MULTIPLE GROWTH TWINNING IN BaTiO$_3$ SINGLE CRYSTALS

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Abstract

A novel form of multiple growth twinning in BaTiO$_3$ single crystals is described. The crystal contains three (111) primary twin planes and one (115) secondary twin interface. The twinned crystal appears to have grown from a nucleus which contained all the twin elements and not by successive twinning separated by intervals of growth. From a hard sphere model of the various forms of growth twinning in BaTiO$_3$, it is suggested that TiO$_6$ octahedra can share up to two faces.

Introduction

The purpose of this paper is to describe a novel form of multiple (111) growth twinning (spinel type) in BaTiO$_3$; to propose some ideas relative to its origin; and to call attention to the type of packing of TiO$_6$ octahedra necessary for multiple twinning in this compound as deduced from a hard sphere model.

Description of the Twin Crystal

A twin crystal which is occasionally found in the crystal assemblage grown from a supersaturated KF-BaTiO$_3$ solution (the Remieka (1954) technique) is illustrated in plan and perspective views, and photographs of the crystals are shown in Fig. 1.

The crystal can be considered as consisting of a twinned spine from which have grown flat plates bounded by {100} faces.* The (111) plane is both the twin plane and composition plane just as has been described for the more common "butterfly" twin. Curien and LeCorre (1955) and White (1955). The plates are identical to the wings of the usual butterfly twin crystals; contrary to the latter, the wings are not paired but alternate right and left along the axis. When viewed down the axis of the spine a V-shaped cross section is seen if the wing growth is approximately equal on both sides (upper plan view, Fig. 1*a* and Fig. 1*b*). In many crystals however, the wing has grown essentially on only one side (lower plan view, Fig. 1*a* and Fig. 1*c*); *i.e.*, in the plan view the wings on one side are very poorly developed. The terminal end of the spine is a (110) plane common to all members of the twinned crystal. In Fig. 2 are shown {110} sections taken along the length of the spine and transverse to the spine axis of a typical multiple twin. The sections were etched and polished simultaneously using a technique described by Kontoleon and

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* BaTiO$_3$ is tetragonal at room temperature, but the crystals are grown in the stability region of the cubic phase and all discussion is in terms of the cubic system.
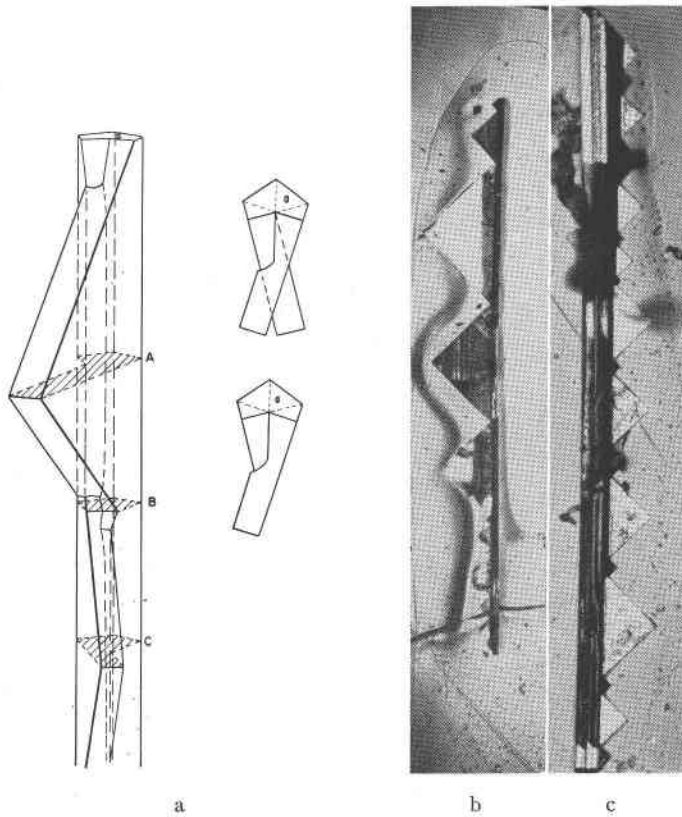
FIG. 1(a). Plan and perspective views of a multiple twin of BaTiO$_3$. The position of the (111) twin planes are shown as light dashed lines in the plan view only. A, B, and C are the approximate locations of the sections in Fig. 2. With the exception of the face "a" which is a (110) plane, all planes are {100}.

(b and c).—Side views of actual twinned crystals. (b) Wing development approximately equal. The small triangular wing at the top points into the plane of the paper; the wing below is tilted slightly up from this plane and so on down the length of the crystal. ×33. (c) Wing development very unequal. The large plates point slightly into the plane of the paper; these alternate with the small wings which are tilted upward. ×140.

Hurd (1956). The sections illustrate the change in crystal shape from one wing to the next where the wing development is approximately equal; Fig. 2b is essentially a section of the spine alone. Three {111} twin plane traces (made visible by etching) divide the crystal into four parts and the relationship to the usual butterfly twin (two twin plane traces) is made clear by comparison with Fig. 3, which is a similar polished section of a typical butterfly twin.
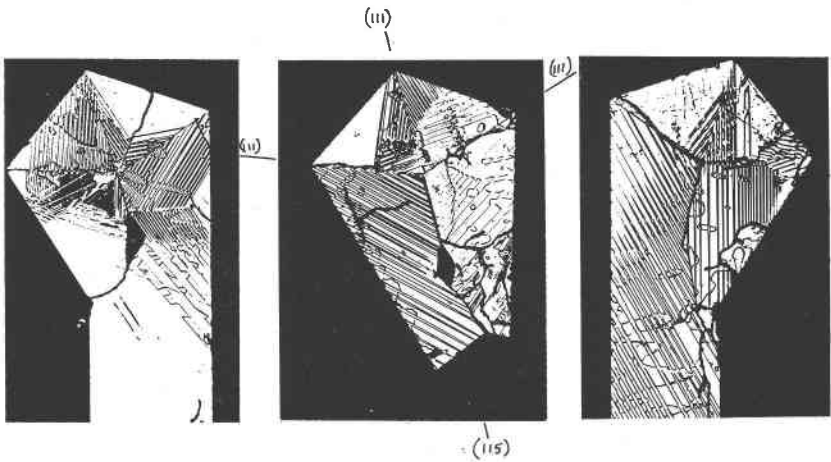
FIG. 2. Polished and etched sections of a multiple twin. Approximate positions of the sections relative to the crystal are given in Fig. 1. The main features of interest to the discussion are indicated. The fine twin structures which show discontinuities at the (111) and (115) traces are (101) tetragonal twins. ×210.
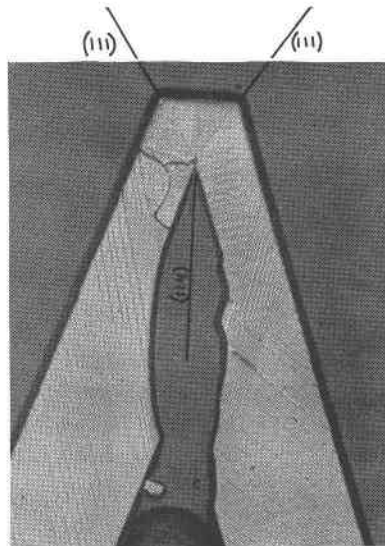

FIG. 3. Cross-section of a typical "butterfly" twin crystal with two (111) twin planes. The "wings" do not converge to form an interface as in the twin with three twin planes. ×50.

In contrast to the usual butterfly twin in which an interface between the wings does *not* develop DeVries (1959) (the most simple interface would be (114)), in the multiple twin under consideration, rapid growth in a [110] direction of the outer wings causes them to converge and a crystallographic interface (115) is formed. As a result, the two outer members of the multiple twin are related as if they were twinned across this plane. As would be expected this interface etches much more easily than the lower energy (111) twin interface. The length of the (115) trace as seen on {110} sections (Fig. 2) varies from a maximum near the region between alternate wings to a minimum near the center of a
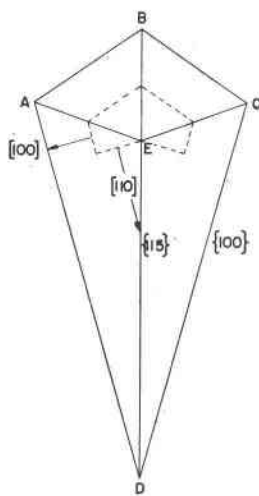

Fig. 4. Ideal cross-section of the multiple twin. AE, BE and CE are traces of (111) twin planes; DE is the trace of a (115) plane. The form described by dashed lines is considered in the text. All external faces are {100}.

wing; in contrast to this variation the length of the {111} traces is essentially constant throughout the length of the crystal. A cavity is often found at the end of the (115) trace (but none has ever been found at the intersection of the twin traces), and the remainder of the grain boundary between the outer members of the twinned crystal is usually noncrystallographic, although occasionally the interface is more regular as seen in Fig. 2a.

As a result of the geometry of the spinel type twinning in the multiple twin of BaTiO₃, the (115) interface is coincident with the central (111) twin plane. The traces of these planes are conveniently shown on a (110) section because all the planes involved are perpendicular to this section, and Fig. 4 is used to prove the coincidence of the (115) and (111) traces.

Thus, given the angle $\{111\} \wedge \{100\}$ equals $54°44'$ (*e.g.*, angles EBC, ECB, ECD) it can easily be shown that the angle EDC of Fig. 4 as computed by difference from $180°$ in the triangle BCD (formed by the extension of BE) is identical to the calculated interfacial angle between $\{115\}$ and $\{100\}$; *i.e.*, $15°48'$.

GROWTH OF THE TWINNED CRYSTAL

It has been established that some of the multiple twins are formed late in the crystallization process; for example, they are found in random orientation on top of the large butterfly twins. However, some have probably grown at the same time as the usual butterfly twins. The microstructural features suggest that the crystal grows from a nucleus which contains all the twinning elements rather than by repeated twinning separated by periods of growth.* If the latter were true, it would be difficult to explain the equal length of the $\{111\}$ traces, the overall symmetry of the cross sections about the (115) trace, and the consistent absence of voids at the center. It seems more reasonable to describe the end result in terms of growth outward from a twinned nucleus.

If it be assumed that in the early stages the crystal has a $\{100\}$ habit with $\{111\}$ twin planes, the outline as seen on a (110) section would be represented by the dashed line of Fig. 4. The potential "wing" portions of this crystal are free to grow rapidly outward along [110] directions (as is characteristic of $BaTiO_3$ grown from a KF flux) while the $\{100\}$ faces grow more slowly. Since the (115) interface does form, there also exists the possibility of the re-entrant angle at E (Fig. 5) serving as a deposition site. As a result the growth rate along the (115) plane would be increased, and at some stage in the growth process the symmetrical form illustrated by the solid lines of Fig. 4 would be reached provided there is no marked anisotropy in growth rates of the potential wings in the [110] direction shown in the figure. Since the alternating wing habit does form, an undefined singularity in growth conditions is assumed. For example, this singularity might be an external condition such as a concentration gradient or a poisoning effect; or it might be an internal singularity such as a dislocation. Whatever the condition which causes one wing to grow more rapidly than the other, the more rapidly growing side serves as a barrier to further growth of the other side, and a noncoherent boundary is formed. The more rapidly growing wing reaches a maximum size which is a resultant of growth both along and away from the spine, and the com-

* This is in contrast to the previously reported Kontoleon and Tomlinson (1956) sequence of events in doubly twinned [211] dendrites and in some butterfly twins in which twin planes are definitely separated as would occur during a period of growth of individual members of the twinned crystal.

pletion of the growth of one wing removes the restriction to growth of
its opposite as the spine advances. Equal development of alternating
wings suggests that neither one has either an internal or external singu-
larity in growth conditions and therefore no marked difference in growth
rates. However, many crystals show very unequal wing growth (i.e., one
side developed almost exclusively, Fig. 1c and lower plan view Fig. 1a)
and barring anisotropic conditions related to position in the solution, *e.g.*,
near sides of the crucible, it is suggested that these crystals most likely
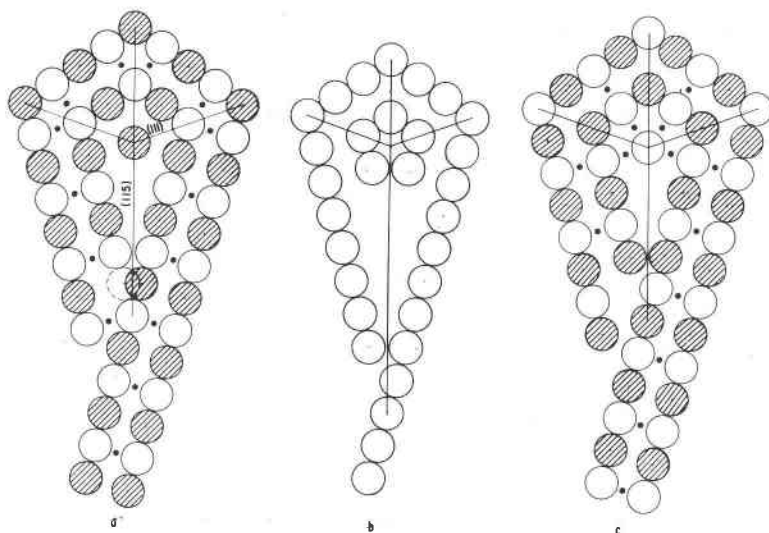have a dominant internal singularity.

FIG. 5. Arrangement of atoms on {110} sections of a multiple twin of BaTiO₃. The
significance of the traces is as previously described. Open circles = oxygen; shaded circles
= barium; solid dots = titanium. Repeated stacking of these layers in the sequence *a, b, c*
develops the multiple twin structure. The central Ba²⁺ and O²⁻ ions of *a* and *c*, respectively,
form a Ba-O-Ba-O chain common to all parts of the twin and the coordination around the
Ba²⁺ ion is shown in Fig. 6.

DEDUCTIONS FROM THE HARD SPHERE MODEL

Oxygen coordination around Ba²⁺

{110} sections showing the atomic arrangement in a hard sphere
model of the twinned crystal are shown in Fig. 5. Repetitive stacking of
these layers in the sequence shown results in a central Ba-O-Ba-O chain
common to all members of the twin. Furthermore, in contrast to the
normal 12-fold cubo-octahedral (f.c.c.) and 12-fold twinned cubo-octa-
hedral (h.c.p.) packing of oxygen ions around a Ba²⁺ ion in untwinned

and singly-twinned crystals, respectively, the 12-fold coordination around a Ba^{2+} ion in the common chain is in the form of a pseudo-pentagonal prism with pyramidal ends (Fig. 6).

Face-sharing arrangements in TiO_6 octahedra

The close approach of Ti^{4+} ions at the twin planes in comparison to the normal Ti-Ti distance is also shown in the {110} sections. In terms of Ti-O groups, the basic unit at the twin plane is the Ti_2O_9 group formed by face-sharing of two TiO_6 octahedra; such a coordination is also found for 2/3's of the octahedra in the hexagonal modification of $BaTiO_3$. Burbank and Evans (1948). The variations in multiple (111) twinning in
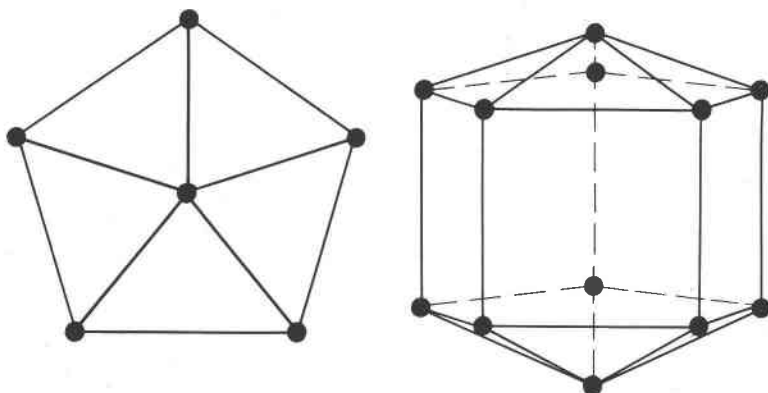

FIG. 6. Plan (left) and perspective view (right) of the type of arrangement of oxygen ions (solid dots) around a barium ion (not shown) common to all parts of the twinned crystal. The packing is in the form of a pseudo-pentagonal prism with pyramidal ends.

$BaTiO_3$ can be described by other still more complex arrangements of TiO_6 octahedra. Thus, a Ti_3O_{12} (three face-shared TiO_6 groups) unit would be a descriptive nucleus of the ordinary butterfly twin (two twin planes); a Ti_4O_{15} group, the nucleus of the multiple twin described here; and the last possibility of this type, a Ti_5O_{18} group as a nucleus of a pseudo-pentagonal shaped crystal ($5 \times 70° \ 32' = 352° \ 40'$) with four {111} twin planes. Schematic illustrations of these arrangements are shown in Fig. 7.

If one considers the ways of stacking octahedra, it will be clear that there are several possible ways of putting together face-shared TiO_6 groups. From the previously reported structures and from the present description of the twinned crystals, the arrangements actually found are (1) face-sharing of two octahedra to form Ti_2O_9 groups as in hexagonal

$BaTiO_3$ and in simple (111) twins; (2) collinear groups of three face-sharing octahedra as found in some impure hexagonal barium titanate forms Burbank and Evans (1948) and (3) cyclic, coplanar groups in which an octahedron can share *two* faces as in the multiple twin described here and in "butterfly" twins (Fig. 7). No morphological evidence has been found which could be interpreted on the basis of the possible forms resulting from a complex group involving face-sharing on more than two faces. This probably represents a limit for this type of coordination for TiO_6 units.

From the external morphology of the twinned crystals it is possible to conclude which of the octahedral faces are more likely to be shared.
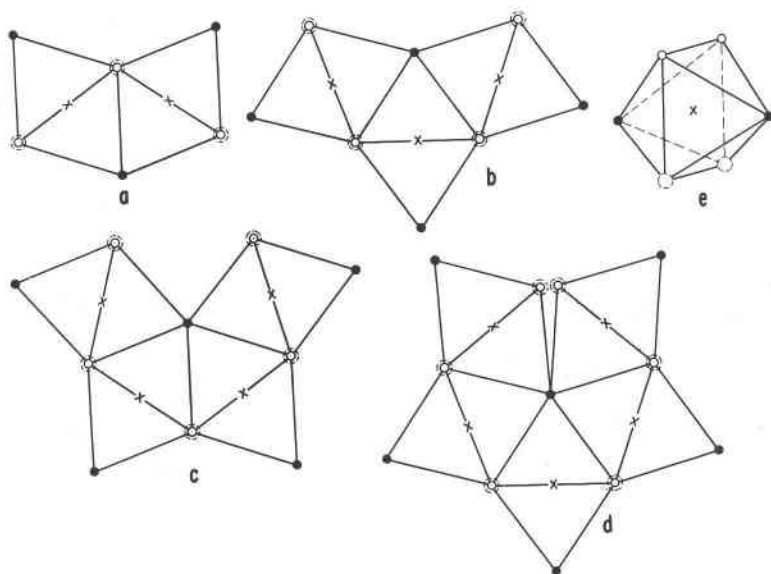

FIG. 7. Schematic representation of the different types of arrangements of TiO_6 octahedra from which the multiple twin structures can be developed. The arrangement of oxygen ions in the projections *a*, *b*, *c*, and *d* is shown in an octahedron in *e*. X = titanium. *a*, Ti_2O_9; *b*, Ti_3O_{12}; *c*, Ti_4O_{15}; *d*, Ti_5O_{18}. Sharing of more than one face of an octahedron is shown in *b*, *c* and *d*.

Given a Ti_2O_9 group formed from two octahedra in twinned relationship as shown in Fig. 8, one can conclude from the multiple twin structures that the faces of the type illustrated by BEC are face-sharing positions. However, there are no crystal forms which can be ascribed to face-sharing of faces of the type ABE or BCF which are sides of re-entrant angles resulting from twinning the octahedral habit. On these planes the orienta-

tion of new material is probably determined by nucleation at the re-
entrant angle growth site and a new twinned relationship would not be
energetically feasible until the crystal had grown somewhat larger. The
evidence for addition of material on the end face of the Ti_2O_9 group such
as CDE is derived not from morphological considerations but from
crystal structure work on impure forms of $BaTiO_3$ in which collinear
groups of three face-sharing octahedra have been reported Blattner *et al.*
(1948).

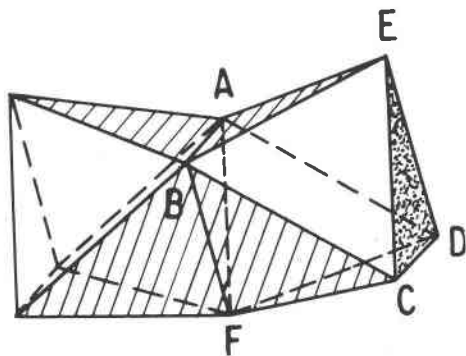Experimentally it has been qualitatively established, again using the

FIG. 8. Perspective view of two octahedra in twinned arrangement as in a Ti_2O_9 group.

external morphology criteria, that the rate of cooling influences which
type of face-sharing will take place in the $BaTiO_3$ structure. Thus under
rapid cooling conditions it is concluded that the single twin (one shared
face) form is the more stable on the basis of profuse amount of singly-
twinned dendrites and the metastable quenching of the hexagonal form
of $BaTiO_3$. Also with rapid cooling there occurs in some dendrites a type
of overgrowth which is related to face-sharing on end faces of the type
CDE (Fig. 8). With slow cooling the multiple twins (two and three twin
planes) predominate; *i.e.*, given sufficient time, the more stable sites for
further twinning are the faces of the type BEC. Why only the unique
cyclic pattern of twinning develops when other equivalent sites are
available is yet another interesting, unanswered question.

SUMMARY

A multiple spinel twin of $BaTiO_3$ with four (111) twin planes grows
from KF-$BaTiO_3$ solutions in the form of flat {100} plates alternating
right and left along an elongated common spine. From an interpretation
of the morphological features of the twinned crystals, it has been sug-
gested that this crystal grows from a nucleus containing all the twinning

elements. With a hard sphere model of this twin and the other variations of (111) twinning in $BaTiO_3$, complex fundamental groups resulting from face-sharing of TiO_6 octahedra can be described. It is suggested from these units and the types of crystals seen, that there is a maximum of two shared faces per octahedron and that certain faces of two octahedra in twinned relationship are more likely than others to participate in face-shared groups.

REFERENCES

BLATTNER, H., GRANICHER, H., KANZIG, W., AND MERZ, W. (1948), Die Kristallstruktur des hexagonalon und rhombischen Barium-Platinat-Titanats; *Helv. Phys. Acta* **21**, (5), 341.

BURBANK, R. D., AND EVANS, H. T., JR. (1948), The Crystal Structure of Hexagonal Barium Titanate; *Acta Cryst.* **1**, 330.

CURIEN, H., AND LeCORRE, Y. (1955), Butterfly-type Twins in Barium Titanate; *Bull. Soc. Franc. Mineral. Crist.*, **78**, 604–607.

DeVRIES, R. C. (1959), Observations on the Growth of $BaTiO_3$ Crystals from KF Solutions; *J. Am. Cer. Soc.*, **42**, (11), 547–558; also *G.E. Research Lab. RL*-2188.

KONTOLEON, D., AND TOMLINSON, J. (1956), Micro-examination of Barium Titanate; *Metal Progr.* **69** (No. 5) 98.

REMEIKA, J. P. (1954), A Method of Growing Barium Titanate Single Crystals; *J. Am. Chem. Soc.*, **76**, 940–941.

WHITE, E. A. D. (1955), Twinning in Barium Titanate Crystals; *Acta Cryst.*, **8**, 845.