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The Inversion Twin: Prototype in Beryllium Oxide*

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The inversion twin is an uncommon fault that potentially can be found in the wurtzite- and sphalerite-type crystal structures and related rhombohedral structures, all of which are hemimorphic and possess a polar axis parallel to the c-axis. The twin structure involves exact inversion of the sense of polarity across a transition region (boundary) of variable orientation and complexity. Although several examples of possible but uncertain occurrence of the twin have been noted in other materials, only in beryllium oxide crystals has it been found to occur with abundance and on a macroscopic scale. The inversion twin, as it occurs in BeO, is described in detail. Existence and geometry of the twin is evident from crystal morphology and chemical and mechanical properties. It is suggested that the twin boundary may be stabilised and its energy lowered by the presence of aliovalent impurities along the boundary. Relation of the inversion twin to other types of faults is considered briefly. Previous discussions and presentation of new data in up-to-date assessment of the inversion twin are reviewed.

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1. Introduction

The concept of twinning in wurtzite-type crystal structures by inversion of crystal polarity was first advanced by Aminoff and Broomé in their pioneering paper of 1931 [1], although they did not report any known example of the inversion twin. The purpose of the present paper is to describe evidence for the existence of inversion twins as they commonly occur in BeO.

The hexagonal wurtzite crystal structure possessed by BeO is one of a series of hemimorphic structures based on tetrahedral co-ordination between the two components of AB-type binary compounds. These structures lack a centre of symmetry, and are electrostatically polar along the c-axis. This series of structures includes the cubic sphalerite structure and many polytypic† hexagonal and rhombohedral forms of SiC, ZnS, and other compounds; these will be discussed in more detail below.

Prior to the finding of inversion twins in BeO, unambiguous examples of this type of twinning in structurally related crystals had not been found. Indirect evidence for possible inversion twinning was reported by Strock and coworkers [2-5]; fine-scale birefringence banding in ZnS (both hexagonal and rhombohedral forms) was interpreted in terms of "polarity reversal". Knippenberg [6] made passing reference to SiC crystals formed under certain growth conditions, that showed etching and morphological character inconsistent with the normal polar structure of SiC. Witzke [7], in reporting growth of AlN crystals, briefly mentioned and illustrated occasional examples of crystal morphology not corresponding to the expected crystal symmetry. Although neither Knippenberg nor Witzke noted the possibility of inversion twinning, its existence might be inferred from their papers. Since the inversion twin has not been observed unambiguously in any other material with the controllability, frequency, and macroscopic size with which it is found in BeO, it appears appropriate to regard BeO as the prototype host material for the inversion twin.

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†See footnote on polytypism, page 258.

It is well recognised that structural flaws, especially stacking faults, in some of these materials probably give rise to electrostatic potential discontinuities [8] that are important to various modes of behaviour, such as, for example, electroluminescence [9], photoconductivity [9, 10], and anomalously high photovoltage [2-5, 11-14]. The inversion twin is another type of fault that potentially may be present in any of the polar tetrahedrally co-ordinated compounds and might have similar effects on electronic properties.

In addition to serving as host for inversion twins, BeO has attracted considerable attention for other reasons. BeO has many properties favouring its use as a high temperature moderator material in nuclear reactors. This interest has been considerably dulled, however, by highly anisotropic growth induced by irradiation [15, 16]. This growth is accompanied by formation of small stacking fault regions and other defects not fully understood at present. Although a discussion of radiation damage in BeO is beyond the scope of the present paper, various aspects of the inversion twin may prove significant to interpretation of radiation-induced defect structures, as those studies progress.

BeO has many other properties that may well be exploited in specialised applications. These include high strength at high temperature [17, 18], piezoelectric character [19], and exceptionally high electrical resistivity [18], thermal conductivity [20], and sonic velocity [19]. High material cost and biological toxicity have hindered widespread exploitation of this material.

Although the finding of inversion twins in BeO and some of its characteristics have been reported in previous papers [21-24], the descriptions were brief and (except for reference 21) incidental to the main purpose of those papers. The emphasis of the present paper, however, is primarily on the inversion twin and its characteristics. It is hoped that the present paper will stimulate further search for examples of inversion twinning and further investigation of its properties.

2. Description of the Ideal Twin

Before discussing other aspects of the inversion twin, we will describe the presently conceived structural features of the twin. The crystal structures in which inversion twins can potentially occur can be regarded most conveniently as follows. Layers of close-packed atoms of one element, which in the case of BeO is taken as the anion because of its large size relative to the cation, are stacked to produce a continuous three-dimensional close-packed structure [25-27]. It is not important in which repetitive sequence the layers are stacked to produce cubic (sphalerite), hexagonal (wurtzite, BeO [28]) or rhombohedral crystal structures. In any of these structures, the anions in adjacent layers define two sets (layers) of tetrahedral interstices: the plus and minus tetrahedral interstices [27], (+)-tet and (−)-tet, as shown in fig. 1. Only one of the two sets is normally occupied by cations.

The anion-cation interlayer separation is either $\frac{1}{4}$ or $\frac{3}{4}$ of the distance between adjacent anion layers. It is this asymmetric location of cation layers between adjacent anion layers that gives rise to the crystal polarity necessary for inversion twinning. In the twin configuration, it is assumed that the anion structure is completely continuous across the twin boundary; on one side of the boundary the cations occupy one set of tetrahedral interstices, and on the other side they occupy the alternate set. Thus, the inversion twin is associated with discontinuity in the cation stacking sequence but not in the anion stacking sequence, as illustrated in fig. 1. For this reason, the structural defect giving rise to the inversion twin has been termed an "Interstice Lattice Stacking Fault" (ILSF). The ILSF concept and its relation to inversion twinning has been discussed recently from a crystal algebraic viewpoint [27].

The interface between twin components of opposing polarity is referred to as the twin boundary. It has no required orientation although specific crystal growth environments favour certain boundary configurations, several of which are represented in fig. 1. The variable boundary configuration is consistent with the notion that the crystallographic "mesh" fits perfectly at the boundary, whatever the orientation, although probably there is slight local strain that influences boundary stability.

Two distinct types of basal twin boundary, *positive* and *negative*, are shown in fig. 1. The names for the two types stem from the naming of interstice lattice stacking faults (ILSF) in terms of the *formal charge* at the twin boundary [27]. In the case of the *positive* ILSF, the negative charge of the central anion layer is overcompensated by having two "close" layers

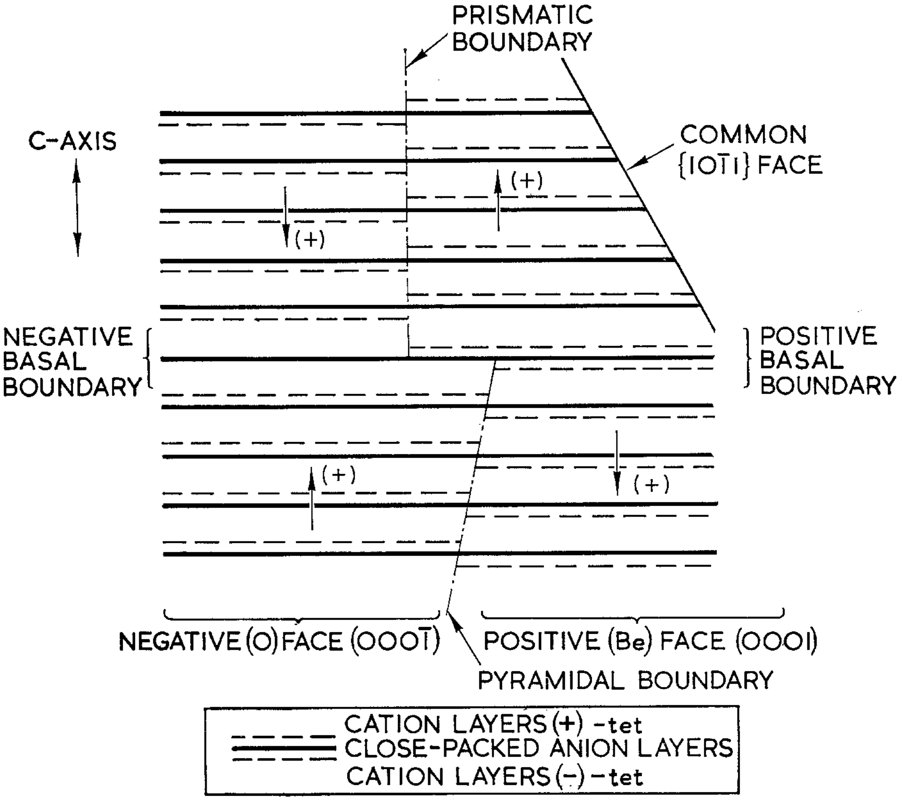

Figure 1 Composite diagram of twin configurations, showing the different types of twin boundaries according to reference 27, and showing relations between cation-anion stacking sequence, crystal polarity, and bounding crystal faces. The arrows are pointing in the positive polar direction.

of cations, which leads to a formal positive charge in comparison to an anion layer in an ideal structure. In the case of the negative ILSF, the two "far" layers of cations lead to an undercompensation of the negative charge of the central anion layer. (Experimental examples of these two types of ILSF are represented in fig. 2.) The formal positive or negative charge may be at least partially reduced by suitable adjustment (not depicted in fig. 1) of cation concentrations in immediate association with the central anion layer. This reduction in charge unbalance would also minimise the boundary energy arising from electrostatic forces.

In fig. 1, the change in occupancy from positive to negative tetrahedral interstices at each boundary is shown as a sharp discontinuity. This may not be the most realistic model; an alternate model would invoke a gradual change of cation occupancy in each layer with distance from the boundary. Thus, the probability of occupancy of the (+)-tet sites would increase while that of the (—)-tet sites would decrease with distance on one side, and vice versa on the other side, of the boundary. At the present time there is neither experimental nor theoretical estimation of the width of such a transition region.

The ILSF discontinuity in the occupancy of the cation sublattice inevitably leads to local electrostatic unbalance regardless of boundary configuration. The nearest neighbour cation-cation distances found in the normal lattice are altered in the transition region, some becoming longer and some shorter (see fig. 2 of reference 27). This electrostatic unbalance is regarded as the primary source of twin boundary energy. As one mechanism for lowering this electrostatic boundary energy, it appears quite reasonable to propose that aliovalent* impurities can concentrate in the boundary and create either atomic interstitials or vacancies. Either interstitials or vacancies would destroy local crystallographic polarity and reduce electrostatic interaction energy between the oppositely directed twin regions. Since no direct experiment has been

*Aliovalency is defined as having valency different than that of either of the host ions.

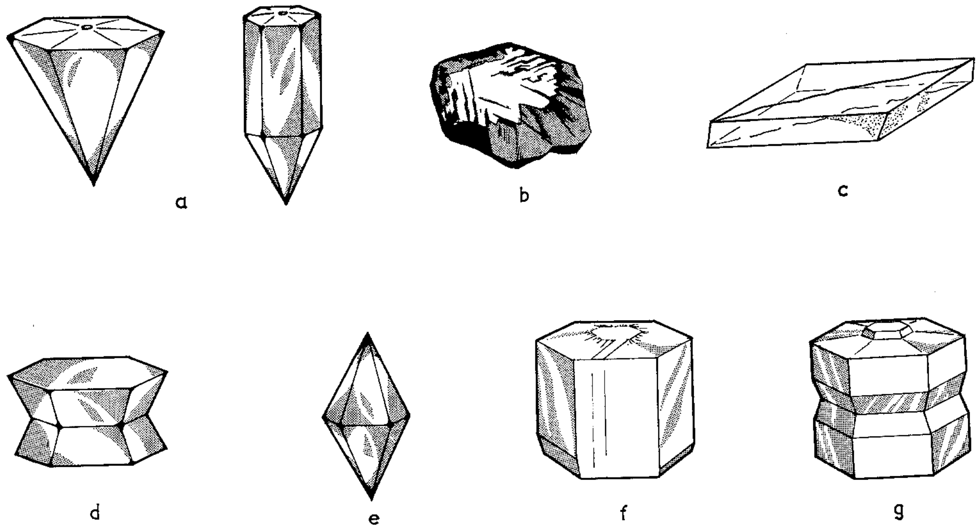

Figure 2 Perspective views of twinned crystals with various crystal habits (c-axis vertical): (a) pyramid and prism; (b) twinned platelet, shown tilted forward; (c) twinned platelet with boundary from tip to tip; (d) crystal containing negative basal twin boundary; (e) crystal containing positive basal twin boundary; (f) prismatic crystal in which "core" is exposed along prism face; (g) multiple twin.

devised to test this notion, it is necessary to leave it as a hypothesis; however, indirect evidence in its support will be cited.

3. Detection of the Inversion Twin

Although the inversion twin has been detected in polycrystalline BeO [29], it has been investigated in detail only in large crystals because of the advantage afforded in these crystals by the macroscopic size of the twin configuration and the ease of identifying crystallographic axes in single crystals. A number of physical properties make the inversion twin amenable to examination. The twin structure was observed initially in the morphology of BeO crystals grown from lithium polymolybdate flux [22-24]. This morphology has been described previously and only a brief description will be necessary here.

For these studies, only relatively symmetrical flux-grown crystals that were free of obvious crystal flaws (intergrowth, inclusions, mosaic misalignment, complex morphology, etc.) were selected for use. Crystals of select quality represented only a small proportion of the total crystal production. Crystal habits to be discussed are illustrated in fig. 2.

The crystals grow in a wide variety of shapes, generally having hexagonal symmetry about the c-axis. The shapes can be classed most broadly as platelets, pyramids, and prisms (fig. 2). They generally have the common crystallographic form $\{10\bar{1}1\}$, $\{10\bar{1}0\}$, (0001), and a curved sloping face approximately parallel to $(000\bar{1})$; this latter face is usually the active *growth face.* Other minor faces sometimes also appear, depending on growth conditions. Twins have been found in most observed crystal shapes and frequently are complex in geometry. Twinning occurs extensively in some groups of platelet crystals and is virtually nonexistent in other groups of platelets, depending upon the growth environment. Twinning occurs universally in crystals of pyramidal or prismatic habit. In the most symmetrical of the pyramidal or prismatic crystals, the typical twin structure extends as a slender core from the apex of the $\{10\bar{1}1\}$ faces to the growth face with a slight angle (~2 to 4°) of divergence within the enclosing crystal as shown in fig. 3. It is this type of crystal that has received the most experimental attention. Whereas prismatic, pyramidal, and many platelet crystals (fig. 2a, b, c, f) contain twins with boundaries that are practically prismatic type, others contain a negative basal boundary (fig. 2d) or a positive basal boundary (fig. 2e). The type of boundary present usually can be identified from crystal morphology.

Relationships between crystal morphology, lattice configuration, and the positive polar orientation have been identified from piezoelectric measurements [19, 28, 30] and are

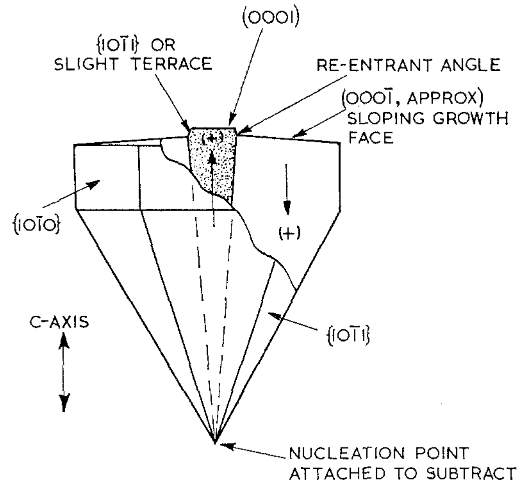

Figure 3 Cross-section of twinned pyramidal-prismatic crystal showing morphological features and polarity orientations.

shown in fig. 1. The negative basal plane face is regarded as the oxygen face and the positive as the beryllium face.

The significance of morphology as an indication of polar direction can be illustrated by reference to figs. 1 and 3. The $\{10\bar{1}1\}$ face is observed on nearly every crystal whatever the general shape, whereas the $\{10\bar{1}\bar{1}\}$ face has never been observed as a natural face by the authors. The direction of positive polarity, therefore, can be identified readily from the direction of convergence onto the c-axis of the $\{10\bar{1}1\}$ faces, as indicated in the upper right-hand part of fig. 1. In most of the habits illustrated in fig. 2c, d, e, g, twinning and local crystal polarity can be identified from the two sets of bounding $\{10\bar{1}1\}$ faces.

Other crystals (fig. 2a, b, f) show only one set of $\{10\bar{1}1\}$ faces. In this case, existence of the twin is made evident by the small central plateau that terminates the twin core on the growth face. In most cases of pyramidal and prismatic crystals, the trace of the twin boundary at the growth surface is evident only as a slight terrace. In some few cases, controlled by flux impurities during growth, the core protrudes far enough beyond the rest of the growth face to exhibit well-formed $\{10\bar{1}1\}$ faces. From other types of tests, as described below, polarity of the core was determined to be inverted relative to that in the enclosing crystal.

When an enclosing crystal lacks $\{10\bar{1}1\}$ pyramidal faces, orientation of the twin components and configuration of twin boundaries can usually be determined from examination of the positive and negative basal faces. Usually the positive (Be) face is nearly featureless and parallel to the crystallographic basal plane, while the negative face slopes at an angle of up to 15° relative to the crystallographic basal plane, as shown in fig. 3. The trace of the twin boundary at the crystal surface is the demarcation line between these components of the nominal basal face. The crystal platelet shown in fig. 2b is one with a very complex pattern of inversion twinning that is evident from these visually obvious differences between the positive and negative faces.

The crystal polarity of each twin component and therefore location of the twin boundary can be determined also by etching the basal face in hot (~175° C) orthophosphoric acid [19] and in molten salts [31]. With the former etchant, the negative surface is readily attacked while the positive face is relatively resistant. An example of the detail shown by etching is shown in fig. 4. A wafer parallel to the basal plane was cut from the centre of a pyramidal crystal, polished on both sides and etched in phosphoric acid. On one side of the wafer (fig. 4a), the enclosing crystal shows etch texture, while on the other side it is the enclosed core that shows the etching effect (fig. 4b). Recent experiments have shown that etching with certain molten salts (such as Li_2MoO_3-$LiBO_2$) also will reveal crystal polarity. In this case, it is the *positive* (Be) basal plane that is preferentially attacked [31].

The trace of a twin boundary with crystal faces *other* than the basal plane is revealed by differences in etching textures on either side of the boundary due to either very light phosphoric acid etching or thermal etching in air. In some cases, particularly on surfaces that are approximately parallel to prism planes, the textural differences are subtle and require careful examination to be seen. With somewhat greater etching in phosphoric acid, the trace of the boundary on $\{10\bar{1}0\}$ faces is revealed as a continuous groove, regardless of the type of boundary (i.e., prismatic, basal, or intermediate).

Still another useful physical property is the difference in hardness on the positive and negative surfaces [32]. This leads to differences in resistance to polishing. As a consequence, polished surfaces approximately parallel to the basal plane show slight but visible relief terraces at intersected boundaries. An example of this

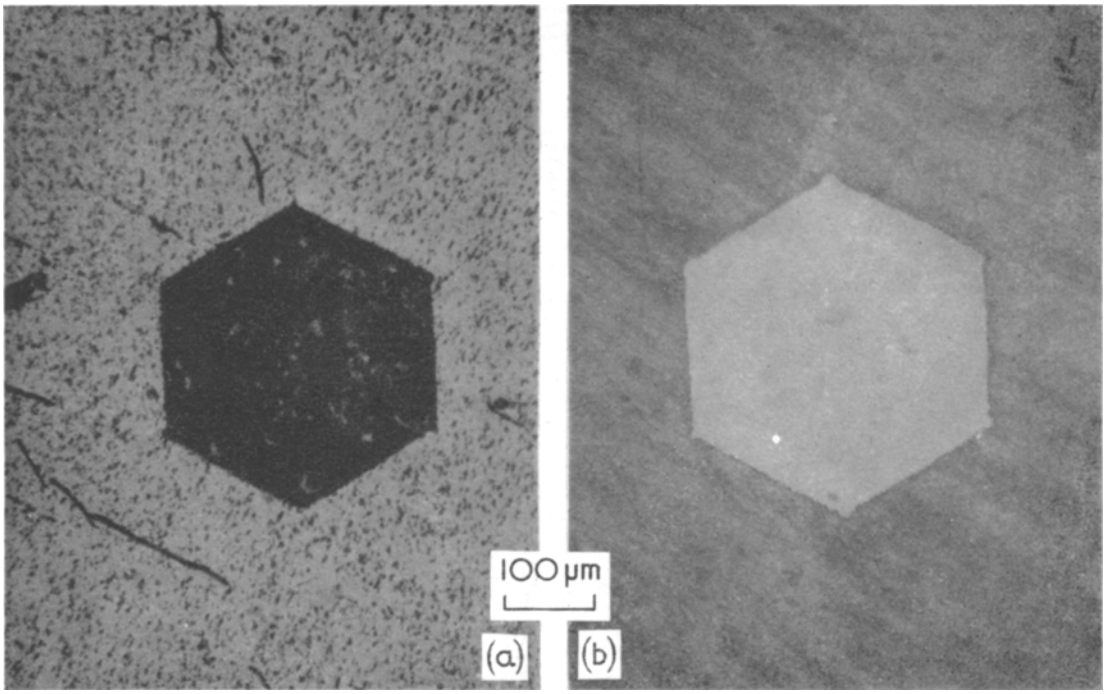

Figure 4 Opposing surfaces of a wafer cut parallel to basal plane of pyramid crystal, polished, and etched in phosphoric acid (175° C).

effect for a platelet having a complex twin boundary configuration is shown in fig. 5. The figure shows the platelet as polished and again after etching in phosphoric acid. The correspondence of boundary patterns in the two photographs is quite evident.

The techniques described above all depend upon surface features for detection; subsurface twin boundaries have been relatively undetectable. One technique that may have some promise of making visible the submerged boundaries is X-ray diffraction topography, although it is relatively difficult to exploit. For example, the twin boundary can be detected under favourable but still ill-defined conditions, as shown by recent Berg-Barrett topographs [33]. It is not known yet whether this detectability is due to local lattice strain or to diffraction effects arising from the cation lattice discontinuity, as discussed by Blank *et al* [34]. In practice, it has been difficult to obtain diffraction topographs that clearly reveal the twin boundary by either the Lang or Berg-Barrett techniques.

4. Inversion Twin Properties

From the model presented here for the ideal twin, some properties of the twin boundary can be predicted; experimental confirmation of some of these predictions, in turn, lends support to the validity of the model.

The origin of the inversion twin probably lies in the *nucleus* from which each crystal grows. In all cases examined, some part of the twin boundary could be traced to the surface which was in contact with the substrate and which presumably included the original crystal nucleus; an example is shown in fig. 6. For the simpler cases of pyramids and prisms in which the nucleus coincided with the sharp apex of the $\{10\bar{1}1\}$ pyramidal termination (fig. 3), the boundary was traced to the tip by several independent methods, including experiments in which the enclosing crystal was etched away from the enclosed core [31]. (Diffraction topography showed that the axial screw dislocation that contributes to crystal growth also intersects the same nucleating point [33].) In those cases in which correlation between the nucleation point and the twin boundary is not quite so obvious, the inference that the twin structure originates in the nucleus is not unreasonable. However, a tendency toward twinning is not always a prerequisite for nucleus formation, since platelet crystals grown under *certain* environments are not twinned.

In less symmetrically-shaped crystals, es-

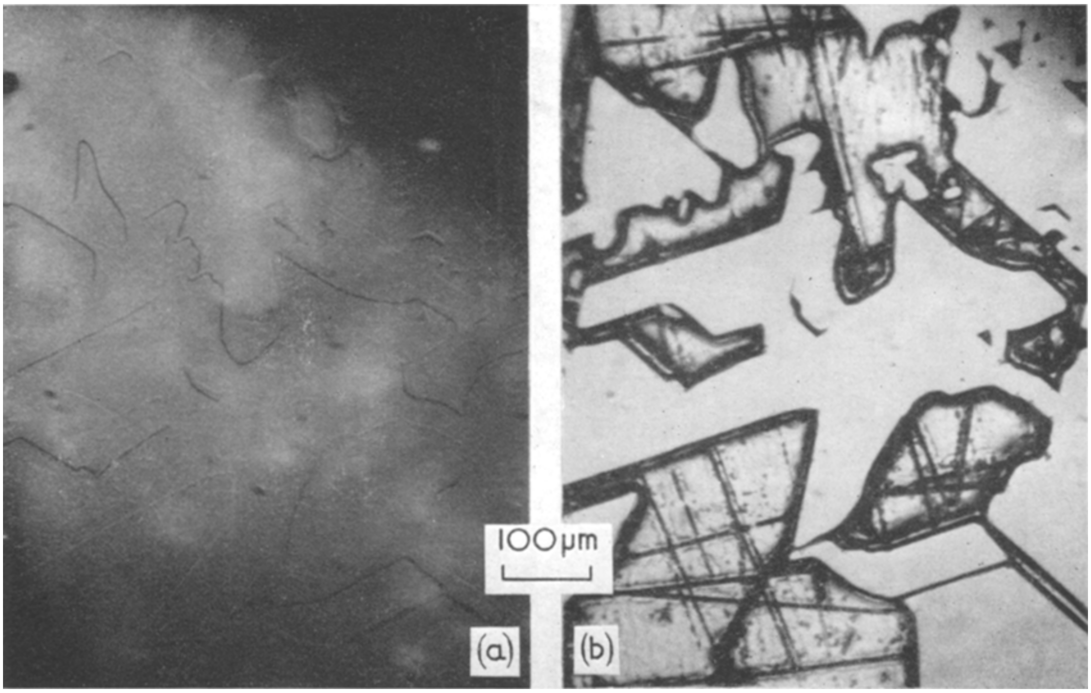

Figure 5 Twinned crystal which has been: (a) polished; and (b) etched, on basal plane. Phosphoric acid (175° C) etchant.

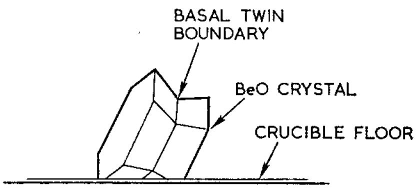

Figure 6 Example of twinned crystal whose twin boundary intersects the surface grown in contact with the substrate (crucible floor).

pecially those that have a broad base rather than a pointed tip, the core often has a broad and irregular cross-section at both ends of the crystal. Occasionally, in these crystals, the core is not entirely enclosed by the surrounding twin component and is exposed along a prismatic side as shown in fig. 2f. From observations such as these it can be deduced that for many crystals: (i) the configuration of twin components in a nucleus or a very small crystal is less symmetrical about the c-axis than in the subsequently larger crystal; and (ii) enclosure of the "core" is not completed until relatively late in the growth period, and occasionally is not completed when the growth run is terminated.

The twin configuration has proved to be significant to the growth mechanism for BeO crystals [35]. The principal effect of the inversion twin boundary is to create, on the growth face, a re-entrant angle (fig. 3) that serves as a favourable site for nucleation of growth layers. The significance of re-entrant angles in crystal growth processes is described in detail by Faust and John [36]. Although the existence of the inversion twin and the associated re-entrant angle are not vital to BeO crystal growth, undoubtedly they contribute to accelerated growth rates.

The twin configuration and orientation of the boundary are quite variable; some of the possible configurations are shown in fig. 2. The reasons for this variability are not fully understood. To some extent, the variability is known to be party temperature-dependent. It may also be partly due to the degree of local supersaturation at the instant of nucleation of the crystal. Still another factor known to affect boundary geometry is the presence of specific impurities in the flux. The impurities that are most significant to crystal habit (B, Al, Si, P) also influence boundary geometries [23]. For example, the presence of approximately 0.1% $LiBO_2$ in the flux during crystal growth at ~1050° C increases several-fold the divergence angle of the inversion twin core. Possibly, this is due to change in relative rates of advance of the $\{10\bar{1}1\}$ and $(000\bar{1}$, approximately) faces that form the re-entrant angle on the growth face (see fig. 3). Another possibility, though, is that boron which enters the lattice substitutionally for beryllium might locate preferentially at the twin boundary [37]. Having an ionic charge of $+3$, the boron ions require cation vacancies for charge compensation, and, as described earlier, it should be expected that the interface energy would be lowered by the presence of the vacancies. This would favour enlargement of the boundary area and therefore of the core diameter, as is observed. Silicon and aluminium impurities, both of which require accompanying cation vacancies for charge compensation, also lead to an increase of boundary area.

Although this discussion deals primarily with simple twin configurations, it should be recognised that multiple twinning also can occur. A relatively uncomplicated and interesting multiple twin is represented in fig. 2g. Within an individual crystal of this type there are co-existing positive and negative basal twin boundaries, as well as pyramidal (nearly prismatic) twin boundaries. The intersection of boundaries inside the crystal is approximately as shown in fig. 1. Crystals of this type are not common, and the critical conditions causing their development have not yet been fully defined.

It has been shown that cation diffusion in BeO proceeds via vacancy migration and is proportional to the vacancy concentration [38]. It is predicted that the inversion twin boundary may be a region of high cation mobility as a consequence of the postulated concentration of aliovalent cation impurities and associated vacancies. Experimental verification of this prediction has not been sought to date. Owing to the limited thickness of the boundary, it is not expected that high diffusivity along the boundary would contribute significantly to overall cation diffusion in BeO.

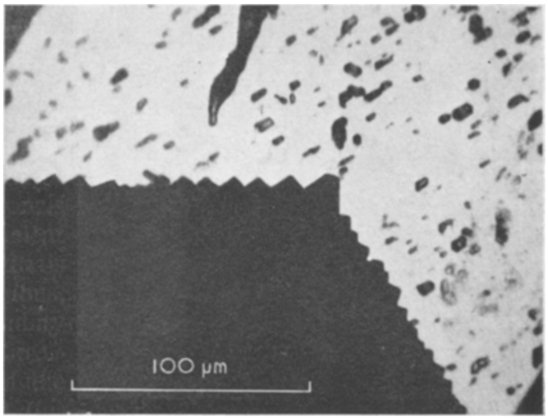

Figure 7 Photomicrograph of sectioned and etched basal plane surface at core boundary, showing jagged boundary contour. Phosphoric acid etchant (175° C).

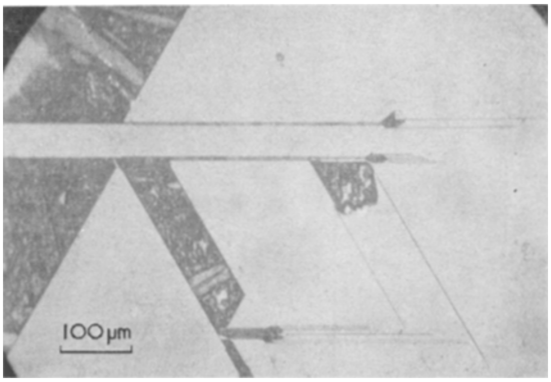

Figure 8 Photomicrograph of sectioned and etched basal plane showing extended twin boundaries. Phosphoric acid etchant (175° C).

The boundary energy associated with the inversion twin appears to be relatively small. This is a qualitative assessment, for no quantitative measurements have been made. In the first place, the energy is low enough that the structure is geometrically stable at the growth temperatures of 1000 to 1100° C, even when the crystal is held at this temperature for long periods of time (up to four months). Other pieces of evidence for low boundary energy (for appropriate boundary orientation) are jagged boundaries such as shown in figs. 4 and 7 and the very long, narrow twin stringers shown in fig. 8. With such irregular boundaries, the ratio of twin boundary area to crystal volume is: (i) not only high relative to that for smooth boundaries; but also, (ii) subject to considerable reduction without requiring the boundaries to sweep through large volumes of the crystal. Observation of boundary stability at growth temperature shows that the boundary energy is not high enough to provide force able to move the boundaries and thus to reduce their total area. Presumably, the resistance to boundary migration is due to a pinning effect of local impurities.

At high temperature, however, the boundaries can migrate, and have been observed experimentally to do so. For example, a pyramidal crystal containing a twin core with an initial boundary and configuration very much as shown in fig. 7 was annealed at 2000° C. The trace of the boundary rapidly became smooth and the core assumed an oval shape. With continued annealing, the boundary migrated toward the centre of curvature, and vanished at the centre after approximately 5 h. Upon disappearance of an inversion twin core by annealing, a twin crystal becomes a true single crystal. At sufficiently high temperature, therefore, the driving force associated with reduction of boundary area (and energy) can override the stabilising effect of impurities. One can only speculate on the role of impurities (presuming their initial presence) as the twin core shrinks in diameter. As one possibility, they may be thermally dissociated from the boundary at high temperature and dissolve into the surrounding crystal volume. This would increase the boundary instability and enhance its mobility. Or, less likely, the impurity atoms might remain associated with the boundary and be pulled along as an impurity "cloud", much as suggested by Pratt *et al* for the drag of impurities by moving dislocations [39].

Motion of the twin boundary involves the jumping of cations from one set of tetrahedral sites to the other, in the immediate vicinity of the boundary. It will be recalled (see fig. 1) that on opposite sides of the boundary the cations occupy alternate sets of tetrahedral sites. If the cations in one set, adjacent to the boundary, were to jump to the alternate set, the boundary between twin regions would thereby be shifted. This statement is equally true for *any* orientation of the boundary, i.e. parallel, normal, or inclined relative to the basal plane.

Since boundary migration depends upon shifting of electrically charged cations, another interesting experiment presents itself, although it has not been performed. The experiment would involve use of a static electric field to direct the cation migration at the boundary. Instead of relying upon built-in boundary curvature for a driving force, an electric field may be applied in either sense of polarity to control the direction of boundary migration at a rate dependent upon field strength and temperature. It is probable that by this means twinned crystals could be converted to single crystals. As an extra feature, reversal of polarity without altering the boundary faces would create crystallographic faces that do not occur as natural growth faces; for example, $\{10\bar{1}1\}$ would become $\{10\bar{1}\bar{1}\}$.

In the preceding discussion, it has been an important assumption that the twin boundary is a favourable location for concentration of impurities in solid solution. This assumption is based on qualitative arguments relating aliovalent impurities and associated vacancies or interstitials with the following experimental observations, previously cited: (i) alteration of twin boundary configurations in the presence of specific aliovalent impurities; (ii) geometrical stability of the boundaries at growth temperatures; and (iii) irregular, high surface-area boundaries indicative of low boundary energy. It is unfortunate, therefore, that no method has been found for directly detecting these impurities. For example, electron beam microprobe methods have proved to be unrewarding [40] for the following reason. Even with sufficient impurities to create a cation wall of 10 interatomic distances (improbably high), an electron beam sampling an area of 1 μm diameter (smaller than typical) would be surveying an impurity concentration of approximately one part in a thousand – an amount which would be very difficult to detect by this method. Detection and analysis of impurity segregation are crucial to a deeper understanding of the local structure of the inversion twin boundary.

The premise that the boundary is a region of higher electrostatic energy than that of the enclosing crystal is based upon examination of cation-cation distances at the boundary [27], as already mentioned. The presence of unusually short and long cation-cation distances with respect to the ideal structure leads to stress and an energy field of electrostatic origin. The above premise is experimentally supported by two effects in addition to boundary motion at high temperature. The first effect is the preferential etching (by either molten salt or acid etchants) along the trace of the twin boundary wherever it emerges on the crystal surface, creating a groove [31]. Enhancement of localised etching is attributed to boundary energy.

The second effect arises from strain relaxation under the influence of electrostatic forces. The extent of relaxation is very slight and appears to require extremely sensitive methods of detection. In a special technique of X-ray diffraction topography, fringes are formed by interference between X-ray beams of slightly different wavelength, and are shifted in position by very slight strain gradients in the sample. Observation by Hart of fringe displacements of this type indicates the presence of strain fields around the core in a sectioned BeO crystal [41].

5. Discussion

At this point, we wish to consider in some detail the crystallographic aspects of the inversion twin found in BeO, and to relate this special type of twin to general twinning phenomena. In this discussion, the review of "Twinned Crystals" by Cahn [42] is valuable.

The term "inversion twin" is used because *only* inversion of crystal polarity is involved. The anion *lattice* is continuous across the twin boundary (ignoring possible but very small lattice strain at the boundary); it is only the distribution of the cations that differs on either side of the boundary. This configuration falls in the classification of *twinning by merohedry*, one of four classifications proposed by Friedel [43], as cited by Cahn [42].

One of the general rules proposed by Aminoff and Broomé states that:

> "The atomic co-ordination in the transition layer is either identical with that in the crystal structure or closely related to it. In the latter case the transition structure is that of a possible polymorphic modification of the structure or else that of a modification which would be plausible for that substance."

This rule is directly applicable to BeO. The atomic (bond) co-ordination in the transition layer is not only the same as that in the normal BeO crystal structure, but also is the same as in the high temperature polymorphic modification, β-BeO [44]. In all three cases, each cation is tetrahedrally surrounded by anions, and vice versa. If consideration is extended to second nearest neighbours, however, the structure of the twin boundary transition region bears a closer resemblance to that of β-BeO than to that of α-BeO.

The structures of α-BeO (the normal low temperature form) and β-BeO (high temperature form) [44] are closely related [24]. In β-BeO, the anions, no longer precisely coplanar, are still close-packed into layers, although the successive layers are no longer so closely packed as in α-BeO. The tetrahedra formed between adjacent anion layers are distorted but have the same general configuration as in α-BeO. Unlike the normal structure in which all cations are in either the (+)-tet or (−)-tet cation layers, the cations in β-BeO are equally distributed between the two layers. The distribution of occupancy in each layer is ordered in such a manner as to give tetragonal symmetry to the crystal structure.

The similarity between β-BeO and the boundary transition structure is that both sets of tetrahedral interstices are partially occupied in both structures. The emphasis of similarity is on this particular point of comparison. The comparison cannot be carried beyond qualitative considerations, though, for several reasons. Firstly, the β-BeO structure is far more distorted than the transition structure. Secondly, the detailed structure of the transition region depends upon whether the distribution of cations in the (+)-tet and (−)-tet layers is disordered or fully ordered as in β-BeO, as well as on the real width of the transition region as already discussed.

The inversion twin is to be contrasted with the far more common faulting found, for example, in the sphalerite and wurtzite forms of zinc sulphide and in the many forms of silicon carbide, and which leads to the well-known extensive polytypism*. In these examples, faults occur by glide (or rotation) parallel to the planes of close packing, thus forming stacking faults, while maintaining the same crystal polarity between twin components. The existence of two types of faulting (i.e. inversion twins and stacking faults) in compounds with comparable crystal structure raises the intriguing question as to why both types are not found in the same crystal. The answer to this may be found, in part, in the observations by Blank *et al* that some structures have negative stacking fault energy (ZnS) and others positive stacking fault energy (AlN) [46]. Owing to negative stacking fault energy in hexagonal ZnS, one would expect to observe conversion from hexagonal to rhombohedral or cubic forms. This expectation

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*"Polytypes" has been used in practice [44a] to designate the series of polymorphs formed by stacking identical two-dimensional close-packed layers of atoms in various cyclical sequences, resulting in cubic, hexagonal, and the many observed rhombohedral structures. This series of polytypes is one of the "homeotect structure types" discussed by Parthé [45]. These layer structures in some materials can be transformed from one polytype to another by accumulation of stacking faults in the original form [46]. Silicon carbide and zinc sulphide are well-known examples of material which exhibit polytypism.

Editorial note See also the paper by D. B. HOLT on page 280 of this issue of *J. Matls. Sci.*

has been confirmed by Kendall [47] for ZnS, as well as structurally-similar CdS, CdTe, and GaP, at room temperature. On the other hand, the positive stacking fault energy in AlN should preclude the stacking faults leading to rhombohedral or cubic forms; this is consistent with experimental findings. Presumably, BeO* also has positive stacking fault energy of relatively high magnitude, since no rhombohedral or cubic forms have been found, and limited electron microscope examination has not revealed any stacking faults in either thin BeO crystals or flakes derived from crushing larger BeO crystals [48]†.

Instead of exhibiting polytypism, BeO is unique in that it exhibits both abundant inversion twinning and a high temperature structure with some elements of similarity to the transition structure of the boundary. It appears, therefore, that the nature of the crystal binding forces leading to the β-BeO structure also may favour the boundary transition structure. However, it is premature to conclude that a necessary correlation exists between the two types of structure in a given material.

Since many materials possess a polar crystal structure similar to that of wurtzite, it might be expected that the inversion twin would be observed in some of these systems. However, it is not evident from the literature that examples of the inversion twin have been discovered (except for those uncertain examples noted in section 1) in spite of extensive crystallographic examination of such compounds as ZnS [1, 50], many other Group II-VI compounds [51], III-V compounds such as GaIn [52], and SiC [6, 53].

It is interesting to note that while the concept of an inversion twin is relatively simple and straightforward, and undoubtedly has occurred to many crystallographers since the 1931 paper of Aminoff and Broomé [1], apparently Nature does not find it easy to form the inversion twin. Such a twin is quite uncommon except for the special case of BeO, which we have taken as the prototype material for inversion twinning.

The special purpose of this paper has been to present an exposition of this novel twin in BeO. Clear recognition of the character of the inversion twin, and careful re-examination of other crystals in which the twin might be expected may lead to further discoveries. It is hoped, too, that further studies of the properties of the twin boundary itself will be stimulated by the discussions presented here.

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*When no prefix is shown, the normal hexagonal form of BeO is implied.

†Rau has presented evidence for stacking faults in very small (100 to 2000 Å) particles of BeO produced by calcining beryllium hydroxide, the stacking fault density decreasing with increase of particle size [49]. From this it can be presumed that the stacking fault energy in BeO is considerably lowered by small particle size and by chemisorbed gases.

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