

A STUDY OF POLYTYPISM IN SILICON CARBIDE

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ABSTRACT

An X-ray study of over 200 single crystals of silicon carbide has established the superiority of transmission Laue photography for rapid polytype identification. The great majority of high-purity crystals grown at temperatures above 2400°C are made up of types 6H or 15R, with frequent syntactic intergrowth of the two. A large number of giant polytypes was encountered, and new modifications 72H, 130H, 408H, 213R, 240R, 242R, 288R, and 1080R were identified. Many of the Laue patterns were found to display anomalous diffuse reflections which are only partially related to the diffraction patterns of the polytypes, and whose nature has yet to be explained.

INTRODUCTION

Over fifty years ago, when Baumhauer (1915) suggested the term "polytypism" to denote the occurrence of a substance in different but closely related modifications, there were three varieties of silicon carbide known. At the time of this writing, an exhaustive literature search reveals a total of nearly 140 polytypes of which roughly one-fifth have been structurally analyzed (Mitchell, 1957; Kuo, 1964, 1965). There can be little doubt that an even larger number await discovery. The nature of this stacking phenomenon is too well-known to require review here. Several excellent papers have been devoted to studies of the causes (still in dispute) of polytypism in SiC, and Verma and Krishna (1966) have summarized the literature and reviewed the known modifications.

This study was an offshoot of the need to develop a method of rapid, nondestructive identification of the polytype composition of a large number of silicon carbide single crystals. After consideration of the optical and x-ray techniques applicable to the problem, we chose transmission Laue photography, using an approach very similar to that outlined by Mitchell (1953), but measuring the *h0.l* reflection positions on the film instead of comparing the patterns with prepared templates.

The crystals were grown in a controlled atmosphere furnace, most of them at 2400–2600°C. From the virtually unlimited number of excellent single crystals we selected a little over 200. All known colour varieties of silicon carbide—blue, black, green, yellow, and even brown—were represented. In a number of cases, as discussed below, colour zoning was prominent. The crystals were all euhedral, generally platy and thin (<0.5 mm), and measured from about 0.5 to 18 mm across. All but a few of the crystals were of very high purity.

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EXPERIMENTAL PROCEDURE

Because of the sensitivity of the Laue method to crystal orientation we required an accurate, as well as rapid means of setting the crystals. After an x-ray image intensifier proved inadequate in registering weak reflections, we decided on photographic film recording, and constructed an optical collimating system with which we can orient well-developed silicon carbide crystals so that c is parallel to the X-ray beam to within about 5 minutes of arc. This is possible because of the excellent reflectivity of the basal faces of most α -SiC crystals. Transmission Laue patterns of each crystal were obtained using unfiltered Cu-radiation at 50 KV and 15 mA, with a crystal-film distance of 60 mm and an exposure time of 1/2 hour. In most cases, such patterns were sufficient for complete polytype identification. The presence of a "giant" polytype in a crystal, however, where the reciprocal lattice consists of a large number of closely spaced points, necessitated lengthening F (the film-crystal distance) to as much as 150 mm, with a concomitant increase in exposure time to 48 hours or more. Under the standard operating procedure, eight to ten crystals can be examined per day, and with some practice, identification of the simpler polytypes (e.g., 4H, 6H, 15R, and β -SiC) can be made from a cursory inspection of the film. Since 6H and 15R comprised the overwhelming majority of the polytypes found in our crystals, the method proved both simple and rapid.

In addition to providing identification of the polytype composition of each silicon carbide crystal, the Laue patterns yielded information on degree of crystallinity and lattice perfection, and made possible a semi-quantitative estimate of the relative proportions of polytypes in a crystal containing two or more modifications.

EXPERIMENTAL RESULTS

Polytype distribution. Of the more than 200 crystals examined in this study, about 90 percent were composed wholly or in part of type 6H. Next in abundance was type 15R, found in a little less than 50 percent of the crystals. Compared with these two, other modifications were relatively scarce. We encountered four instances of type 4H, ten of 8H, two of 10H, eleven of 21R, and seven of 33R. Twelve crystals containing β -SiC were discovered. There was a remarkable scarcity of type 4H, a polytype common in most silicon carbide. It has been reported (Hamilton *et al*, 1960) that type 4H is unstable above 2500°C, and that 6H is the most stable variety above this temperature, with 15R occurring throughout a wide temperature range. Our results are certainly in harmony with these statements.

By far the most unexpected discovery, however, was the appearance of

“giant” polytypes in 26 crystals. Considering that such modifications, though not rare, are rather infrequently noted in the literature, it was surprising to encounter them in 13 percent of crystals selected more or less at random. There is nothing to indicate whether this high incidence is simply a characteristic of silicon carbide previously unobserved, or whether it is a function of the way in which these crystals were synthesized.

Suzuki (1958), Hamilton *et al* (1960) and Knippenberg (1963) have reported a relationship between the colour of SiC crystals and their polytype composition. To a limited extent we also found a correlation. All of the yellow crystals which we encountered contained type 15R in substantial amounts (though often in syntactic growth with 6H or other modifications), while all but one of the blue crystals were made up largely or wholly of 6H. In addition, the green crystals of our sample showed a 3:1 incidence of 6H over 15R. However, the fact that each of the colour categories was found to contain examples of every common polytype emphasizes that these findings are trends only and do not represent exclusive conditions.

Colour zoning is prominent in several SiC crystals and is of two types. Irregularly zoned crystals are usually composed of patches of two, and in one case, three differently tinted portions when viewed on a platy (0001) face. Frequently different colour zones comprise different polytype assemblages. In regular, concentrically zoned crystals, on the other hand, the polytype distribution is generally homogeneous, and in fact the zoning is often of different shades of the same tint rather than sharply distinct colours.

Syntaxis. This term was introduced by Ungemach (1935) to describe the intergrowth of polytypic modifications of a substance in crystallographic congruence; Thibault (1944) termed this phenomenon “coalescence.” In the case of silicon carbide, syntaxis is achieved through contact of polytype individuals on their (0001) faces, with parallel orientation of their crystallographic axes. This phenomenon is consistent with the concept of growth of silicon carbide crystals by stacking along the *c* axis.

Syntaxis proved to be very common in our experimental material; in fact, in the 203 crystals we examined we observed a total of 349 syntactically related polytype individuals. The most common syntactic relationship was that of 6H and 15R, and Figure 1 is a Laue pattern produced by such a combination.

Crystals containing more than two modifications were less common—we discovered 27 crystals containing three polytype individuals—and the simultaneous occurrence of as many as four different varieties was def-

initely rare, being observed in only two crystals. In each of the last two cases, careful study of the pattern enabled all four to be clearly separated and identified.

In a few instances, the syntactic individuals were of different colour, with green and yellow the most common combination.

Twinning. Because this study was concerned solely with euhedral, platy, "single" crystals of silicon carbide, and because the Laue photographs

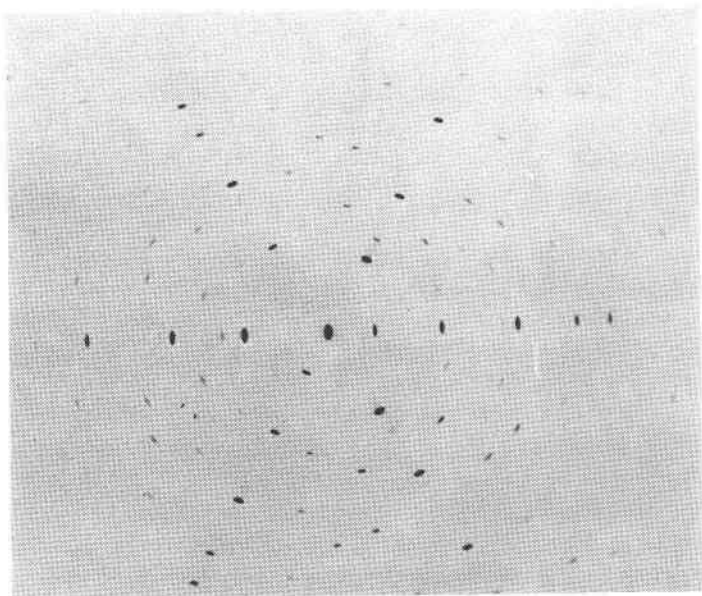


FIG. 1. Transmission Laue pattern of syntactically related 6H and 15R polytypes. X-ray beam parallel to c ; copper radiation, 50 KV, 15 mA; $F=60$ mm.; exposure $\frac{1}{2}$ hour.

used in polytype identification were all taken down the c -axis, we encountered only instances of 180° c -axis rotation twinning of rhombohedral polytypes. This type of twinning was observed for several 15R individuals, and when both twin sections are of about the same mass, the resulting diffraction pattern bears a superficial resemblance to a hypothetical type 30H. Such twinning of 15R was first reported by Thibault (1944), who recorded two examples.

All of the β -SiC crystals we encountered were platy (0.5 to 2 mm across) and otherwise similar to α -SiC in their gross morphology. In their case, however, the cubic crystal axis normal to the platy surface is $[111]$, and the resulting Laue pattern can be regarded as that of a 3R modification. However, most of these crystals were twinned about the 3-fold axis,

under the same law which governs the rotational twinning of 15R. As a result, the diffraction pattern of the twin simulates a pattern of type 6H α -SiC, except for certain missing $h0.l$ reflections such as 20.3 of 6H. An excellent study of twinning in β SiC has been presented by Kohn and Eckart (1962) in which this and higher-order twinning about several [111] directions is discussed; in our crystals we observed twinning about only one of the four 3-fold axes.

Giant polytypes. Without doubt the most surprising feature of this study was the discovery of such a large number of "giant" polytypes—those with a c -axis periodicity of over 100 Å. As is well known, these modifications represent a precisely periodic sequence of many tens or even hundreds of individual layers of Si-C tetrahedra; the question of just how they nucleate and grow is still in dispute (Mitchell, 1957; Krishna and Verma, 1963, 1966). Those recorded in the literature range in size up to 594R (Honjo *et al.*, 1950), and Mitchell (1954) has reported a polytype of either $\sim 1200R$ or $\sim 400H$.

Of the 26 examples which we encountered, we were able to identify nine with certainty. One of these, 174R, has been previously reported by Tomita (1960); the other eight are not mentioned in the literature. They are: 72H, 130H, 408H, 213R, 240R, 252R, 288R, 1080R.

We were able to identify another five giant polytypes only approximately: 60H; 420R; 2400R; 165H or 495R; 1560H or 4680R. In the remaining twelve cases, the patterns were too poor for identification. Either the polytype was of such a gigantic size that the reflections simply could not be resolved, or the specimen was too poorly crystallized, yielding diffuse reflections which could not be accurately measured. In still other cases, c -axis disorder led to smearing of the $h0.l$ reflection zones (Fig. 2).

In most cases identification was difficult. Even with a large F the $h0.l$ reflections of the giant modifications are frequently very closely spaced on the film. This is well illustrated by Figure 3, a c -axis Laue pattern of type 408H syntactically intergrown with type 6H. The reflection separation can be so small that our error in setting F (± 1 mm) would preclude accurate determination by film measurement alone. Errors in film shrinkage were also uncontrolled. Thus, in the case of the polytype which lies in the neighbourhood of 2400 R, our instrumental errors prevented accurate determination despite our possession of a pattern comprising a truly amazing array of superbly sharp and well-resolved reflections.

Because the great majority of these giant polytypes occur syntactically intergrown with one or both of 6H and 15R, our most effective procedure was to calculate the number of reflections from the unknown modification which lies between reflections of the known type. This technique has

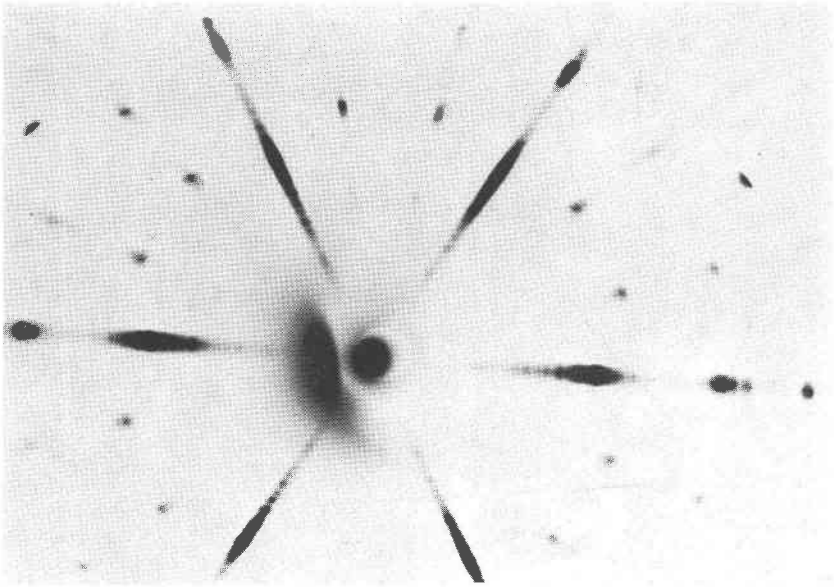


FIG. 2. Transmission Laue pattern of SiC crystal showing c -axis disorder. $F=120$ mm; exposure 30 hours.

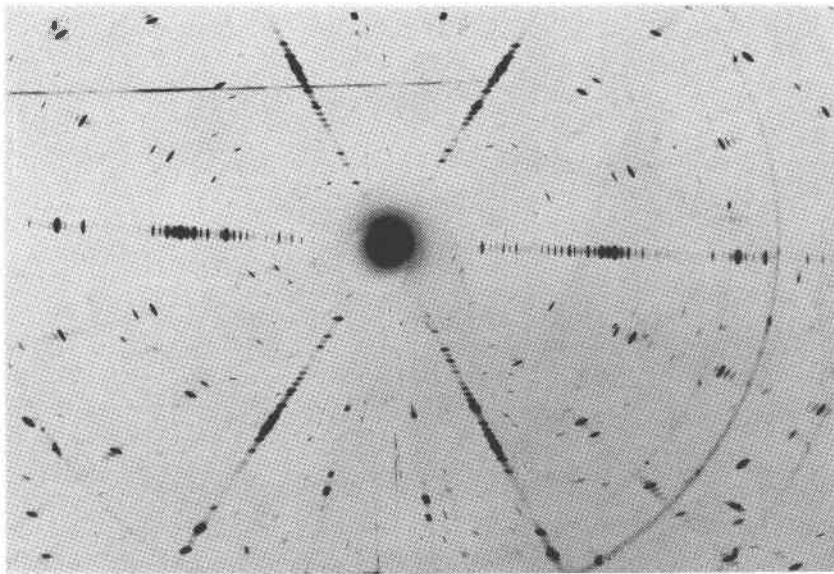


FIG. 3. Transmission Laue pattern of syntactically related 6H and 408H polytypes. X-ray beam parallel to c ; $F=120$ mm; exposure 30 hours.

been lucidly discussed by Honjo *et al* (1950) and Mitchell (1954). Sometimes a double check could be made. In the case of 130H, we found 21-2/3 reciprocal lattice spacings of the large modification between the 10.1 and 10.2 reflections of type 6H, and 26 spacings between various adjacent 10.*l* reflections of 15R. An inspection of the symmetry (both geometry and intensity relations) of the six *h0.l* zones is almost always sufficient to distinguish the symmetry of the polytype.

Type 72H occurs in a pale watery green crystal, transparent and free of inclusions. The crystal is platy, 3.5 mm across and 0.36 mm thick. The large modification is syntactic with 6H.

The crystal containing type 130H is pale olive green, transparent and free of inclusions, and measures 4 mm across and 0.76 mm in thickness. Types 6H, 15R, and 10H are in coalescence with the giant form.

Type 408H is syntactically intergrown with 6H and 15R. The crystal containing them is a transparent, flawless green plate 5 mm across and 0.76 mm thick.

Type 174R occurs in a crystal which is visibly a syntactic intergrowth of two plates, both of which are pale blue in colour. The larger of the two coalesced plates is 4.5 mm across, and the combined thickness is 0.25 mm. The giant polytype is syntactic with 6H and 15R.

The crystal containing type 231R also contains types 6H and 33R. It is an irregularly colour-zoned yellow and green plate which is transparent but bears brown surface inclusions, and one face is severely etched and resorbed. The crystal is 7 mm across and 0.32 mm thick.

Type 240R occurs in a transparent, yellow and green irregularly zoned crystal; one face shows marked etching and resorption. The crystal, which is 10 mm across and 0.58 mm thick, also contains types 6H and 15R.

An extremely thin, transparent pale green crystal contains types 6H and 252R syntactically intergrown. The crystal is 5 mm in diameter and only 0.04 mm thick.

Type 288R is syntactic with 6H and 15R in a transparent, irregularly zoned yellow and green crystal which is 5 mm in diameter and 0.5 mm thick.

Type 1080R is found in a thick, transparent dark green and yellow crystal showing irregular colour zoning. One basal face is strongly etched and resorbed. The crystal is 8 mm across and 0.5 mm thick. Types 6H and 15R are syntactically related to the giant modification.

During this study, the question arose as to whether the diffraction patterns of these giant modifications could not be produced by complex *c*-axis twinning of simpler polytypes. Sandanaga and Takeuchi (1961)

have examined a related phenomenon in connection with polytypism in micas. However, a careful check revealed that no known type of rotational twinning could generate these long c -axis polytypes from the commoner ones.

Anomalous diffuse reflections. More than half of the crystals we examined produced Laue patterns containing a puzzling feature. Situated on the $h0.l$ zones of these patterns are two broadly diffuse spots. They possess the following characteristics:

- 1) With $F=60$ mm, they occur invariably at distances of 36 and 42 mm from the centre of the pattern.
- 2) They occur on each of the six $h0.l$ zones, but often their intensities vary from one zone to the next, in the same pattern, without regard for the crystal symmetry of the polytypes.
- 3) The spots are always diffuse, rather large, and ill-defined. In some patterns they are of great intensity, while in others they may be barely discernible; some patterns show no trace of them.
- 4) Their disposition precisely on the $h0.l$ zones indicates that the spots bear some relation to the crystal, and yet even when slight misorientation of the crystal shifts the positions of the true lattice reflections by a few millimetres, these diffuse spots remain at about the same distances from the centre of the pattern. A pattern containing reflections of this type is shown in Fig. 4.

We could find no reference to this or any comparable phenomenon in the literature on silicon carbide. Suspecting that a quasi-crystalline surface coating of an oxide of silicon (Finch and Wilman, 1937; Verma, 1952) might be responsible, we subjected several crystals whose patterns display this feature to a bath of CP-4 etchant in order to remove all surface contamination. No change whatsoever was found when new Laue patterns were taken under identical conditions to the first set. If the diffuse reflections are indeed produced by a foreign substance, then it must be within the crystal, inaccessible to a surface chemical treatment. However, these crystals are transparent and apparently free of inclusions, and consequently we believe that the cause of the anomalous reflections is still to be found.

Limitations of the Laue method. We have already noted that c -axis rotational twinning of two identical rhombohedral polytypes having the same mass can produce a pattern which mimics a hexagonal modification of twice the c -spacing. Careful inspection of the pattern, however, combined with knowledge of the patterns of the common polytypes, will usually

prove adequate in detecting this situation. In applying the Laue method to discrimination of SiC polytypes, however, there exists a more serious limitation. As is well known, every reflection of an n -layer structure will have systematic coincidences with those produced by a multiple n -layer structure. For example, each of the reflections of 6H will be coincidental with certain reflections of, say, 18H (provided, of course, the two are identically oriented). Similarly, since β -SiC viewed down [111] can be regarded as 3R, its reflections will coincide at all points with those of any

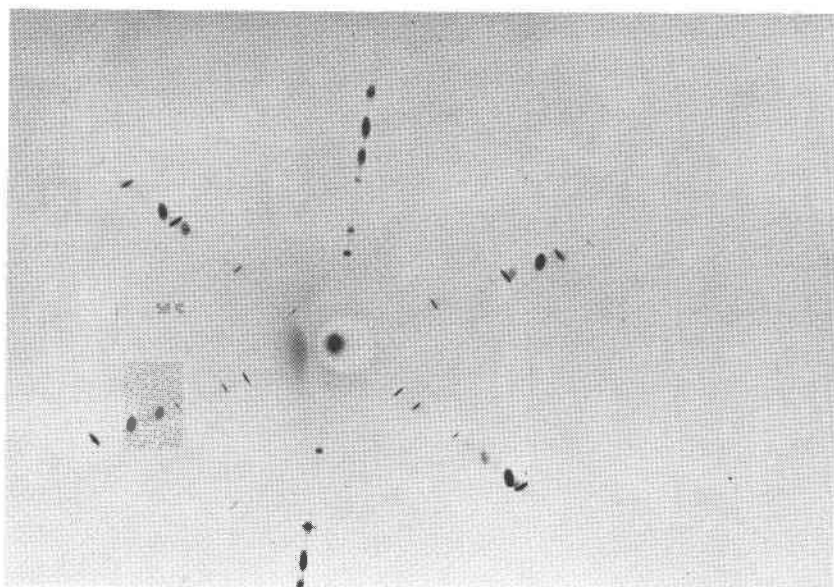


FIG. 4. Transmission Laue pattern of syntactically related 6H and 15R polytypes showing the presence of anomalous, diffuse reflections. X-ray beam parallel to c ; $F=60$ mm; exposure $\frac{1}{2}$ hour.

rhombohedral modification of silicon carbide, since all the R-types are composed of a whole-number multiple of three layers of Si-C tetrahedra.

In our study this limitation was most obtrusive where the recognition of type 4H was concerned, because 10.1_{4H} and 10.2_{4H} coincide with 20.3_{6H} and 10.3_{6H} , respectively. The presence of 4H can therefore go unnoticed in a crystal containing 6H, unless the former is present in sufficient quantity that its 10.1 reflection is too strong to be mistaken for 20.3 of 6H, which is significantly weaker than the other $h0.l_{6H}$ reflections.

Conclusions. This study established the fact that, using Laue photog-

raphy, a large sample volume of silicon carbide single crystals can be rapidly examined, and that even rather involved syntactic polytype combinations can be sorted out with a little care. The approach proves particularly powerful in identifying giant polytypes. In that connection, our discovery of eight new modifications lends credence to the statement, "With the discovery of each new polymorph of silicon carbide it becomes more evident that there is no limit to the possible modifications of this substance" (Mitchell, 1954). Unfortunately, because of the limited scope and objective of this study, we were unable to examine or cast light upon some of the more fundamental questions concerning the existence of this fantastic variety of polytypes.

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