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Preparation and Properties of Crystals of Barium Titanate, $BaTiO_3$

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A technique is described for the preparation of 'single' crystals of $BaTiO_3$. At room temperature the crystals are complexes of habit appropriate to cubic symmetry, but consisting of multiply-twinned tetragonal components with orientation very sensitive to externally applied pressure or electric fields. Optical and X-ray observations have been used in a detailed study of the nature of the transitions occurring near 120° C., near 0° C., and near −90° C.

Introduction

A number of workers have described researches on the electrical properties and structure of $BaTiO_3$ and related materials. Among the more recent papers reference may be made to Harwood, Popper & Rushman (1947), von Hippel, Breckenridge, Chesley & Tisza (1946), Megaw (1946, 1947), Rushman & Strivens (1946), and Wul (1946). In all these investigations, however, the material has been in the form of a fine-grained polycrystalline ceramic mass, and the only X-ray method applicable has been that of the Debye-Scherrer pattern. Recently, Rhodes and the present author (Kay & Rhodes, 1947) succeeded in preparing 'single' crystals of $BaTiO_3$, and these have been subjected to detailed X-ray and optical examination. The present paper describes some of the more important facts which have emerged in the course of the investigation.

Production of the crystals

Blattner, Matthias & Merz (1947) have recently produced crystals approaching the composition $BaTiO_3$ by dissolving either $BaO + TiO_2$ in a mixture of K_2CO_3 and Na_2CO_3, or $BaCO_3 + TiO_2$ in $BaCl_2$, and then slowly cooling the solution from about 1000° C. This method was adopted in the work described here, except that in all cases the solute was $BaTiO_3$ previously prepared by sintering together $BaCO_3 + TiO_2$ at temperatures of about 1300° C. The optimum conditions of growth have not yet been established completely, and work is continuing, but the following observations are of value.

Platinum appears to be the best container, but it has recently been stated that carbon is even more satisfactory (Matthias, 1948). Preliminary tests with aluminous porcelain showed no obvious signs of crucible corrosion at the temperatures employed. Above 950° C. carbonate solution reacts with platinum and the maximum temperature should never exceed 900° C. Using chloride solutions higher temperatures are required, but the limit is set by evaporation and platinum corrosion which become serious at 1200° C. The rate of solution is quite slow, and a period of about 20 hr. at 1150° C. is required to ensure the solution of 1 part of finely powdered $BaTiO_3$ to 4 parts, by weight, of $BaCl_2$; solution in carbonates at 900° C. is a little more rapid. A cooling rate of 3–4° C./hr. produced the most satisfactory crystals, whose sizes range from 0·01 to 2·0 mm., although this size does not seem to depend only on the cooling rate and solution concentration of $BaTiO_3$.

The process involving fusion mixture, while requiring lower temperatures, is more difficult to control owing to the reactive nature of the solution and the wide variety of phases which can be obtained under different conditions of temperature and solute purity; hexagonal, rhombohedral and tetragonal products have been obtained, all except one of which have pseudocubic symmetry. Of these, only the tetragonal product shows a symmetry change at temperatures up to 200° C.

The use of $BaCl_2$ gives more consistent results, and the products always show tetragonal pseudocubic internal symmetry characteristic of $BaTiO_3$ made by the powder-sintering process. However, their habit, colour and twinning complexity depend on the temperature of formation, duration of firing process and the $BaO : TiO_2$ ratio of the initial solute material. Small parameter differences have been observed.

Very pure $BaTiO_3$, '$BaTiO_3$' having 0·31 mol. % excess TiO_2, and '$BaTiO_3$' having 5 mol. % excess TiO_2 have been used as solute. Of these the highest purity material seems preferable for use with carbonate solvent, whereas 5 mol. % excess TiO_2 gives consistently better results if $BaCl_2$ is used, pure material giving darker, red to black crystals which show a higher degree of semi-conductivity. This suggests that molten $BaCl_2$ may tend to produce crystals with an excess of Ba over Ti, and that this effect can best be compensated by an initial excess of TiO_2, but it is conceivable that darkness in crystals may result, at least in part, from dissolved platinum (Matthias, 1948), an effect which may be reduced by excess of TiO_2.

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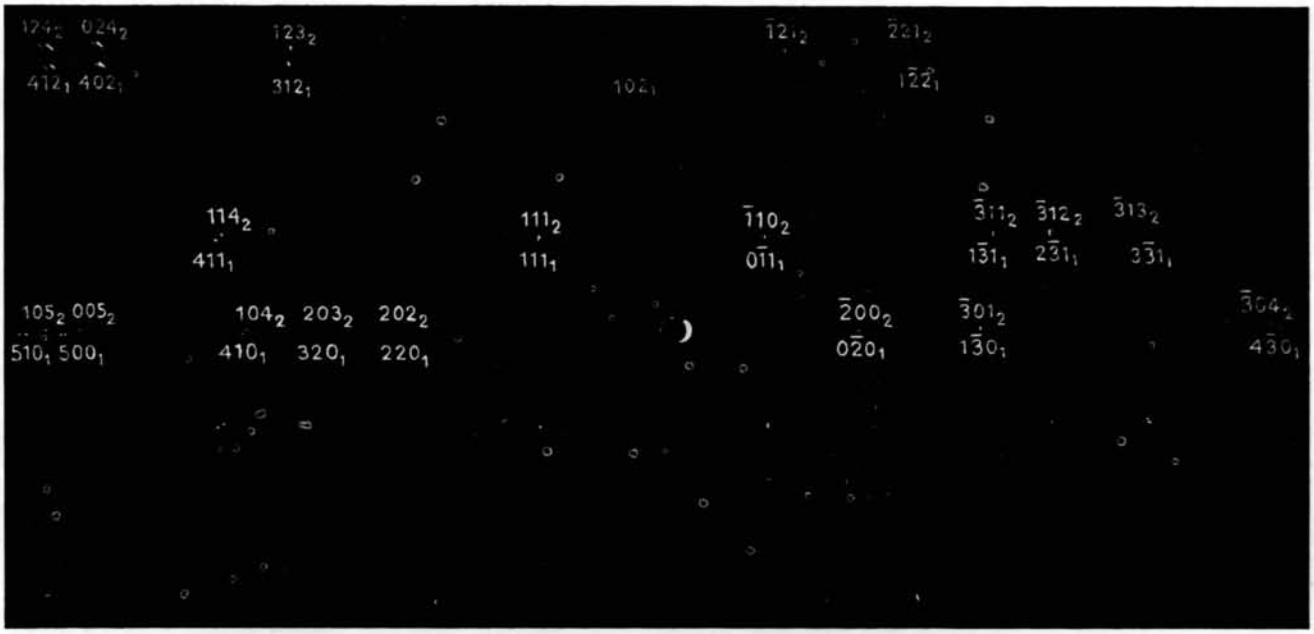

Fig. 1. 15° oscillation photograph of a small cube of $BaTiO_3$. Oscillation about a cube-axis with the incident beam parallel to another cube-axis at the extremity of the range of oscillation. Subscripts to the indices indicate reflexion from the two components. Filtered Cu K radiation. Camera diameter 6 cm.

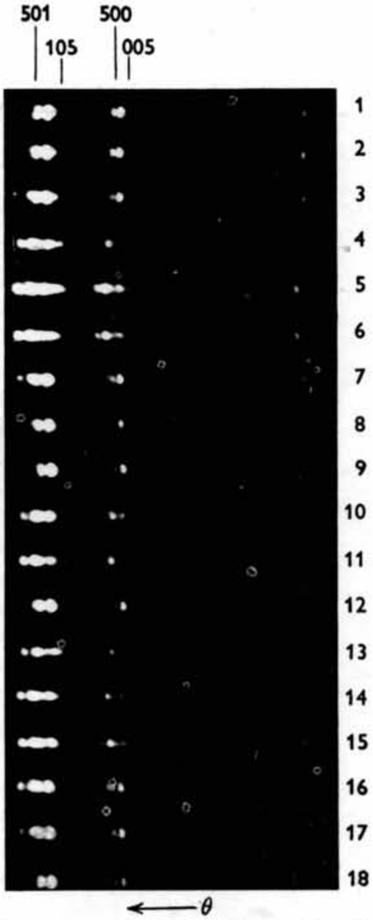

Fig. 2. High-angle portion of zero layer-line photographs of $BaTiO_3$. X-ray beam nearly parallel to the x cube-axis at the extremity of a 15° oscillation about the z cube-axis. Electric fields applied along the y cube-axis (Table 1). Radiation Cu K. Camera diameter 6 cm.

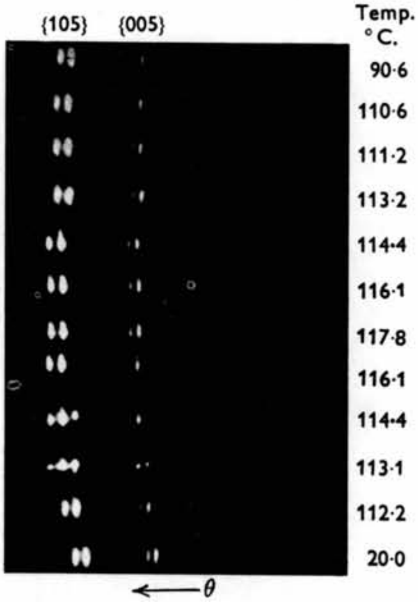

Fig. 3. High-angle portion of zero layer-line photographs of the $BaTiO_3$ crystal sketched in Fig. 10(a). X-ray beam nearly parallel to the x cube-axis at the extremity of a 15° oscillation about the z cube-axis. Crystal at different temperatures. Radiation Cu K. Camera diameter 6 cm.

General characteristics

At the temperature of formation the structure of $BaTiO_3$ is cubic, so that at room temperature the habit of the crystals corresponds to cubic symmetry. Perfect cubes have been observed, other crystals also show {111} face development, while others show {110} faces in addition. The majority, however, are cubes, orthogonal prisms or plates. The colour of crystals from different 'melts' varies from very light yellow, yellow, brownish, reddish wine, to black, and it is possible that the pure material is water-clear.

At room temperature the internal symmetry is tetragonal, and all but a very small number of the crystals are intimately twinned, the composite showing 'straight-extinction'. The degree of twinning is greater for the darker crystals and the average twin size correspondingly smaller. The uniaxial interference patterns observed in large twins indicate that the material is optically negative, and if c is oriented along the microscope axis no birefringence is observed. This fact, when taken together with the X-ray data, indicates that the material is certainly tetragonal. The refractive indices are high (probably $\sim 2{\cdot}3$). The crystals are fairly hard and show no preferential cleavage direction. They are piezoelectric (established in co-operation with Dr W. A. Wooster by using the apparatus of Giebe and Scheibe), but simple tests for pyroelectricity were inconclusive.

In view of the differences in colour, semi-conductivity, twin complexity, and probably of slight variations in composition, only those crystals were selected for study which were clearest and had the best insulating properties, but it is to be emphasized that no chemical analysis was made.

Twinning

A very small number of truly single crystals are observed, invariably in the form of very thin flakes or needles, usually with the tetragonal c axis parallel to the smallest cube-axis dimension of the crystal specimen. All others are twinned to varying degrees, and X-ray photographs of such crystals oscillated about any cube axis show only layer lines indicating a repeat distance of $\sim 4{\cdot}0$ A. Since $a = 3{\cdot}9932 \pm 0{\cdot}0002$ A., and $c = 4{\cdot}0341 \pm 0{\cdot}0003$ A., this indicates that all the component twins lie with c axes parallel to one of the cube-axes of the macrocrystal. The diffraction spots from such a crystal occur in groups; for example, reflexion 500 arising from one twin component lies close to 005 of another, and, since $c > a$, $\theta_{005} < \theta_{500}$.

In many crystals the c axes of the component twins lie in only two of the cube-axis directions. Fig. 1 is a 15° oscillation photograph of a small crystal of this type. The reflexions are indexed in the figure with subscripts 1 and 2 indicating the two components. It can be seen that two discrete sets of layer lines are discernible, indicating that the c axes of the two components are oriented at an angle of $90° - \gamma$, where $\gamma = 35'$. This angle corresponds to that between planes (011) and $(0\bar{1}1)$ of the tetragonal lattice, and is numerically equal to $2 \tan^{-1} a/c = 89° 25'$ or $90° - 35'$. Therefore twinning occurs about the (101), $(\bar{1}01)$, (011) or $(0\bar{1}1)$ planes, and the angle γ lies in the (100) or (010) planes.

It will be convenient to describe the orientation of an individual component of a twinned crystal by the direction of its c axis relative to the cube axes x, y, z of the macrocrystal. Thus a [100] component has c parallel (within a few minutes) to the macrocrystal x axis.

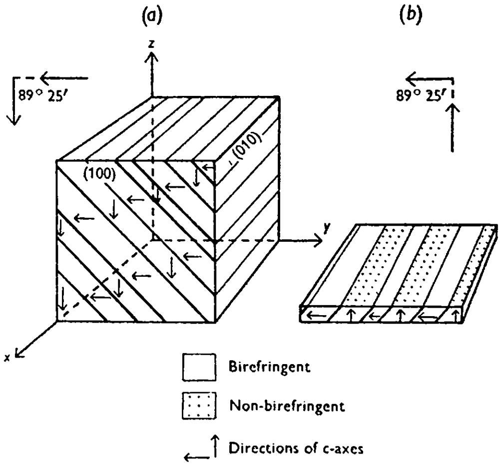

Fig. 4. Diagram of simply-twinned crystals of $BaTiO_3$ showing the twin boundaries. Short arrows indicate the c-direction of the individual components. (a) Cubic-shaped crystal. (b) Platey crystal.

If a small crystal composed only of [010] and [001] twins (as determined by X-rays) is viewed under the microscope along the x axis, fine dark lines are observed which extend normally into the crystal as (011) planes, and the crystal appears uniformly birefringent (see Fig. 4(a)). On viewing along the y and z axes no lines can be seen, but, especially in the case of smaller crystals, variations in birefringence colours can be seen with lines of equal birefringence extending parallel to the x axis. These lines, therefore, represent boundaries between adjacent [010] and [001] twins, and in Fig. 4 the c directions of the individual twins have been marked by arrows which make an angle of 89° 25′ with each other. This twin arrangement is verified by the optical appearance of many thin flakes, which, when viewed perpendicular to the plate surface, are often seen to consist of alternate birefringent and non-birefringent lamellae such as would be expected for individuals with c directions oriented as shown by the arrows in Fig. 4(b). Such flakes can be considered as thin sections from the (010) face of the crystal of Fig. 4(a).

These crystals give X-ray reflexions apparently arising from two components only, although the number of individuals may be large. On the other hand, twin boundaries (011) and (0$\bar{1}$1) may both be present, i.e. γ occurs in both positive and negative sense in the plane (100). This gives X-ray reflexions corresponding to three components, two of which are inclined at an angle of 1° 10′ to each other. Such crystals are usually built up of blocks having (011) boundaries (with γ positive) next to blocks having (0$\bar{1}$1) boundaries (with γ negative); the boundaries rarely interpenetrate.

Larger crystals usually show a more complex twin arrangement with c lying parallel to all three cube axes, and [100], [010] and [001] twins may coexist along a boundary parallel to the [111] cube-direction. Fig. 5 shows a fairly simple crystal of this type, the interpretation of which is possible in view of its thinness in the x direction. In thicker crystals a detailed interpretation becomes difficult; the twins are usually smaller, and the crystal often exhibits signs of greater strain. Even in relatively simple crystals strain effects are sometimes observed as curved contours of equal birefringence, the exact interpretation of which is not yet certain.

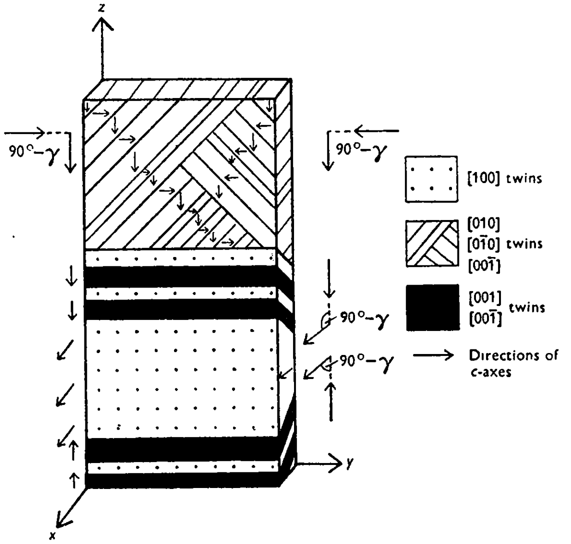

Fig. 5. Diagram of thin crystal of BaTiO$_3$ exhibiting complex twinning with γ in a positive and negative sense in both the (100) and (010) planes.

The twin dimensions vary considerably. Small, simply-twinned plate-like crystals may have twins with dimensions in the x, y and z directions up to 1·5, 1·5 and 0·02 mm. respectively, and in simple cubes the dimensions may be $0{\cdot}3 \times 0{\cdot}3 \times 0{\cdot}04$ mm. In more complex crystals they may be less by a factor of 10–20. Figs. 4, 5 and 6 are slightly simplified in that they show adjacent [010] and [001] individuals as having approximately equal size. In some cases this regularity is observed to a marked extent, but it is more usual to find one orientation taking preference. For instance, in one locality, or perhaps even in the whole crystal, the [001] twins may occupy a much greater volume than twins having c in other directions, so that c is oriented essentially along the z axis.

Investigations by Vousden and the present author have revealed that in the {110} planes many dark striations occur for which c is parallel on either side. Moreover, such striations may terminate within the crystal and not at its bounding surface. Using a microscope of magnification 100, such striations are invariably found to be a close pair of striations separated by a distance of about 0·0005 mm., a figure which is very frequently observed in the crystals so far investigated. Between each close pair is a thin sheet of the crystal having c oriented nearly at right angles to the main c direction, so that these double striations are essentially a close pair of the type of twin boundaries already described. A discussion of finer structural details will be dealt with in a future publication.

Effect of pressure

Unidirectional pressure was applied along the y axis of well-formed crystals by means of a small screw clamp, and the effects produced were studied by viewing along the x axis. Fig. 6(a) shows sketches of a crystal initially composed only of [010] and [001] twins subjected to successively increasing pressure P. As the pressure increases the [001] twins (having c perpendicular to the compression) grow in volume at the expense of the [010] twins (having c parallel to the compression) by a migration of the twin boundaries in a direction perpendicular to their own plane. The boundaries become progressively less numerous, and in the later stages, observation of the colour contours provides increasing evidence of the presence of [100] twins, until eventually the appearance of the whole crystal is that expected from a combination of [001] and [100] twins only, as shown in the last sketch of Fig. 6(a). Irregular strain effects are also frequently observed.

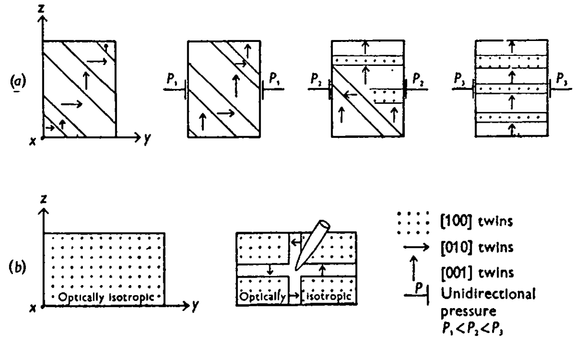

Fig. 6. Diagram showing the effect of unidirectional pressure on BaTiO$_3$ crystals. (a) Simply-twinned crystal having [010] and [001] twins only. Pressure applied along y axis. (b) Single crystal with c parallel to x. Point pressure applied along x.

The boundary migration may be by way of a sudden jump, but is often quite slow, and after application of the pressure, 1 or 2 sec. may elapse before equilibrium is attained, while further small variations may be observed after some hours. Relaxation of the pressure tends to reverse the process, but the crystal rarely returns to the original condition, and usually retains some [100] twins. Repeated compression and relaxation causes an increase in the number and complexity of the twins, but a small 'annealing' effect is observed afterwards.

Point pressure applied along the x axis of a perfectly single [100] crystal produces a birefringent cross of [010] and [001] twins on a dark background corresponding to the remaining [100] twins, as shown in Fig. 6(*b*).

As the temperature of the crystal is increased it becomes more susceptible to applied pressures, and above the transition point, when the crystal is normally isotropic, small pressures will make it anisotropic. The experiments suggest that unidirectional pressure will raise the transition temperature of a single crystal.

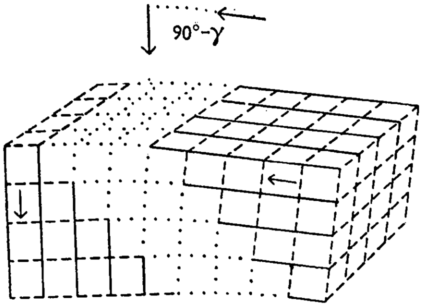

Fig. 7. Probable lattice array occurring at a twin boundary in $BaTiO_3$. Continuous lines show c directions of unit cells, broken lines show a or b directions, and dotted lines show slightly distorted near-cubic lattice at the boundary.

These experiments show that the compressibility of c is greater than that of a, which is to be expected in view of the relative atomic density in these two directions. When pressure is applied along the c axis it presumably forces the cell into a slightly distorted cube of roughly the same volume, which then forms a new c axis in another cube axis direction offering less resistance. This process occurs as a twin boundary migrates, so that the boundary itself consists of a layer of slightly stress-distorted cells as depicted in Fig. 7. Support for this suggestion is obtained from X-ray photographs of materials having a vast number of very small twins, which show anomalous scattering at positions on the film corresponding to diffraction from material with a cubic structure of the same volume as the tetragonal structure.

It should be possible to produce single crystals from twinned crystals by simultaneous pressure along the x and y directions, especially if the crystals are at the same time cooled slowly through the transition temperature. Preliminary experiments were unsuccessful, owing probably to manipulative difficulties associated with the very small crystals available.

Effect of electric fields

Electric fields were applied along the y direction between opposite cube faces of well-formed crystals, and the effects were studied microscopically by viewing along the x direction.

Application of a d.c. field encourages the preponderance of [010] twins, i.e. those having c parallel to the field. As in the case of compressional stress, the reorientation is effected by a migration of the twin boundaries in a manner similar to that depicted in Fig. 6(*a*), except that the relative proportion of [010] to [001] twins increases in this case. The effects of electric and compressional stresses are in opposition, and greater fields are required to produce the same degree of orientation if the crystal is compressed parallel to the field direction.

The stronger the field the more effective is the alining process, and, if care is taken to ensure that the electrodes do not apply any mechanical stresses, complete saturation may be obtained in the case of small simply-twinned crystals, i.e. c becomes completely oriented in a direction parallel to the applied field and all boundaries disappear. The voltage required for saturation depends on the complexity of the specimen and the time of application of the field, the process being encouraged if the field is occasionally relaxed slightly. When the field is completely relaxed the crystal may remain perfectly single if complete saturation was previously achieved, but more often partial relaxation of the orientation occurs, although the crystal never returns completely to its original twin configuration. A crystal composed entirely of a [001] component changes to [100] by the sudden appearance, in parts of the crystal, of diagonal twin boundaries which proceed to migrate in the usual way. In such a case, complete reorientation through 90° and saturation have been achieved with 15,000 $V.cm.^{-1}$.

Slow reversal of the field usually allows some [001] twins to appear, and these finally reorient in the opposite direction parallel to $-z$, but reversal of the field applied to a completely saturated crystal may show no visible effect, i.e. the domains reorient through 180° directly. If the field is rapidly and repeatedly reversed, other twin directions invariably occur, and saturation cannot be achieved so readily. Increasing the frequency to 50 $cyc.sec.^{-1}$ renders the crystal much more opaque, owing to the decrease in domain size and the increase of relative proportion of boundary material. The boundaries are seen to be in a state of violent agitation, and stresses involved with high voltages often crack the crystal in an irregular way which does not obviously conform to single crystallographic directions.

As the temperature is raised the orientation becomes more sensitive to applied electric stress, but the crystal rapidly becomes semi-conducting and stable d.c. conditions of field are difficult to obtain. Just above the transition temperature a d.c. field will produce strong birefringence in the crystal, indicating that the field may force the crystal back to the polar state with c oriented along the field. The application of a strong field may therefore be expected to raise the transition temperature.

X-ray photographs were taken of small ($\sim$0·4 mm.) crystals which were subjected to electric stress. Opposite cube faces were silvered and the crystal was supported by two thin copper wires mounted on the goniometer head of a standard single-crystal camera. The crystal was oscillated 15° about the z axis with the X-ray beam nearly parallel to the x axis at the extremity of the oscillation. This gave high-angle groups {500} and {510} with Cu K radiation. Only the zero layer line was recorded so as to allow multiple exposures on the same piece of film. Fig. 2 shows the high-angle portion of a series of such photographs, and Table 1 indicates the field applied during successive exposures.

Table 1. *Electric fields corresponding to the photographs of Fig.* 2

Exposure	Field in V.cm.$^{-1}$	Time sequence
1	0	
2	3,000 d.c.	
3	6,000 d.c.	
4	12,000 d.c.	
5	15,000 d.c.	
6	$-$15,000 d.c.	
7	0	15 min. after (6)
8	0	40 min. after (6)
9	3,000 50 cyc.sec.$^{-1}$ a.c.	
10	6,000 50 cyc.sec.$^{-1}$ a.c.	
11	7,500 50 cyc.sec.$^{-1}$ a.c.	
12	0	
13	16,500 d.c.	
14	16,500 d.c.	15 min. after (13)
15	16,500 d.c.	11 hr. after (13)
16	0	15 min. after (15)
17	0	1 hr. after (16)
18	0	24 hr. after (17)

Although the crystal contained all twin orientations, the (100) face exposed to the X-rays fortuitously contained only [100] twins having c parallel to the incident radiation, and other twins below the surface did not contribute reflexions because of the heavy absorption ($\mu = 1540$ cm.$^{-1}$). Only reflexions 005 and 105 are therefore recorded in exposure (1).

Application of 3000 V.cm.$^{-1}$ produces a small [010] component (with c parallel to the field) as shown in exposure (2) by the appearance of a faint 501 reflexion. Exposures (3), (4) and (5) show increasing proportions of [010] components as the field is increased to 6000, 12,000 and 15,000 V.cm.$^{-1}$ respectively. Parameter measurements are not of high absolute accuracy, but measurement of the films shows with certainty that c/a increases with increasing d.c. field, as can be seen by the increasing separation of reflexions 105 and 501 of exposures (2)–(5). This variation of c/a results primarily from an extension of the c-parameter while the a-parameter remains sensibly constant, and is further demonstrated in exposure (6) in which the reversal of the maximum applied field causes a large spread of the 105 reflexion while the 501 reflexion remains sharp. The cell volume, therefore, increases when a field is applied, a fact which must be interpreted as an electrostriction effect, and a block of $BaTiO_3$ will expand in the direction of an applied field owing both to the reorienting of twins with c along the field, and to the increase of c/a.

When the voltage is reduced to zero, relaxation of the crystal is very slow provided it is kept in a closed electrical circuit. Exposures (7) and (8) were taken 15 and 40 min. respectively after removal of the field, and exposures (16), (17) and (18) are further examples taken 15 min., 1 hr. and 24 hr. after the field had been removed. On the other hand, relaxation proceeds as far as it ever will within the 15 min. of the first exposure if the crystal circuit is 'broken'. The analogy to a 'keeper' in the ferromagnetic case is evident. Exposures (13), (14) and (15) taken after a fixed d.c. field had been applied for 15 min., 30 min. and 11 hr. show a sharpening of the 105 reflexion, indicating a gradual attainment of equilibrium.

The effect of applying 50 cyc.sec.$^{-1}$ a.c. voltages of 3000, 6000 and 7500 V.cm.$^{-1}$ is seen in exposures (9), (10) and (11), and greater a.c. fields aline a greater proportion of the twins parallel to the field. The average c/a value is less than for corresponding d.c. voltages, and the crystal rapidly settles down to an equilibrium condition which does not vary with the time of application of the field.

These experiments show that individual twins are ferro-electric domains having an electric dipole parallel to the c axis. It may be that each individual twin is composed of smaller sub-units with c axes in antiparallel orientation, a condition which would not be observable by X-ray or optical methods, but this seems unlikely.

Effect of temperature

The effect of temperature changes on the crystals was investigated by both optical and X-ray methods.

The transition near 120° C.

In order to ensure uniform temperature in the optical observations crystals were placed in a massive, well-lagged copper chamber having small glass apertures to transmit light. This was placed on the microscope table together with a small heating stage.

It was found that as a crystal is slowly heated the birefringence decreases, and very near to the transition temperature the twin boundaries often become slightly curved, i.e. they no longer conform exactly to simple crystallographic directions. At this same temperature some of the boundaries begin to migrate irregularly through the crystal. As the symmetry transition takes place, parts of the crystal become optically isotropic, the proportion of isotropic material increasing until the transition is complete. On cooling, the crystal returns to a composite of tetragonal twins whose arrangement usually varies after each cycle; the more rapid the cooling, in general, the greater the complexity. There is no fracture or obvious reduction in the crystal strength, however often the cycle is repeated.

After repeated cycles, performed very slowly, the twinning becomes less complex, i.e. the average number of twins decreases, and the average volume of each twin component increases. There is, therefore, an annealing effect if the transition is continually repeated, but slow cooling by itself has rarely produced truly single tetragonal crystals. This is probably due to strain centres resulting from local lattice imperfections characteristic of each individual crystal.

For X-ray photographs at different temperatures it was considered essential to use a crystal with minimum twin complexity. The specimen was a thin flake of dimensions parallel to x, y and z of 0·02, 0·28 and 0·8 mm. respectively, composed essentially of a perfect [100] single crystal except for three [001] twin lamellae extending across the plate in the y direction (Fig. 10 (*a*)). The crystal, and thermocouple placed 2 mm. from it, were surrounded by a small cylindrical heater, with temperature control of the thermocouple to $\pm 0{\cdot}1°$ C. Further details of this and other apparatus used in these researches are to be found elsewhere (Kay, 1947). The crystal was oscillated about z, with the beam nearly parallel to the x or y axis at the extremity of the oscillation, thus giving reflexions 005, 500, 105 and 510 at high angles with Cu K radiation.

A series of seventy-eight photographs was taken at temperatures from 18 to 200° C. A multiple-exposure technique was employed giving only the zero layer line, and a photograph at room temperature was taken on each film to provide a standard of known parameter. Fig. 3 shows a series including the transition for both increasing and decreasing temperatures. The high-angle group of reflexions 105 and 510 is sketched in Fig. 8 with a common θ abscissa in order to clarify the discussion.

The crystal was principally composed of the [100] component, so that the high-angle reflexions are 105 and 005, as seen in the exposure at 90·6° C. A very faint 510 reflexion can be observed from the small [001] twins. At 110·6° C., θ_{105} has increased, i.e. c has decreased. At 111·2° C., c has again decreased very slightly, but a faint satellite has appeared above it with a higher θ value. This is the 150 reflexion from cubic material; the faint tetragonal 510 reflexion is seen to occur with θ_{510} slightly greater than θ_{150}. This is not easily visible in Fig. 3, but ample evidence has been obtained of the occurrence of tetragonal 105 and 510 reflexions together with the cubic 150 reflexion. At 113·2 and 114·4° C. the reflexions 105 and 150 remain at the same angle θ, but a greater proportion of cubic material is indicated by the increase in relative intensity of reflexion 150. At 116·1° C. the transition is complete, only reflexion 150 is present, and this is the case up to 117·8° C. and higher temperatures.

If the temperature is reduced to 114·4° C. about 20 % of the volume has reverted to the tetragonal phase, as is seen from the relative intensity of 105 and 150 reflexions. At 113·1° C. about 50 % is tetragonal, compared with 95 % tetragonal at this same temperature on heating; this demonstrates the phenomenon of temperature hysteresis. At 112·2° C. the transition is complete, and at 20° C. the crystal again consists largely of the [100] component, but the doubled 510 reflexion indicates a slightly different distribution of twin orientation in that the angle γ occurs in both a positive and negative sense in the plane (010).

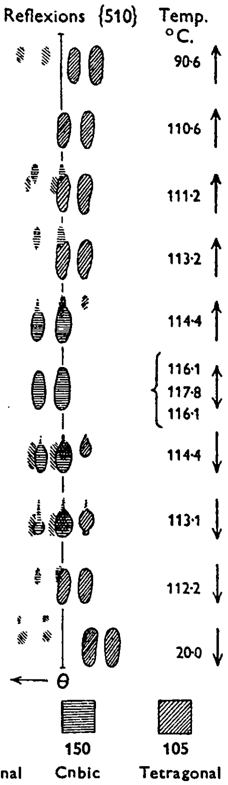

Fig. 8. Sketches of the high-angle group of reflexions occurring in the series of photographs shown in Fig. 3 reduced to a common θ abscissa. Reflexions of different indices are shown differently shaded. Faint reflexions are not bounded. Arrows indicate rising or falling temperatures.

It is impossible to differentiate between 510 and 501 tetragonal reflexions because of their small difference in spacing, so that the occurrence of small amounts of [010] twins at some stage of the transition cannot be completely excluded. The changes in distribution of intensity perpendicular to the layer-line indicate the bodily reorientation of small units of the crystal at the transition.

All photographs reveal that there is a minimum separation of tetragonal 105 and cubic 150 reflexions, and also of tetragonal 510 and cubic 150 reflexions. This indicates a discontinuity of c/a with temperature, i.e. the transition is effected by a change in the relative proportion of two different phases within the same crystal, rather than by a continuous and gradual approach of the tetragonal a and c parameters to a common cubic parameter. At the transition the tetragonal parameters are $a=4\cdot0051\pm0\cdot0008$ A., and $c=4\cdot0206\pm0\cdot0007$ A., and the cubic parameter is $a=4\cdot0096\pm0\cdot0002$ A. The minimum value of $c/a \neq 1$ is $1\cdot0039\pm0\cdot0002$. There is no change in volume of the two phases within the experimental error of $\pm0\cdot1$ (A.^{3}), but more accurate measurements are intended. Fig. 9 shows the parameter values plotted against temperature, and the accuracy throughout is of the same order as that quoted above. The temperature scale has been adjusted to make the transition temperature conform with the results of the more accurate optical measurements, and it should be noted that this is lower than that usually stated for powder materials, a consequence which may result either from small compositional differences or from the intense strain effects inherent in polycrystalline aggregates produced by the powder-sintering process.

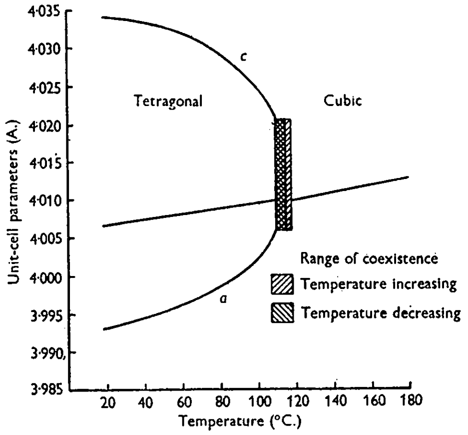

Fig. 9. Relation between cell parameters and temperature for a single crystal of $BaTiO_3$. The cube root of the cell volume is shown for the tetragonal phase. The tetragonal and cubic phases coexist in the shaded region.

Comparison, by eye, of the intensities of the tetragonal 105 and 005 reflexions (below the transition) with the cubic 150 and 050 reflexions (above the transition) gives no indication of a change in atomic coordinates between the two phases, although such reflexions would be most susceptible to any change of atomic co-ordinates along the c axis.

This same crystal was attached directly to a thermocouple within the microscope heating chamber, and when viewed along the x axis had the appearance shown in Fig. 10(a). When heated slowly the birefringence gradually decreased owing to the reduction in the value of c/a, and this became particularly noticeable above 65° C. The twin boundaries became less distinct at 100° C., and at 108° C. the [001] twins decreased in size, their contours becoming rounded. At the same temperature other irregularly shaped slightly birefringent patches having straight extinction appeared in the main [100] component (Fig. 10(b)). The boundaries of these regions were diffuse and only rarely coincided exactly with any simple crystallographic direction. These patches migrated irregularly over the crystal as the temperature increased (Fig. 10(c)), becoming smaller and fainter, and eventually disappeared leaving the crystal completely isotropic at 117·4° C. (Fig. 10(d) and (e)).

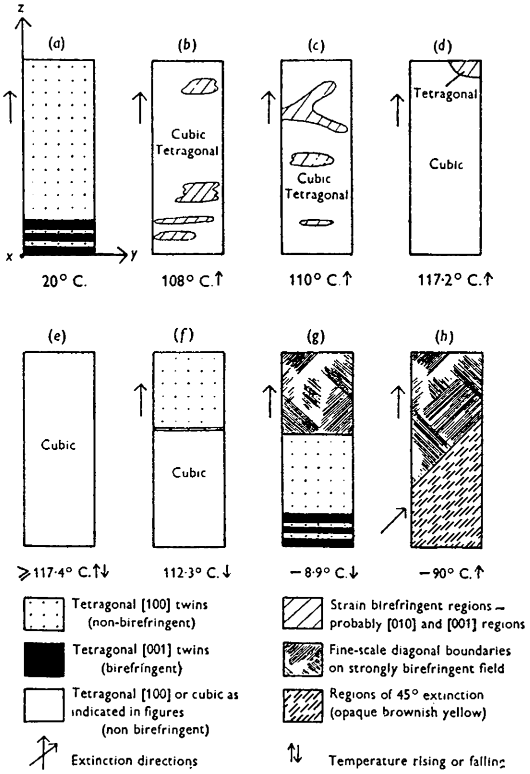

Fig. 10. Appearance between crossed nicols in a thin flake of $BaTiO_3$ at different temperatures.

An unambiguous interpretation of these phenomena is at present impossible, but it is probable that the following explanation is correct in general outline. The [001] twins transform early in the process, since their a directions are parallel to the thinnest dimension of the plate and so are able to expand as the transition temperature is approached, and no restriction is placed on the associated contraction of c. On the other hand, the large [100] twins have both a and b in the plane of the plate and the necessity for their expansion opposes the transition. The migrating birefringent patches occur when the two phases coexist. The discontinuous transition from tetragonal to cubic symmetry of any small region of the large [100] component will necessitate a local expansion of this area, since the plane of the plate includes the expanding a and b cell dimensions. This will result in stresses restricting the transition of neighbouring portions of the [100] tetragonal component, thus explaining the temperature range of the transition, and will result also in the reorientation of small regions of tetragonal material in such localities as might tend to relieve the stresses involved. This local reorientation from [100] to [010] and [001] directions produces birefringent patches with 'straight' extinction which disappear as they in turn become cubic and the transition proceeds from the area. The X-ray photographs show a slight increase in the relative proportion of components other than [100] at temperatures within the transition range.

The coexistence of two phases, for which there is no common lattice parameter, cannot be quite analogous to the coexistence of two orientations of the same phase in which the boundary is composed of slightly curved lattice rows, each row having the same distortion as the boundary is traversed. The tetragonal–cubic boundary must be composed either of a series of 'dislocations' or 'faults' occurring on an average at least once in a thousand unit cells

$$(a_{\text{cubic}}/(a_{\text{cubic}} - a_{\text{tetragonal}}) = 1081),$$

i.e. about every 4×10^{-5} cm., or the boundary must be composed of continuous unfaulted lattice rows having strains which vary considerably from point to point of the boundary. In either event the observed differences and irregularity of the transition might be expected, together with the obvious extreme susceptibility to crystal flaws and strain centres.

If the temperature is reduced from above the transition, the phenomena are not exactly reversed. No analogous strain patches are observed to migrate over the crystal, and the transition occurs in sudden jumps in which relatively large areas suddenly become tetragonal (Fig. 10(*f*)). This is explicable when it is remembered that whereas both cubic–tetragonal and tetragonal–cubic transitions produce anisotropic stresses in the surrounding lattice, thus favouring some symmetry other than cubic, only in the case of decreasing temperature is the stable phase anisotropic, and in this case temperature change and strain effects will tend to co-operate and produce the anisotropic phase. The temperature range of transition might therefore be expected to be less in the case of falling temperature, as is found to be the case.

The transition to the original (or very nearly the original) twin arrangement is complete at 109·8° C. after about three jumps, but the small [001] twins always persist for no apparent reason. This indicates the probable existence of local strain centres characteristic of this crystal, perhaps arising from the circumstances of the formation of the crystal from solution.

Summarizing the results of these experiments, we may say that for rising temperature the temperature range of transition is 109·6 to 117·5° C., while for falling temperature it is 114·8 to 109·8° C. The mean transition temperature is thus 112·9° C., and the temperature ranges are 7·9 and 5·0° C. for rising and falling temperatures respectively. The magnitude of the temperature hysteresis of the all-cubic condition is 2·7° C. (=117·5 – 114·6° C.), whereas there is no appreciable hysteresis for the all-tetragonal condition (109·8 – 109·6° C.). This difference may well be due to the strain associated with the twin boundaries in the low-temperature state.

Low-temperature changes

On cooling the specimen below room temperature, by dripping liquid air on to the thermal lagging of the specimen chamber, another crystal change was seen to occur in the range –8·0 to –9·8° C. (=1·8° C.) for decreasing temperature, and in the range 0·6 to 0·8° C. (=0·2° C.) for increasing temperature. The mean transition temperature is –4·1° C., and the mid-points of the temperature ranges of the transition have a hysteresis of 9·6° C.

For both rising and falling temperature the transition occurs very suddenly in jerks, in which small areas of the crystal change their optical appearance radically. For decreasing temperature, areas of the [100] component (which appear isotropic) suddenly become strongly and non-uniformly birefringent. Such areas are characterized by a criss-cross array of fine-scale dark boundary lines which suggest very small twins (~0·0005 mm.) of the type [001] adjacent to [010] (Fig. 10(*g*)). When the whole crystal has transformed, further cooling increases the birefringence. On heating, the phenomena are exactly reversed, but at –4·0° C. the fine-scale boundaries become unstable and begin to move bodily in directions normal to their own plane. This is probably a slight annealing effect. The transition proper then commences at 0·6° C.

It is very probable that a further discontinuous change in cell parameters occurs at these temperatures, and the cell symmetry may no longer be tetragonal, for present evidence suggests that the material is biaxial. The large separation of the transition ranges for rising and falling temperatures, and the small transition range in each case, indicate that the change is much smaller than that occurring at 113° C., while the narrower range for increasing temperature suggests that the distortion from isotropy is greater above the transition than it is below, i.e. the unit cell probably becomes more nearly cubic as the temperature is reduced through the transition, and then the distortion probably increases as shown by the increasing birefringence.

At even lower temperatures a further transition occurs in the range –92 to –89° C. (±0·5° C.), which has been measured for rising temperature only. As in the previous two cases, two phases coexist in the crystal and the transition is jerky and occurs in blocks as indicated in Fig. 10(*h*). Above –89° C. the crystal shows bright birefringence colours with closely spaced diagonal boundaries, and with the extinction direction parallel to the cube edges as in all cases discussed so far. The phase in equilibrium below −92° C., however, shows no signs of twin boundaries, and the birefringence colours have disappeared leaving a rather opaque, brownish yellow crystal which shows extinction inclined at 45° to its previous direction. The crystal remains in this condition down to the lowest observed temperature of −183° C.

X-ray photographs taken at −183° C. with this crystal oscillated about the z axis show the same general pseudocubic diffraction array as that which occurs at room temperature, but the spots are extremely diffuse and are elongated particularly along the layer-lines. This diffuseness cannot be explained in terms of temperature variations, and must result from large strains which occur particularly in the cube-axis directions. It is impossible to determine whether the symmetry is really tetragonal or otherwise, but if it is tetragonal, then $c/a = 1{\cdot}002 \pm 0{\cdot}001$ with $a = 3{\cdot}990 \pm 0{\cdot}002$ A.

These detailed observations at various temperatures were made on a thin crystal flake composed almost entirely of a single [100] domain. Thicker crystals cannot be studied in such detail owing to the overlap of twins and the complicating factor of the existence of more than two twin orientations which tend to make the transition more diffuse and strained in character. Furthermore, although identical phenomena have been observed in similar crystals, others show more complex characteristics. For instance, many crystals show gradual and very diffuse transitions for both increasing and decreasing temperatures, but the evidence suggests that in such cases dissolved impurities cause such a large number of lattice strain centres that local 'supercooling' and 'hysteresis' effects become impossible. In addition, each crystal shows features which depend on its own characteristic array of imperfections laid down during formation from solution. Further investigation of a large number of crystals is in progress, and it seems probable that a complete interpretation will be arrived at only by a study of the properties of the single domain.

Fuller details of the research into the production and properties of $BaTiO_3$ and related compounds, together with a more comprehensive survey of the literature, are to be found elsewhere (Kay, 1945, 1947).

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