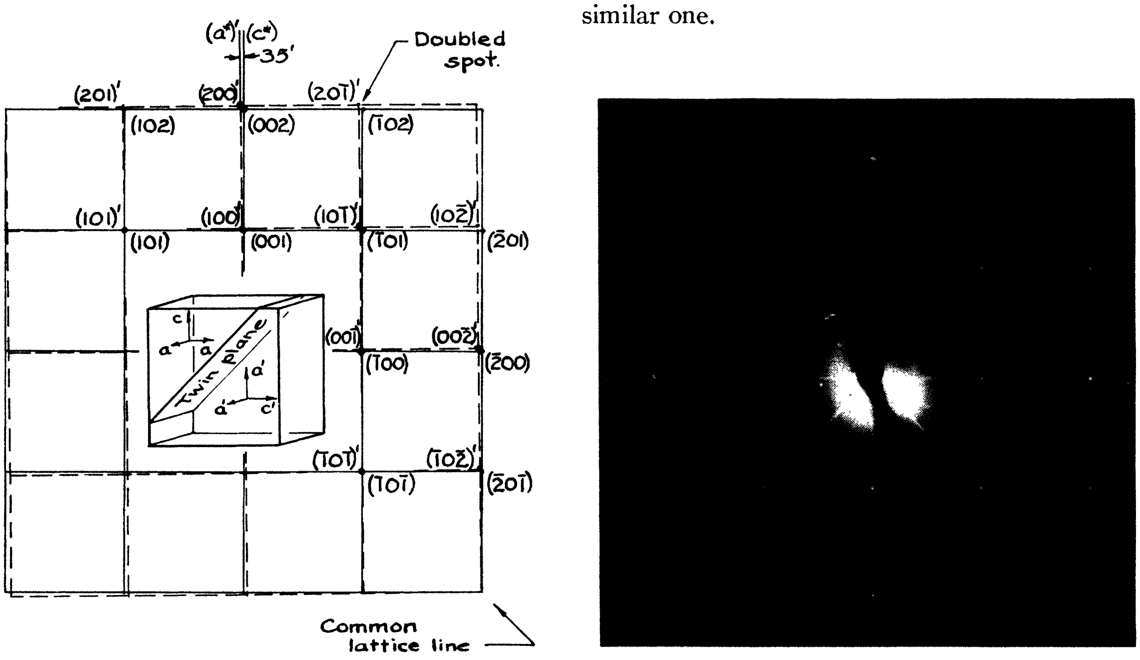


FIG. 7. Effect of electric field on domain structure of $BaTiO_3$ crystal. (A) No field applied. (B) +2000 volts/cm. (C) Field removed. (D) −2000 volts/cm.

regions of anomalous dielectric response near 5°C and −70°C, which become pronounced in the ceramics at higher field strength.

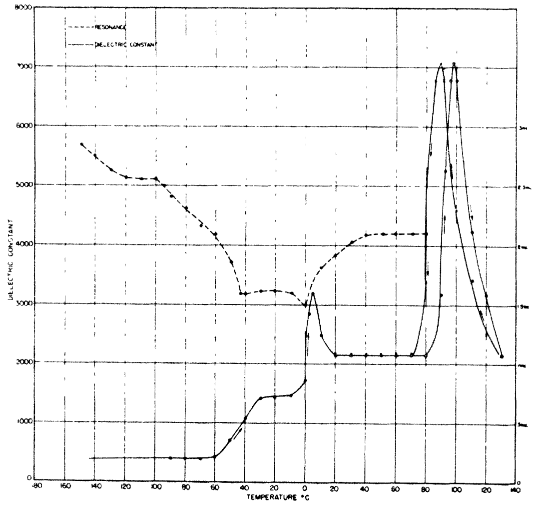
In observing single crystals on a heating stage, it was found that with rising temperature near the Curie point the 45° stripes and the broad parallel bands disappear; the plates become completely clear and isotropic. *Vice versa*, in lowering the temperature into the ferroelectric region, first the widely spaced bands begin to subdivide the field of view, next the shading by 45° stripes develops and a pattern builds up which is more or less different from the original one (Fig. 6).

Lowering the temperature through the second and third transition regions does not affect the ferroelectric state as such, but rather the position of the optical axis. Near 5°C this axis seems to rotate by 90°; simultaneously, crystals consisting of a single domain which previously showed a uniaxial interference figure, become strongly birefringent. This might be due either to a rotation of the optical axis, or to a reduction of crystal symmetry. Passing below the third transition point near −70°C seems partly to reverse this effect. The transitions may proceed rather gradually, starting at one corner and propagating throughout the crystal; sometimes they appear delayed, and sometimes they are extremely sluggish. Returning from any of these transitions to room temperature, one obtains, in general, not exactly the initial pattern, but a similar one.

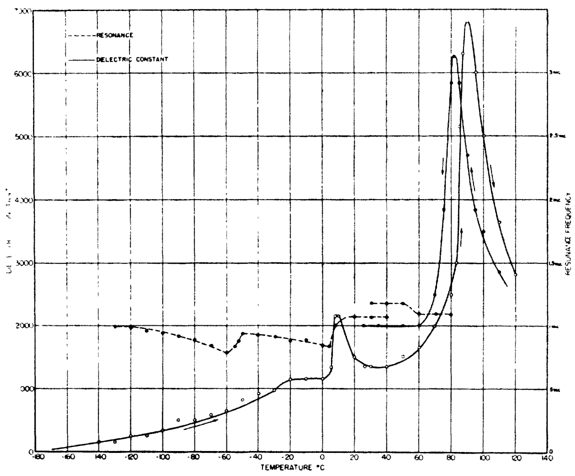


A B

FIG. 8. Precession photograph of a two-domain crystal.



(100)



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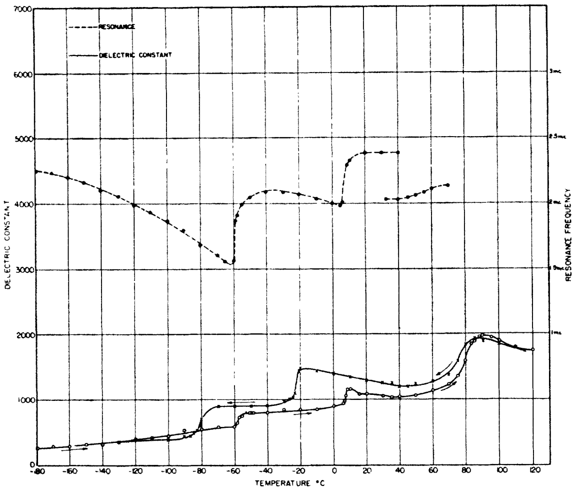

(001)

FIG. 9. Dielectric constant and piezoelectric resonance of $BaTiO_3$ single crystal in its three axis directions. (Curie point lowered by impurities.)

These observations make one already suspect that the patterns are a visual expression of domain structures which develop in the ferroelectric crystals by the aligning of dipole groups in various directions. The action of electric fields on these structures leads to a closer correlation.

4. EFFECT OF ELECTRIC FIELDS

Figure 7 shows in sequence: the initial pattern of a crystal at room temperature, the effect of a d.c. field, the crystal after removal of the field, and finally the structure with the voltage reversed. One observes clearly how areas grow or contract, how sections of new shading suddenly appear, and how disconnecting the voltage leaves a remanent state which requires a counter voltage for removal.

Closer inspection in polarized light with the field parallel or perpendicular to the crystal plate leads to a correlation between the visual structure of a crystal section and the direction of the polar axis. With a moderate electric field parallel to the crystal plate, the areas covered with 45° stripes expand or contract, but are preserved, while the regions initially free of the striation tend to assume it. At very high field strength, the lines disappear, the crystal clears up and gives, between crossed Nicols, the picture of a uniaxial crystal observed perpendicularly to the optical axis. If, on the other hand, the field is applied perpendicularly to the crystal plate, and one observes through semitransparent electrodes, the regions without striations are seen to grow at the expense of the 45° line regions; strongly colored bands parallel to the crystal edges appear, and with increasing field, the crystal darkens until the centered uniaxial cross appears showing the optic axis to be parallel to the line of sight.

Below the Curie point, a single crystal breaks up into spontaneously polarized domains oriented with their polar axes in one of the three cube-edge directions. The lattice expands parallel to the axes and contracts perpendicularly to them; hence, the counteracting stresses of different domains produce a complicated stress pattern. An external field of sufficient intensity can turn all axes into the field direction, thus creating a tetragonal crystal with the polar axis identified as the optical axis. The rotation of an axis may be seen in stroboscopic light when a.c. fields are applied by observing the changing pattern of domains. The biaxial pattern disappears when the polar axes become aligned in the field direction.

Further information as to the axis orientation has been obtained from Weissenberg and from Buerger precession x-ray patterns. Figure 8 gives the precession photograph of a small crystal which contained only two domains; it shows the tetragonal lattice of one superimposed on that of the other. These reciprocal lattices have the points (101) in common, thus demonstrating that this plane of the direct lattice is a twin plane. Since the reciprocal lattice is not perfectly square, reflection of the lattice across this plane causes other points to split into double spots, as one lattice deviates from the other. The twin angle shown (35′) corresponds to the c/a ratio of 1.010 reported by Megaw[10] from x-ray studies on powdered ceramics.***

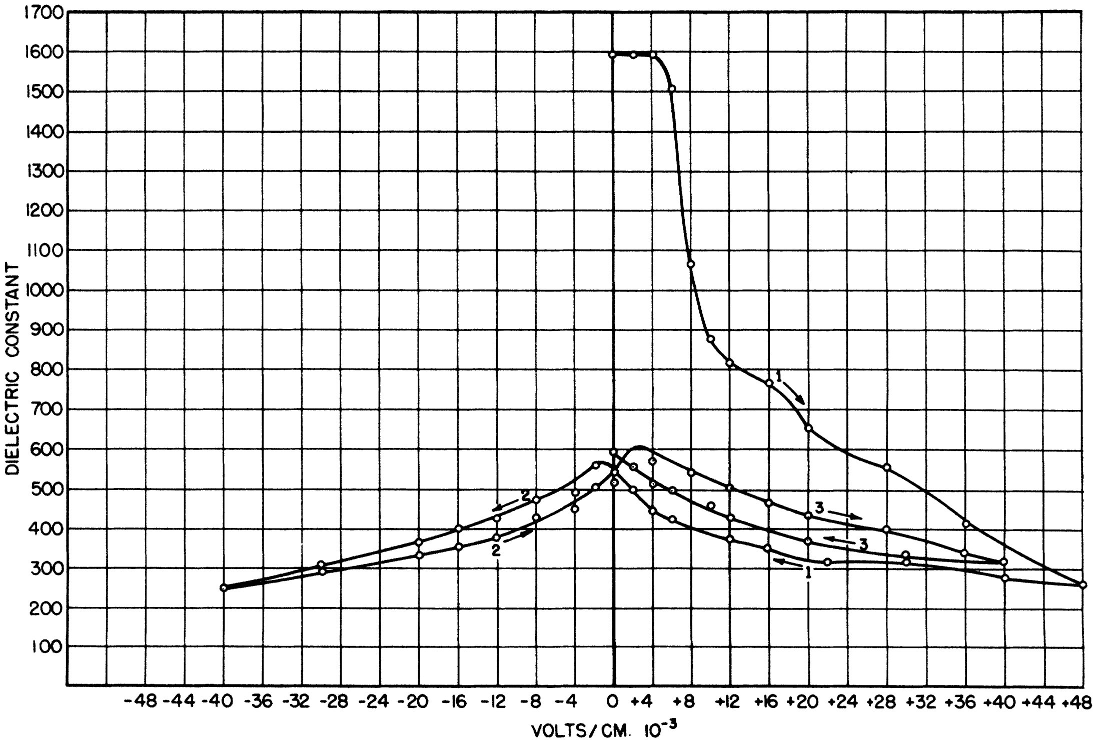

FIG. 10. Dielectric constant as function of biasing field.

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[10] H. D. Megaw, Trans. Faraday Soc. **42A**, 224 (1946).

*** Detailed x-ray investigations on single crystals are being made by H. T. Evans, Jr.; the results will be published at a later date.

5. DIELECTRIC AND PIEZOELECTRIC MEASUREMENTS

Figure 9 shows the dielectric constant and piezoelectric resonance frequency measured on the same crystal in the three cube-edge directions as a function of temperature in a small a.c. field of less than 10 volts/cm at 1 kc/sec. The piezoelectric resonance frequency reaches a minimum and the dielectric response a maximum at the two lower transitions because the deformability under electric stress becomes high at these points.[11] When the Curie point is approached, the anisotropy begins to disappear and the piezoelectric response ceases. Two of the three characteristics are nearly identical since most of the domains had their polar axes perpendicular to the major plane of the crystal.

More quantitative information can be obtained by selecting crystals exactly oriented with their polar axes either perpendicular or parallel to the plate surface, i.e., either type 3 or 2. The dielectric constant parallel to the polar axis amounts to about 550 and perpendicular to it about 1600–1800 at room temperature. This anisotropy can be demonstrated by the following experiment (Fig. 10). A small a.c. field is applied perpendicularly to the polar axis and the dielectric constant determined. Then a biasing field is superimposed in the same direction and gradually increased, thus rotating the polar axis by 90° into the parallel position. From here on, a decrease and reversal of the bias voltage changes only the sign of the polar axis but not its angular position. Hence the a.c. field measures now the first derivative of the hysteresis loop for the parallel orientation.

The total charge density bound by a crystal saturated in field direction was about 12×10^{-6} coulomb/cm^2, in relatively good agreement with a value 16×10^{-6} coulomb/cm^2 reported by Hulm.[12]

By attaching small mirrors to the edges of a single crystal, the mechanical deformation under the stress of a d.c. field could be observed. Due to the domain structure, the results cannot be evaluated unambiguously, but show the superposition of a linear and a quadratic piezoeffect. By evaluating the linear effect, which will be largest with the field applied parallel to the optical axis, one obtains a piezomodulus which seems at least one order of magnitude higher than d_{14} of rochelle salt. This large piezoeffect is even audible when one excites a crystal by an alternating field.

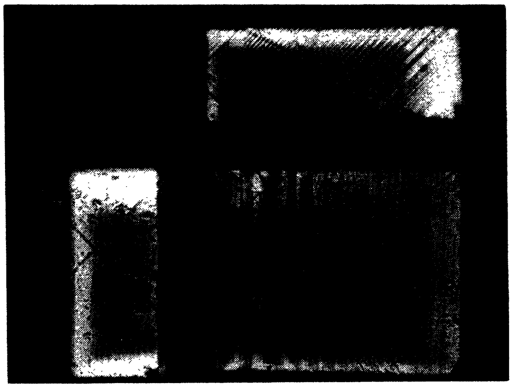

FIG. 11. Striation on a crystal seen from three perpendicular directions.

6. DETAILS OF THE DOMAIN STRUCTURE

Figure 11 shows the same crystal viewed from three perpendicular directions. This picture demonstrates the correlation between the 45° lines and the parallel regions of crystal types 1, 2, and 3. Furthermore the x-ray results indicate that the polar axis turns 90° in crossing each of the 45° lines. These facts lead to the arrangement of domains as shown schematically in Fig. 12.

Increasing field strength reduces the width of the domains that lie with their polar axes perpendicular to the field until they disappear and a completely clear crystal results. At an intermediate stage of domain formation wedge-shaped areas may be observed (Figs. 12 and 13).

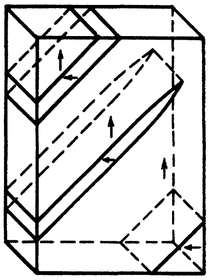

FIG. 12. Correlation between striations and directions of polar axes.

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[11] B. Matthias, Helv. Phys. Acta 16, 99 (1943).

[12] J. K. Hulm, Nature 160, 126 (1947).

FIG. 13. Wedge-shaped domains.

The pattern of type 4 has a mesh size of the net equal to about twice the thickness of the crystal.†

7. DISCUSSION

The results thus far obtained suggest the following concept: in the cubic structure above the Curie point the Ti^{+4} ions oscillate about the centers of the $Ti-O_6$ octahedra with large induced dipole moments, but without effective mutual coupling. As Eucken and Büchner[13] have pointed out, the Ti ion has a tendency to change from ionic to covalent bonding as its distance to an oxygen atom decreases; hence, we expect the largest induced moments in the direction of the valence vibrations. When the Curie point is approached, the interaction between these induced dipoles overcomes the thermal agitation and the Ti ions are locked in an eccentric position displaced toward one of the six oxygen neighbors. This displacive transformation,[1, 14] a case analogous to that of rochelle salt, causes the unstrained crystal to become tetragonal, but generally it subdivides into domains.

In rotating the polar axis, six minimum positions are observed in the cube-edge directions toward the six oxygen neighbors. In a strong external field all intermediate positions may be assumed by the polar axis, and it is not surprising that the high symmetry of the $Ti-O_6$ constellation allows barium titanate ceramic materials to approach the behavior of single crystals.

With decreasing temperature, two polymorphic transitions seem to take place near 5°C and −70°C which change the symmetry of the crystal. Such transitions might be anticipated when one considers that the Ti ion can use the *3d*, *4s*, and *4p* orbitals for the formation of covalent bonds. The experimental indication is that below the Curie point, first octahedral bond orbitals are preferred, but as the structure contracts, and the thermal vibrations decrease, other hybrid bonds may become dominant.

If the situation is as described, the ferroelectric group of the titanates may bear a true relationship to those of the tartrates and phosphates. The ferroelectric state in the latter two groups is presumably caused by hydrogen bonds, which may be described as covalent in one direction and ionic in the other. This description seems also to apply to the titanium-oxygen bond, hence such dual bond character may be a prerequisite for ferroelectricity. Permanent dipoles in solids cannot ordinarily line up freely because of hindered rotation, but dipoles induced by vibrations may do so. The dual bond character can impart high dipole moments and, by mutual coupling under favorable structure conditions, may overcome the thermal agitation of the lattice even above room temperature.

Investigations are in progress which we hope will lead to a more quantitative treatment of the ferroelectric state of $BaTiO_3$.

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† A detailed study of domain structures as equilibrium arrangements is at present being undertaken by P. W. Forsbergh, Jr. The wedge-shaped areas were first observed by him.

[13] A. Eucken and A. Büchner, Zeits. f. physik. Chemie **B27**, 321 (1934).

[14] L. Tisza, Phys. Rev. **72**, 532 (1947).

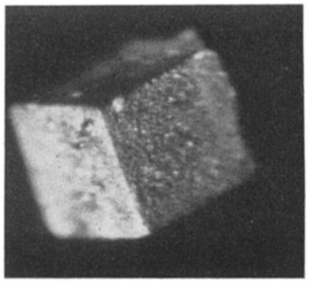


FIG. 1. Cubic $BaTiO_3$ crystal.

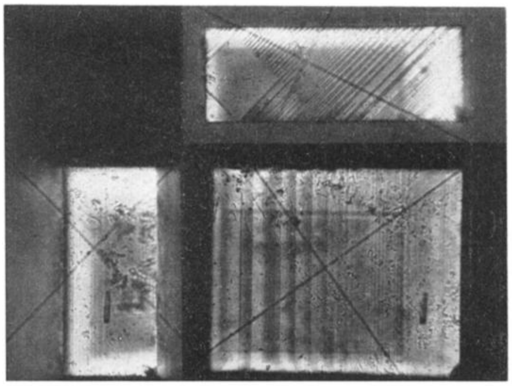


FIG. 11. Striation on a crystal seen from three perpendicular directions.

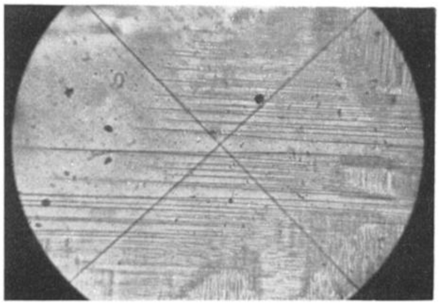


FIG. 13. Wedge-shaped domains.

FIG. 2. Crystal type 1 (45° stripes).

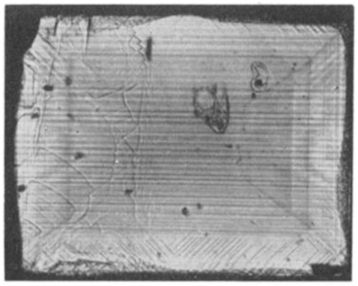


FIG. 3. Crystal type 2 (stripes parallel to one cube edge).

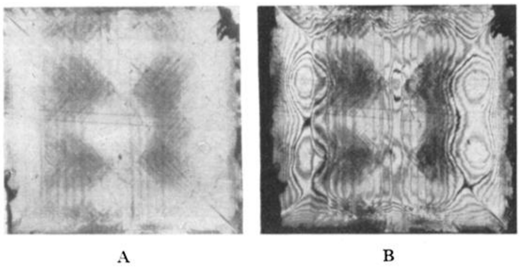


Fig. 4. Crystal type 3. (A) Natural light. (B) Polarized light.

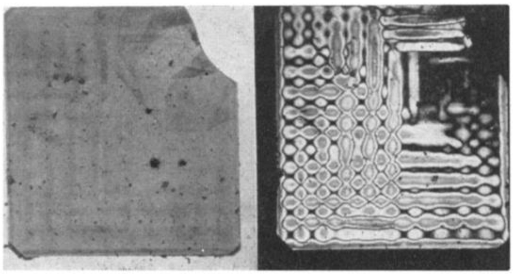


FIG. 5. Crystal type 4. (A) Natural light. (B) Polarized light.

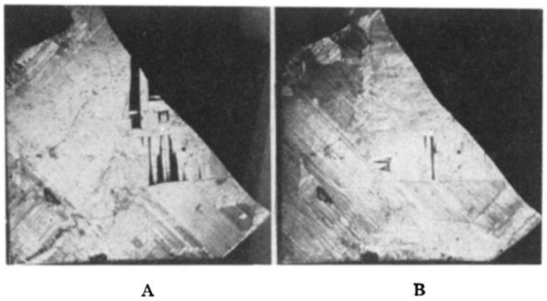


Fig. 6. (A) Initial pattern at 25°C. (B) The same crystal at 25°C after heating above Curie point.

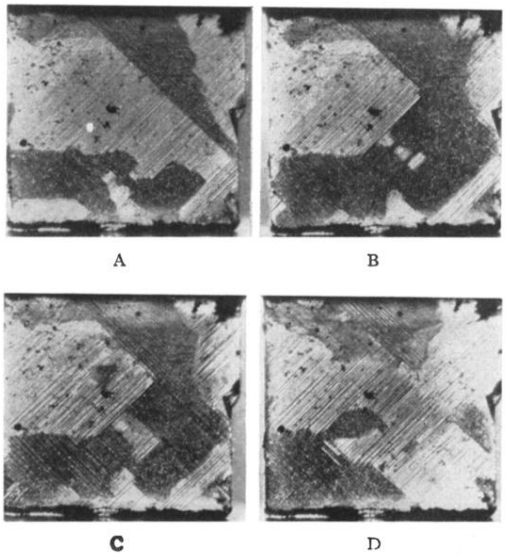
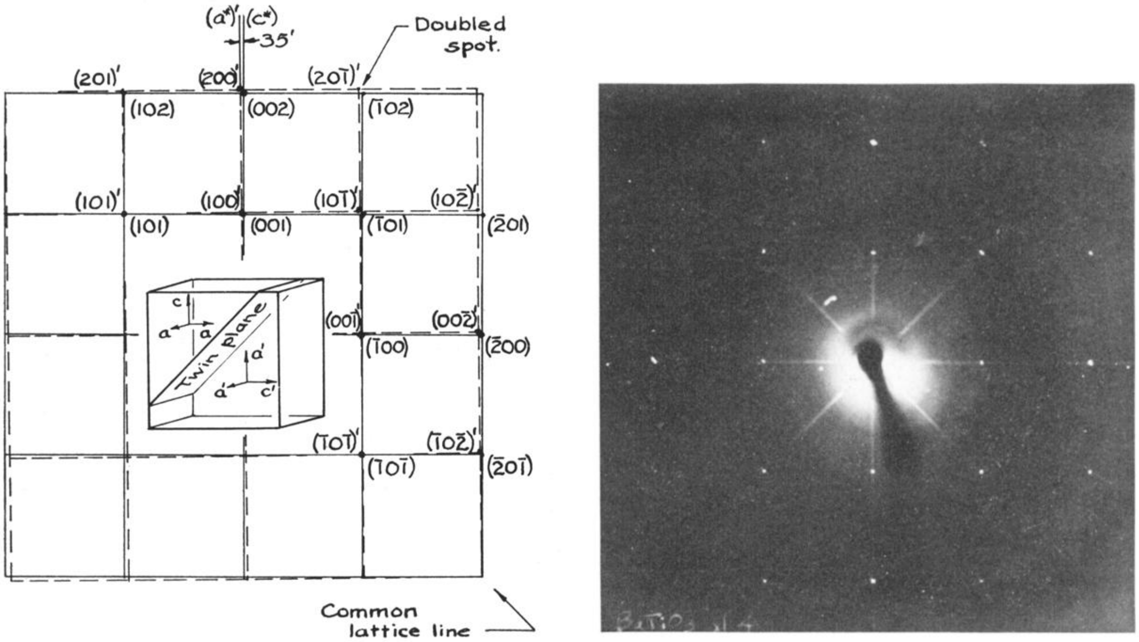


FIG. 7. Effect of electric field on domain structure of $BaTiO_3$ crystal. (A) No field applied. (B) +2000 volts/cm. (C) Field removed. (D) −2000 volts/cm.



A

B

FIG. 8. Precession photograph of a two-domain crystal.