Canadian Mineralogist
Vol. 16, pp. 347-352 (1978)

PENETRATION TWINS IN HEXAGONAL BARIUM TITANATE: A PROPOSED MODE OF NUCLEATION

HOWARD T. EVANS, JR.
U.S. Geological Survey, National Center 959, Reston, Va. 22092, U.S.A.

ABSTRACT

In a synthethic preparation of hexagonal $BaTiO_3$ many multiple penetration twins were observed. In the morphology of a fourling, based on reflection in $(10\bar{1}2)$, the four hexagonal plates imitate a cuboctahedron. Structural integrity is shown to exist across the normal composition planes $(10\bar{1}2)$ and $(\bar{1}014)$. It is proposed that such twin groups originate, not by overgrowth of a twin component on a crystallographically developed crystallite, but by crystallographic extension from a nuclear molecular group in which the double octahedral Ti_2O_9 group, characteristic of the hexagonal $BaTiO_3$ structure, occurs in four different orientations.

SOMMAIRE

Parmi les cristaux d'une préparation synthétique du $BaTiO_3$ hexagonal, on a observé beaucoup de macles multiples avec pénétration. Dans la morphologie d'un quadruplet où l'opération de macle est la réflexion dans $(10\bar{1}2)$, on distingue quatre plaquettes hexagonales simulant un cuboctaèdre. On montre que l'intégrité de la structure subsiste quand celle-ci franchit les plans d'accolement normaux $(10\bar{1}2)$ et $\bar{1}014)$. On émet l'hypothèse que l'origine de pareilles macles est à chercher, non pas dans la cristallisation d'un des cristaux de la macle sur cristallite porteur cristallographiquement bien développé, mais dans l'extension cristallographique d'un groupement moléculaire jouant le rôle de noyau, dans lequel le groupe bi-octaédrique Ti_2O_9, caractéristique de la structure hexagonale de $BaTiO_3$, se présente dans quatre orientations différentes.

(Traduit par la Rédaction)

INTRODUCTION

During the early years of the study of barium titanate as a ferroelectric substance, much effort was directed toward the preparation of single crystals, usually from carbonate or halide fluxes. Large crystals of the tetragonal form were readily grown from $BaCl_2$ fluxes (Matthias 1948), but the hexagonal form also appeared occasionally in small amounts. When $BaCl_2$ was replaced largely with Na_2CO_3 or K_2CO_3, hexagonal crystals predominated (Burbank & Evans 1948). Burbank & Evans described the crystal structure of this modification, which is centrosymmetric and without polar properties.

One of these early preparations yielded a group of multiply twinned crystals of hexagonal barium titanate (Fig. 1). These twins have interested the author, not only because of their striking beauty, but also because they suggest a possible mechanism for the genesis of penetration twins in general. The twin morphology of hexagonal $BaTiO_3$ and its probable mode of origin are described in this paper.

MORPHOLOGY AND TWINNING OF HEXAGONAL BARIUM TITANATE

Hexagonal barium titanate (point group $6/mmm$, $c/a = 2.4499$) typically forms hexagonal plates bounded by c $\{0001\}$ and m $\{10\bar{1}0\}$, bevelled by r $\{10\bar{1}2\}$ (Burbank & Evans 1948). Twinning occurs by reflection in r, commonly growing in penetration forms (Fig. 2a). A single crystal may be related to three other individuals by this twin law, occasionally resulting in remarkable fourling groups. The crystals are red in color, and all faces give sharp, bright optical signals. When equally developed, the four interpenetrating hexagonal plates form a cuboctahedron in outline, with reentrant depressions on each face (Fig. 2b). The measured optical signals show that the internal faces of these depressions, which correspond to the c faces of the various twin components, form dihedral angles of 109°28′, in accord with the twin law stated above. It is noteworthy that, although there are six equivalent planes r in a single crystal, twinning occurs only on three alternate planes.

TWINNING AND STRUCTURE

Much has been written concerning the relationship of twinning and lattice coherency (Friedel 1926, Cahn 1954). In order adequately to understand the twinning phenomenon, as Cahn in his comprehensive review of twinning

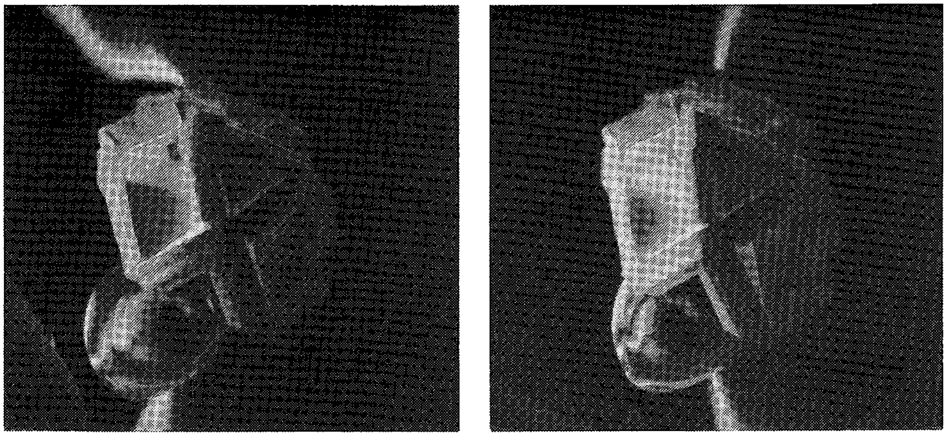

FIG. 1. SEM stereophotograph of a fourling of hexagonal $BaTiO_3$. The diameter of the cuboctahedrally shaped composite is 0.3 mm.

points out, a structural integrity must be found at the contact surface of crystal twin components. Then it may be said that the various lattice relationships that can be defined among twin components must follow as a corollary to this structural integrity.

The most common type of growth twin is that in which the two individuals meet in a crystallographic plane, the twin plane, which relates them by a mirror reflection. In the spinel crystal (perhaps even at nucleation), the is that of the oxygen layer in the cubic close-packed structure, and is common to both individuals. At some time in the growth of the spinel crystal (perhaps even at nucleation), the polar cation arrangement normal to (111) chose to orient itself on one side of this plane in a direction opposite to that on the other side. The structural integrity is maintained by the close-packed oxygen arrangement, which prevails unchanged throughout the twin edifice.

In terms of lattice planes, the components of such a twin have one crystallographic plane in common [(111) in spinel] in which the twin reflection takes place. But the same twin configuration will also be produced by a reflection in a plane normal to the plane of contact (composition plane), which may also correspond to a common lattice plane [$(11\bar{2}$ in spinel)]. In a contact twin, structural integrity will be required on only one of these planes, the composition plane, which is coincident with the twin plane.

In a *penetration* twin the same twin law prevails, but contact occurs on both the normal mirror twin planes. In some species (*e.g.*, staurolite) this type of twin is so prevalent that some additional structural criterion beyond that of the ordinary contact twin must be required. Sadanaga *et al.* (1963) emphasized that this additional criterion is the necessity of structural integrity over both composition planes. It seems obvious in the case of hexagonal $BaTiO_3$ that some mechanism of twinning beyond mere contact on one common structural plane is needed to account for the prevalence of such elaborate twin edifices as shown in Figure 1. Therefore, we must examine in detail both of the interfaces involved on an atomic scale. The corresponding twin lattice planes are $(10\bar{1}2)$ and $(\bar{1}014)$. In this lattice the angle between these planes is 90.01 ± 0.03°, and both may be considered as composition planes.

The crystal structure of hexagonal $BaTiO_3$ has been determined and described by Burbank & Evans (1948). They reported a hexagonal unit cell with *a* 5.735, *c* 14.05Å, and a structure in space group $P6_3/mmc$ based on six close-packed oxygen–barium layers. The sequence of layers is *ABCACB*, thus relegating the interlayer Ti atoms to both single octahedra and double, face-shared octahedra (Fig. 3). When we view this structure along the a_2 direction (twin plane on edge), we find that the oxygen–barium layers interact across the composition plane in a complex manner. One mode of coalescence (the only reasonable one) is shown in Figure 4. Extensive structural integrity can be seen to exist across both planes $(10\bar{1}2)$ and $(\bar{1}014)$. We observe, incidentally, that although the macroscopic twin law is a reflection in either one of these planes, the operation relating the crystal structures in the twin is a mirror operation in $(\bar{1}014)$ and a diagonal glide in $(10\bar{1}2)$.

Along the $(10\bar{1}2)$ contact we find a har-

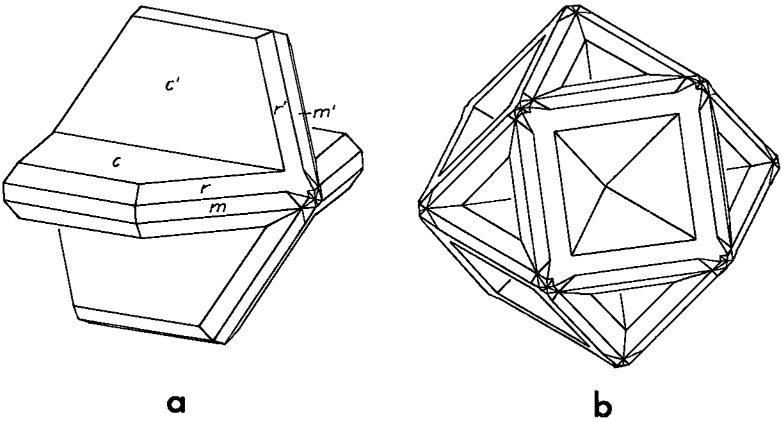

FIG. 2. Twinned hexagonal $BaTiO_3$: (a) typical habit showing c $\{0001\}$, m $\{10\bar{1}0\}$ and r $\{10\bar{1}2\}$, and a single twin on r; (b) a fourling as observed in Figure 1, consisting of three twins on alternate r planes of one crystal.

monious though somewhat complex interaction. Along the $(\bar{1}014)$ contact the interaction contains irregular regions, left as gaps in Figure 4. Much of the contact can be readily joined by local regions of cubic structure (between the gaps in Fig. 4), but periodically regions are encountered in which the regular arrangement of oxygen atoms is interrupted. Some compromise local adjustment of the structure could be postulated here, but not with any certainty. Thus, whereas considerable integrity does exist across the two composition planes, it does not appear to be complete. It is questionable whether this degree of matching of structure is enough to account for the imminent formation of the observed fourlings. Curien & Kern (1957) noted that penetration twins of fluorite may arise at the very start of growth, when conditions are different from those found when a twin is formed on a crystal already well developed. We now examine more closely possible nuclear configurations for hexagonal $BaTiO_3$ in this primeval stage.

NUCLEATION OF TWIN STRUCTURES

As shown in Figures 3 and 4, a prominent feature of the hexagonal $BaTiO_3$ structure is the double octahedral Ti_2O_9 group. In Figure 4 we note that in the contact zones triple Ti_3O_{12} groups are also formed, in which a central octahedron shares two of its nonparallel faces with adjacent octahedra. The imminent appearance of these face-shared octahedra suggests a mechanism of nucleation that can account for the initiation of such multiply-twinned groups.

Arguments based on lattice-energy concepts have been advanced to explain the appearance of face-shared octahedral groups in stable structures (*e.g.*, Al_2O_3), in apparent violation of Pauling's basic crystal-chemical rules (Gorter 1970, Zemann 1972). If we accept the presence of some driving force that encourages the formation of double and multiple octahedral groups without at present concerning ourselves with its origin, we may inquire what happens when such a crystal is nucleated. Thus, beginning with a $[TiO_6]^{8-}$ group, we may expect up to four Ba^{2+} cations to become associated in a $[Ba_4TiO_6]^0$ group (Fig. 5a). At this point octahedron doubling will set in, which can occur on four of the original octahedron faces alternating with Ba atoms, forming a $[Ba_4Ti_5O_{18}]^{8-}$ group (Fig. 5b). Now, further Ba^{2+} ions will be attached on the outer exposed faces of the last-added TiO_3 groups, forming a $[Ba_8Ti_5O_{18}]^0$ group (Fig. 5c). A further development of this nuclear cluster is shown in Figure 6. These stages of nuclear growth will probably extensively overlap each other. Beyond this point, further growth will revert to the formation of the normal hexagonal $BaTiO_3$ structure. Continued growth will be mainly in a lateral direction around each of the four Ti_2O_9 groups in the nucleus. This group appears in four different orientations in the nuclear complex we have postulated in Figure 5c. It is clear that twins on only alternate $\{10\bar{1}2\}$ planes will be possible by this means. In this way the foundation of the four members of the fourling shown in Figures 1 and 2b is established.

Once the four individual crystals in this complex begin to develop, the contact surfaces will form as a consequence of normal crystal growth.

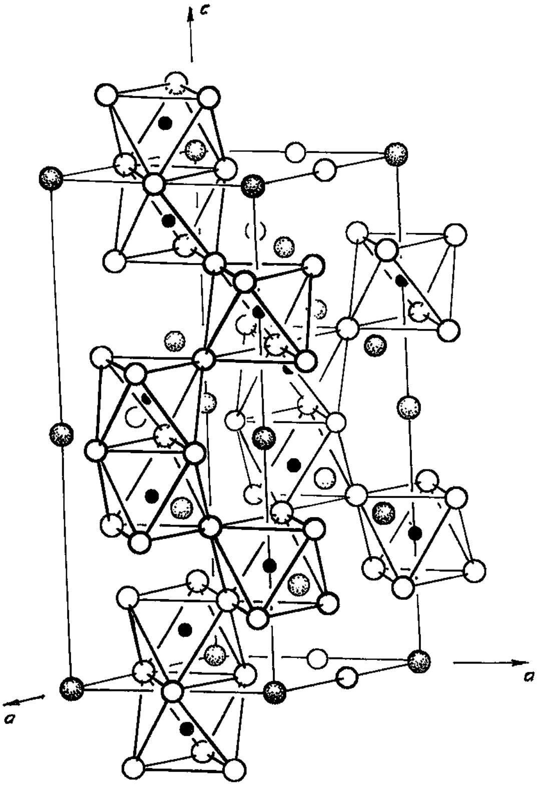

FIG. 3. The crystal structure of hexagonal $BaTiO_3$ as illustrated by Burbank and Evans (1948). Large shaded circles are Ba atoms.

Whereas a harmonious structure fit at the contacts will certainly contribute to the interpenetration twinning phenomenon, complete and extended integrity would not be necessary. On these contacts there are many triple Ti_3O_{12} groups, but at the very centre of the fourling crystal aggregate there is a single quintuple Ti_5O_{18} group, which initiated the whole growth process.

DISCUSSION AND CONCLUSIONS

One of the notable properties of twinned crystals is their consistent and persistent appearance depending on circumstances. Their nature and morphology are as characteristic of a substance and its conditions of formation as its crystal habit. The commonly observed fact that in a given environment most crystals show the same complex twin morphology indicates that their origin is not an accidental process. Among the few contributions that deal directly with penetration twins, some (Hartman 1956, Curien & Kern 1957) interpret the phenomenon in terms of lattice geometry without much concern for the structure itself. Others (Sheftal′ 1971, Senechal 1976) discuss growth kinetics on an atomic scale, but always assuming that a twin individual forms on an already crystallographically developed crystallite, and then overgrows the edges of the latter, thus initiating the interpenetrating growth. It is suggested now that such haphazard events are inadequate to account for the high prevalence and nearly perfect form of such twins in many cases.

It seems much more reasonable to seek the origin of the characteristic twin edifices in the nucleation process itself, though little attempt seems to have been made to do so. Interesting twin properties were described recently for orthorhombic pentagonite, $CaVOSi_4O_{10}\cdot 4H_2O$ (Evans 1973). Twinning occurs on (110), with perfect structural integrity across this plane (its polymorph cavansite, also orthorhombic, could produce nearly the same twin geometry, but there is no structural integrity on this plane, and no twins are observed). The angle of twinning is close to 72°, and nearly perfect prismatic, star-shaped fivelings are common. Evans suggested that these characteristic fiveling forms arise from nucleation on a tubular silicate core, which is the first (noncrystallographic) element of the structure to be formed from the surrounding medium. Continued crystal growth on this core then proceeds in five different directions to form the five segments of the fiveling. This is not a case of penetration twinning, but is perhaps the first case where the twin morphology is attributed to a special noncrystallographic nucleation process.

The interpretation of multiple twinning phenomena in hexagonal $BaTiO_3$ and other substances leads to the following conclusions:

(1) The occurrence of crystal pairs or groups in specific orientation with respect to each other is a consequence of their structural integrity at the contact zone. The lattice relationships follow from structural relationships. (2) When penetration twins are common, extensive structural integrity should exist over both normal contact planes (Sadanaga *et al.* 1963). (3) The characteristic twin pair or group will be determined by the precrystallographic nucleation process, through the formation of complex molecular groups in the growth medium. (4) The nucleation process will provide the creative force for interpenetration and multiple twinned groups, and structural integrity at the contact surfaces will be a factor supporting but subordinate to this force.

The hypothesis presented above should be

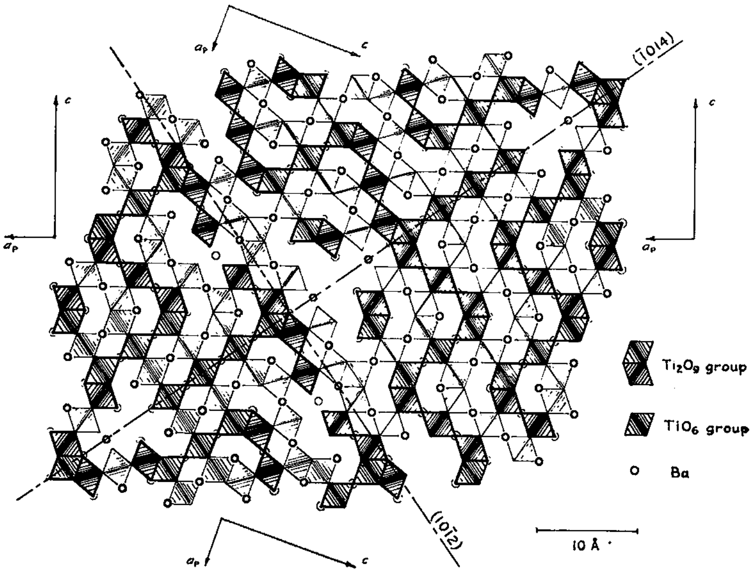

FIG. 4. The crystal structure of hexagonal $BaTiO_3$ projected along the a_2 axis and parallel to the twin composition planes ($10\bar{1}2$) and ($\bar{1}014$). The a_p (a projected) and c axes for each component are shown drawn to scale. Light features are displaced ½a relative to the dark features, parallel to the direction of projection.

tested on many outstanding examples. Noncrystallographic nuclear groups may be conceived in each case (as for hexogonal $BaTiO_3$ and pentagonite) and studied to determine whether extended crystal growth on these nuclei will lead to the observed twin group. The concept of nuclear groups applied to contact twin pairs will not provide support for the hypothesis, but when applied to penetration twins (staurolite, pyrite, fluorite) or other complex multiple twins (rutile), some insight into the process of twin formation may thus be gained. Energy calculations should also assist in determining which nuclear molecular arrangements or clusters may be expected to have transient stability as a substrate for subsequent crystal growth. It is proposed that studies following the approach outlined above may provide new insight into twin-crystal formation, and crystal nucleation and growth in general.

ACKNOWLEDGEMENT

It is a pleasure to dedicate this paper to

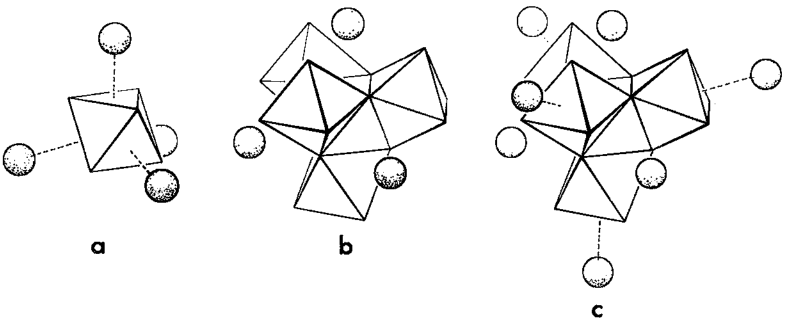

FIG. 5. The proposed nuclear groups from which the fourlings originate: (a) initial $[Ba_4TiO_6]^0$ group; (b) second stage $[Ba_4Ti_5O_{18}]^{8-}$ group; (c) third stage $[Ba_8Ti_5O_{18}]^0$ group.

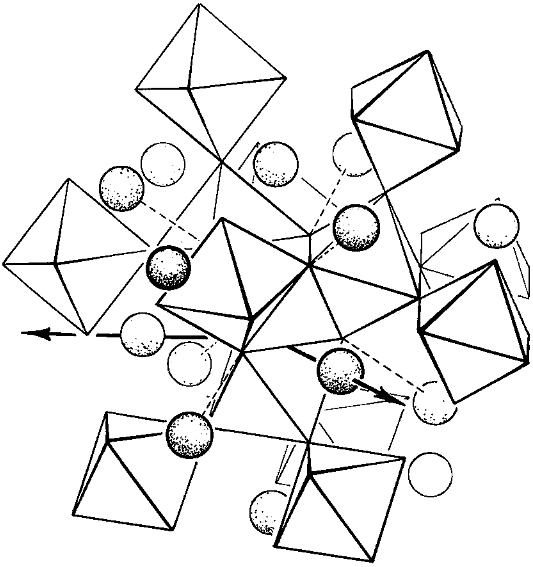

FIG. 6 A probable further development of the fourling nuclear group of Figure 5c. Crystal growth will continue for one individual (with *c* axis vertical) in the direction of the arrows.

J.D.H. Donnay on the occasion of his 75th birthday. The author is especially grateful to him for his vigorous and helpful discussion and criticism of the manuscript prior to publication. Thanks are also due to Richard R. Larson, who made the SEM photographs of Figure 1.

REFERENCES

BURBANK, R.D. & EVANS, H.T., JR. (1948): The crystal structure of hexagonal barium titanate. *Acta Cryst.* **1**, 330-336.

CAHN, R.W. (1954): Twinned crystals. *Adv. Phys.* **3**, 363-445.

CURIEN, H. & KERN, R. (1957): Macles par contact et par pénétration. Essai d'interprétation causale. *Soc. franç. Minéral. Crist. Bull.* **80**, 111-132.

EVANS, H.T., JR. (1973): The crystal structures of cavansite and pentagonite. *Amer. Mineral.* **58**, 412-424.

FRIEDEL, G. (1926): *Leçons de Cristallographie.* Berger-Levrault, Paris.

GORTER, E.W. (1970): Classification, representation and prediction of crystal structures of ionic compounds. *J. Solid State Chem.* **1**, 279-305.

HARTMAN, P. (1956): On the morphology of growth twins. *Z. Krist.* **107**, 225-237.

MATTHIAS, B. (1948): The growth of barium titanate crystals. *Phys. Rev.*(2) **73**, 808-809.

SADANAGA, R., TAKÉUCHI, Y. MORIMOTO, N. & TAKANO, Y. (1963): Structural aspects of penetration twins. *Acta Cryst.* **16**, A144 (Abstr.).

SENECHAL, M.L. (1976): The mechanism of formation of certain growth twins of the penetration type. *Neues Jahrb. Mineral. Monatsh.* 518-524.

SHEFTAL', N.N. (1971): The mechanism of penetration twin formation. *Sov. Phys. Cryst.* **16**, 322-326.

ZEMANN, J. (1972): Crystal chemistry of corundum type structures. *Sov. Phys. Cryst.* **16**, 1039-1041.

Received March 1978.