Detwinning Ferroelectric Crystals

By **ELIZABETH A. WOOD**

Unstrained single crystals of barium titanate can be detwinned under the influence of an electric field at elevated temperature, but strained crystals cannot. It seems probable that this is also true of crystals in a polycrystalline body such as a ceramic.

EACH of the ferroelectric[1] crystals so far discovered has a structure which closely approaches a more symmetrical structure into which it transforms at the Curie temperature. In all of them, the deviation from the more symmetrical structure is so slight (Table I) that the application of mechanical stress or electric field can produce a shift from one orientation of the lower symmetry structure to another. Since, in crystals grown from the melt, such as barium titanate, inhomogeneous mechanical stresses resulting from inhomogeneous cooling or differential thermal contraction of the surrounding flux material are present in the crystals as they pass through the Curie temperature, these crystals commonly comprise regions of two or more orientations of the lower-symmetry structure, symmetrically related. They are, in other words, twinned.

In this condition the electrically polar direction differs in orientation from one individual of the twin to another[2]. Since it is frequently desirable to have the polar direction oriented uniformly throughout the crystal, it is of interest to determine under what conditions this state can be achieved. It is not possible in all crystals.

The discussion in this paper will be confined to barium titanate because more experimental data are available for this crystal, but it is probable that similar considerations are applicable to the other ferroelectric crystals.

The process of causing the polar axis in a ferroelectric crystal to have the same orientation throughout the crystal has been called "poling." It is the process of detwinning the crystal. As C. J. Davisson and others pointed out in connection with the problem of detwinning quartz crystals during World War II, if the crystal is subjected to a stress which will be lessened if the "misoriented" regions change to the desired orientation and if the activation energy of the change is not too great, the crystal will be detwinned.

---

[1] Ferroelectric crystals are those crystals which exhibit, with respect to an electric field, most of the phenomena exhibited by ferromagnetic crystals with respect to a magnetic field, such as spontaneous polarization, domain structure, hysteresis of response to an alternating field and a Curie temperature above which these unusual characteristics are not present.

[2] By the ferromagnetic analogy each twin individual is called a ferroelectric "domain."

TABLE I

Substance	Stable Structure at lower temperature	Closely allied more symmetrical structure and the Curie Temperature above which it is the stable structure	Differenc:
Barium titanate	Tetragonal $c = 4.04$, $a = 4.00$	Cubic, $a_0 = 4.00$ $T_c =$ ca. 120°C	1% of the length of the c axis
Potassium niobate	Orthorhombic $a = 5.70$, $b = 5.74$, $c = 3.98$ equivalent to special case of monoclinic in which $a = c = 4.04$, $b = 3.98$, $\beta = 90°, 20' \pm 5'$	Cubic, $a_0 = 4.04$ $T_c =$ ca. 435°C	1.5% of the length of the c axis + a shear angle of about 20′
Rochelle Salt	Monoclinic	Orthorhombic $T_c =$ ca. 24°C	A shear angle of about 3′
Potassium dihydrogen phosphate	Orthorhombic	Tetragonal $T_c =$ ca. -152°C	Small shear

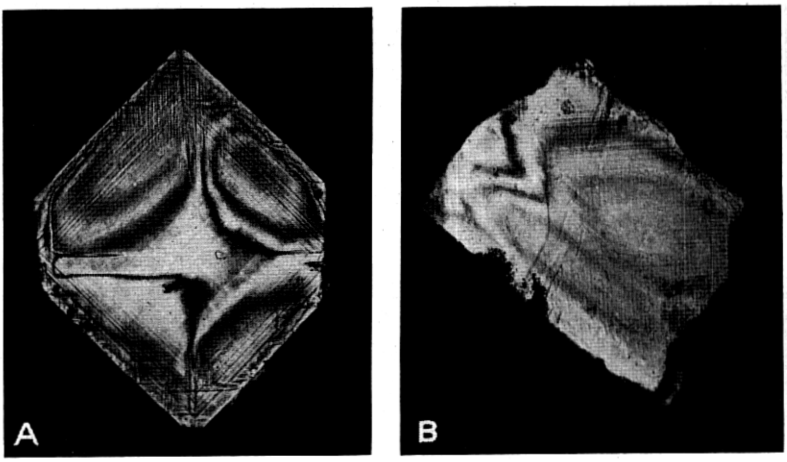

Fig. 1—A. Crystal a as received from the melt. Edges at 45° to polarization directions of crossed nicols. Dimensions of surface: .2 x .2 mm.
B. Crystal b as received from the melt. Edges at 45° to polarization directions of crossed nicols. Dimensions of surface: .15 x .2 mm.

With barium titanate as with quartz, the activation energy of this change can be reduced to zero by heating the crystal through a polymorphic transition above which its symmetry is such that the twinning can no longer exist. It is then cooled through the transition under the influence of the applied stress which favors one of the possible twin-orientations.

SINGLE-CRYSTAL EXPERIMENTS

Parts A and B of Fig. 1 are photomicrographs of barium titanate crystals, both grown from the same melt by B. T. Matthias. The composition of the melt was 26 grams $BaCO_3$, 6.5 grams TiO_2, 50 grams $BaCl_2$, and the method followed was that described by Matthias in 1948[3]. Each of the crystals shows several domains and some inhomogeneous strain as indicated by birefringence evident between crossed nicols when the crystal is at the extinction position, Fig. 2, A and B, i.e. when its edges are parallel to the polarization directions in the polarizer and analyzer. An unstrained crystal in this position appears black between crossed nicols.

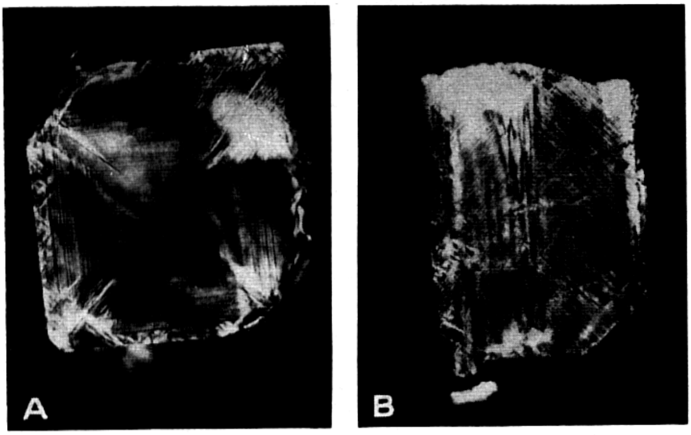

Fig 2—A. Same as Fig. 1A, but at extinction position.
B. Same as Fig. 1B, but at extinction position.

OPTICAL EVIDENCE OF THE EFFECT OF A HIGH FIELD

However, crystal *a* can be made to assume essentially a single orientation throughout by the application of a high field at elevated temperature as shown in Fig. 3A, but the same treatment applied to crystal *b* results only in the formation of a large number of domains, as shown in Fig. 3B. A field of 16000 volts per cm. was applied across each crystal at 125°C. and continued until the crystal had cooled to less than 50°C. Parts A and B of Fig. 4 are the extinction-position photographs corresponding to Parts A and B of Fig. 3.

X-RAY EVIDENCE OF INHOMOGENEOUS STRAIN

The reason for the difference in behavior of the two crystals is suggested by their back-reflection Laue photographs. Parts A and B of Fig. 5 are Laue

---

[3] Matthias, B. T., *Phys. Rev.* 73, 808–9, 1948.

photographs taken before the attempt was made to pole the crystals. Whereas a Laue photograph of a perfect single crystal would show a pattern of single spots, crystal *a* shows a pattern of groups of spots joined by fainter streaks and crystal *b* shows a pattern of short streaks. In both cases, the streaks indicate crystal material of continuously varying orientation, but in the case of crystal *a* it is transitional in orientation between two or

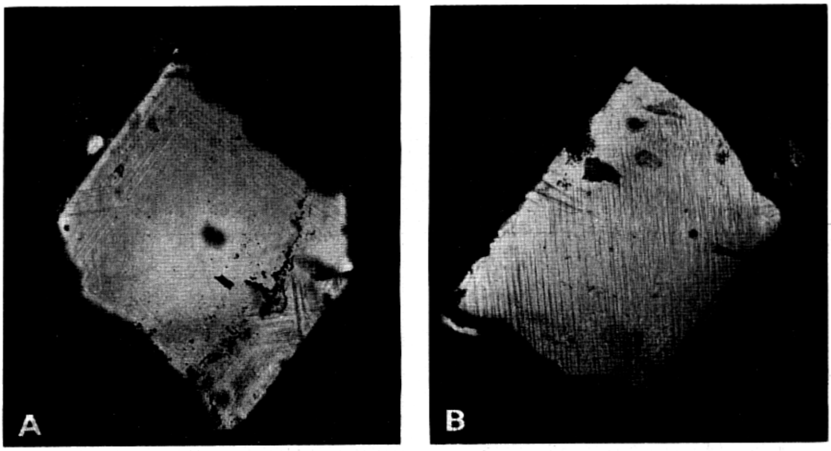

Fig. 3—A. Crystal *a* after the application of a high field at elevated temperature. Edges at 45° to polarization directions of crossed nicols

B. Crystal *b* after application of a high field at elevated temperature. Edges at 45° to polarization directions of crossed nicols.

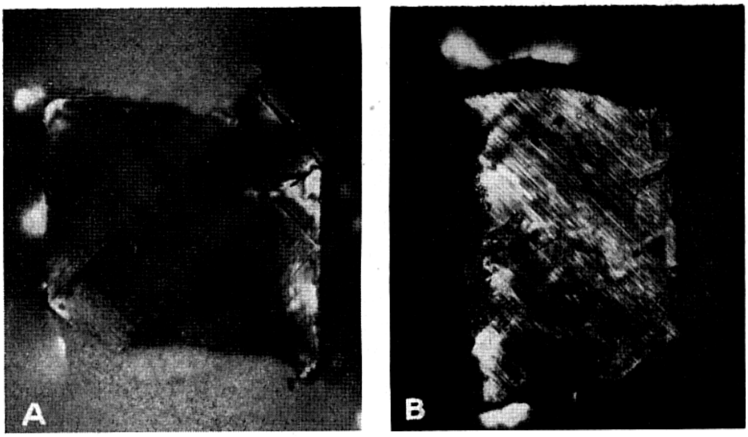

Fig. 4—A. Same as Fig. 3A, but at extinction position.
B. Same as Fig. 3B, but at extinction position.

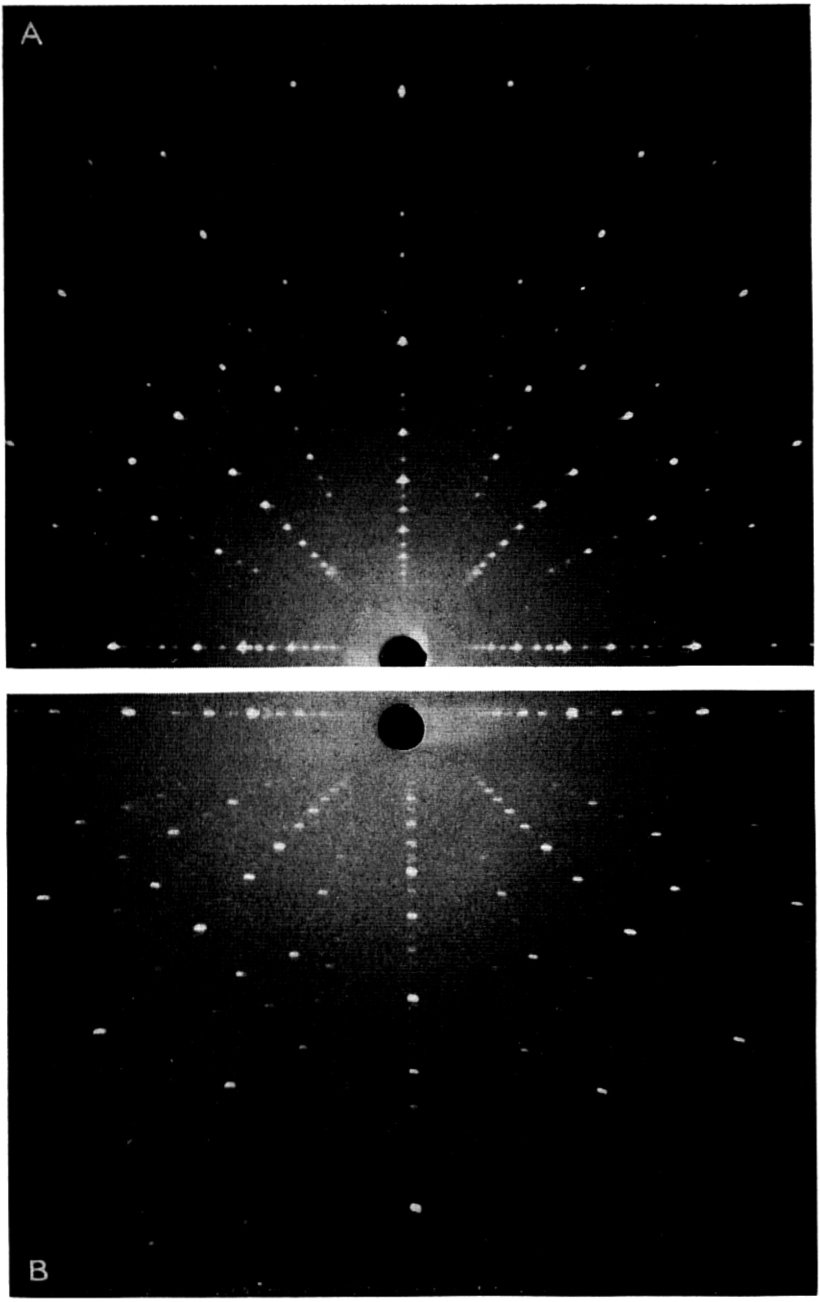

Fig. 5—Laue photographs of the two crystals before treatment. The symmetrical half of each photograph has been removed to facilitate close comparison. A: from crystal *a*; B: from crystal *b*.

more twin-related orientations and is probably twin-boundary material, whereas crystal *b* is a bent crystal.

The evidence for this interpretation lies in the facts that (1) the streaks in Fig. 5A converge at the reflections from the various (101) planes which are twin planes, whereas those in Fig. 5B do not; (2) the streaks in Fig. 5B show only that variation in length which is due to the use of a flat film whereas those in Fig. 5A show greater variation; and, finally, (3) the streaks in Fig. 5B are of nearly uniform intensity throughout, whereas those in Fig. 5A are faint streaks between strong end points. These three points are discussed in the following section.

DISTINCTION BETWEEN TWIN-BOUNDARY AND OTHER INHOMOGENEOUS STRAINS IN CRYSTALS

The spots on a back-reflection Laue photograph may be considered as the intersections of the film with normals to atomic planes in the crystal, modified by a non-linear scale factor. The position of any spot is independent of the wave-length of the x-rays producing it and dependent only on the orientation of the reflecting plane.

When the x-ray beam falls on a twin boundary two families of twin-related spots appear on the film. In barium titanate twin-related spots from equivalent planes are close to each other. If the two spots of such a pair are joined by a line these lines will all converge toward the spot from the (101) plane which is the twin plane, the plane across which reflection of the structure would produce the twin configuration. (See Fig. 6, a back-reflection Laue photograph of a barium titanate crystal with only 2 twin-related orientations.) That this must be so will be clear from Fig. 7. With the exception of the twinning plane the planes in this figure represent zonal planes, planes containing two or more atomic-plane normals. The zonal planes on the two sides of the twin plane represent the zonal plane orientations in the two parts of the twin. The only zonal plane directions common to both parts of the twin are those normal to the twin plane since these are the only directions not changed by reflection across the twinning plane. The one direction common to all these unchanged zonal planes is the normal to the twin plane. Thus the zonal arcs on the plane photograph which are common to spots from both parts of the twin intersect in the reflection from the twin plane.

Referring now to Parts A and B of Fig. 5, we see that the streaks in Fig. 5A lie along the zonal arcs common to both parts of any given twin pair and are intermediate between the spots of the twin pair. They are therefore reflections from material transitional in orientation between the two twin orientations. The streaks in Fig. 5B, however, do not converge toward a

(101) plane-normal, but rather, when the non-linear scale factor has been taken into account, are all normal to the (100) axis which lies parallel to the film in a top-to-bottom direction. They therefore come from crystal planes bent around this axis of a twinned barium titanate crystal.

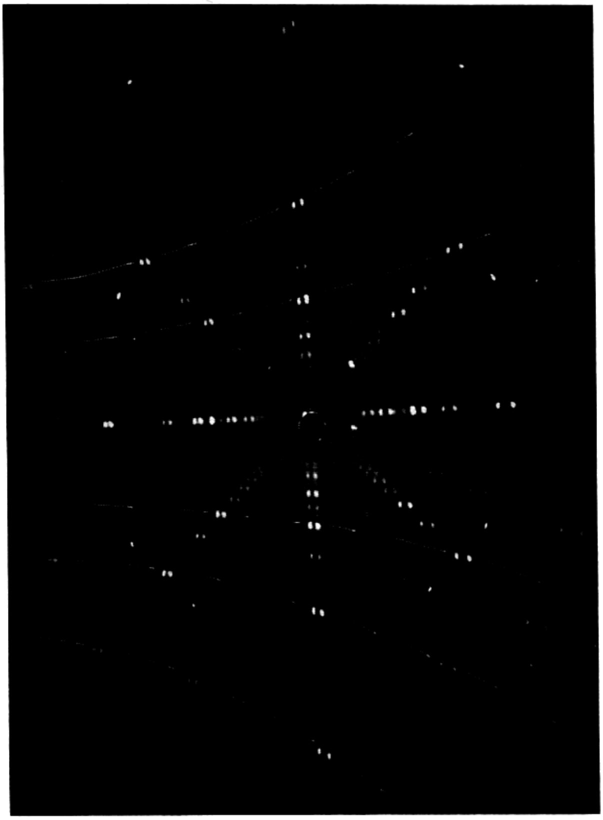

Fig. 6—Laue photograph of a barium titanate crystal with only two twin-related orientations.

A section through the reciprocal lattice of a twinned barium titanate crystal is shown in Fig. 8A: that of a bent crystal, in 8B. In the reciprocal lattice of a tetragonal crystal the direction of each point from the origin is the same as the direction of the normal to the set of planes it represents and the distance of each point from the origin is proportional to the reciprocal of their interplanar spacing. Since the back reflection Laue photograph shows only orientations of the atomic planes it may be thought of as a shadowgraph of the reciprocal lattice, illuminated by a point source of light at the origin, as indicated by the dashed lines in Figs. 8A and 8B.

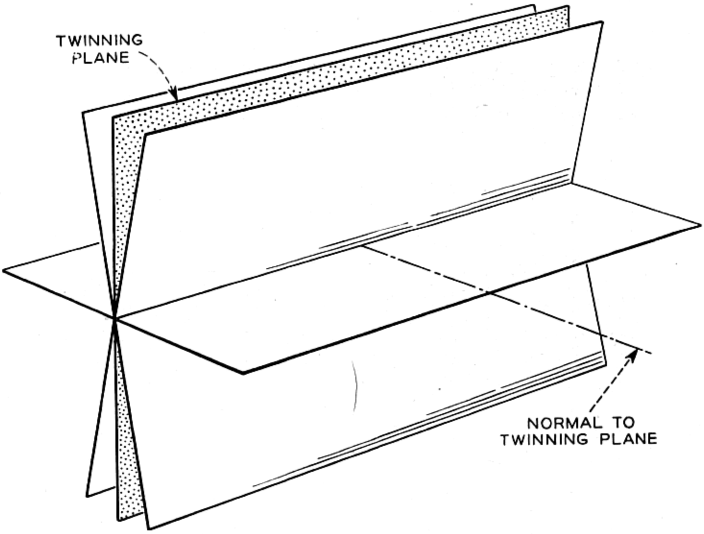

Fig. 7—Diagram of zonal relations between the two parts of a twinned crystal.

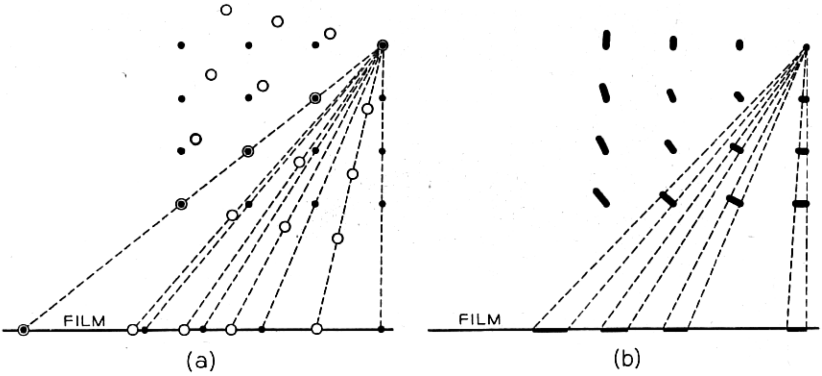

Fig. 8—A. Section of the reciprocal lattice of a twinned crystal and its Laue photograph.
B. Section of the reciprocal lattice of a strained crystal and its Laue photograph.

From these figures the second point of difference between Laue photographs 5A and 5B becomes clear, namely, that in the case of the bent crystal viewed normal to the bending axis the streaks appear rather uniform in length, whereas the streaks from the inter-twin oriented material

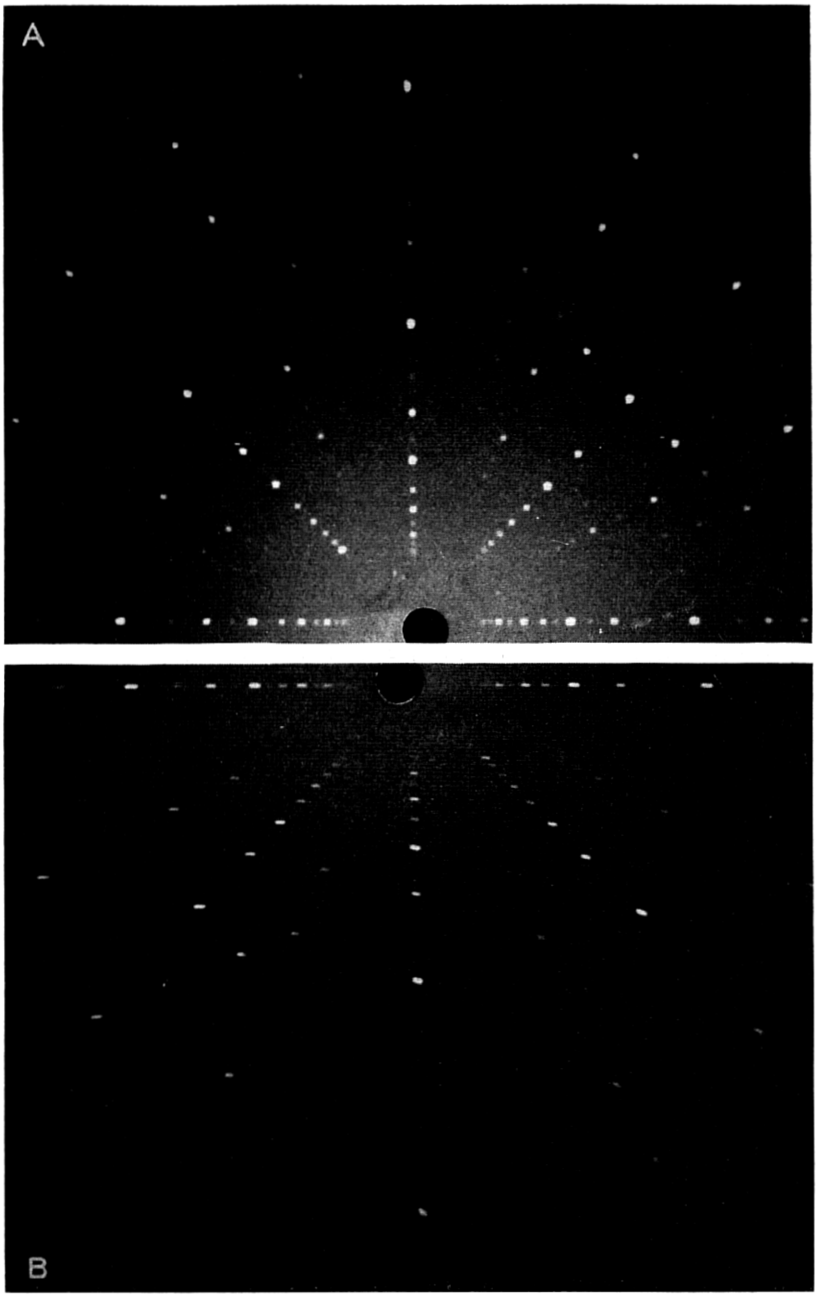

Fig. 9—Laue photographs of the two crystals after treatment, paired as in Fig. 5. A: from crystal *a*; B: from crystal *b*.

diminish in length as they approach the twin-plane normal. This is perhaps more obvious in Fig. 6 where only one pair of twins is shown.

Finally, the streaks from bent crystals are more uniform in intensity than those with intertwin-oriented material, but if the bending were non-uniform or the intertwin material more abundant this might not be so.

X-RAY EVIDENCE OF EFFECT OF HIGH FIELD

The Laue photograph of crystal *a*, taken after the poling process had caused it to become a single untwinned crystal, Figs. 3A and 4A, is shown in Fig. 9A. It shows a pattern of single spots. The absence of streaks agrees with the paucity of birefringent regions in Fig. 4A in indicating very little inhomogeneous strain in the crystal.

The Laue photograph of crystal *b*, taken after the poling attempt had produced only a regular multiple-twin pattern in it, Figs. 3B and 4B, is shown in Fig. 9B. The inhomogeneous strain has not disappeared, as indicated also by the birefringent regions in the photograph of Fig. 4B.

SUMMARY OF RESULTS OF SINGLE-CRYSTAL EXPERIMENTS

From the experiments described above it is concluded that barium-titanate crystals with only twin-boundary strain can, under the influence of a high field at elevated temperatures, be caused to have a single crystallographic orientation whereas barium titanate crystals otherwise strained cannot.

APPLICATION TO BARIUM TITANATE CERAMICS

Single crystals of barium titanate large enough for practical applications have not yet been grown. Therefore all practical applications using barium titanate have so far used it in the ceramic form.

Ceramics have been made for two different applications: condensers and electromechanical transducers. For the first, the maximum electrical polarizability for a given applied electric field is desired, since this results in a high dielectric constant. For the second application, however, it is desirable to have a ceramic which will deform mechanically in an electric field according to its own polarity. With this end in view, ceramics intended for electromechanical transducers have been poled by being subjected to a high field (roughly 15000 v/cm.) as they were cooled through the Curie temperature to room temperature.

In a series of unpublished experiments W. P. Mason and R. F. Wick of the Bell Laboratories have found that certain barium titanate ceramics, when poled in this way, retain their polarization in spite of high reverse fields ($\frac{1}{6}$ to $\frac{1}{3}$ the poling fields), i.e. require a high coercive force to change the direction of their polarization. Such ceramics can be used in piezoelectric devices with high alternating fields without "depolarization" and can therefore achieve electro-mechanical coupling at higher power levels than ceramics that do not retain their polarization under the influence of a reverse field. Only a small proportion of ceramic specimens could be poled in this way and the factor common to these has not yet been ascertained.

In the light of the single-crystal experiments reported in this paper, it seems apparent that ceramics composed of inhomogeneously strained crystals (excluding twin-boundary strain) could not be poled. Three ceramic specimens whose poling history was known were available. Of these only one could be poled. X-ray diffraction photographs of the two unpolable ceramics showed streaked reflections from the individual grains, indicating strain. The grain-size of the polable specimen was much smaller, so small that reflections from individual grains could not be identified.

It is anticipated that ceramics for different uses should be differently fired and perhaps even differently composed as well as subjected to different electrical treatment subsequent to their formation.