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Application of Modulated Structure Analysis to Polytypes. II. Determination of a 66*R* SiC Polytype

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Abstract

A new polytype structure of 66*R* SiC (*R*3*m*, a = 3·078, c = 166·188 Å) was determined by the use of the method of modulated structure analysis described in part I [Yamamoto (1981). *Acta Cryst.* A**37**, 838–842]. The R factor smoothly converged from 0·68 for an initial state to 0·031 for a final result after 26 cycles and the stacking sequence described by the Zhdanov symbol $[23233333]_3$ was obtained. To confirm that the final result is independent of initial parameter selection, the least-squares program was initiated from another starting point and different final parameters describing the same stacking sequence were obtained. Therefore, this method can be used for SiC polytype analysis without special consideration for initial parameters.

Introduction

In the first part of this series [Yamamoto, 1981; referred to as (I) in the following], the theoretical basis of the method used here was given and analyses based on this theory were applied to the known structures of 21*H* SiC and 66*R* ZnS polytypes. In this paper, we describe the application of this method to the determination of the stacking sequence of a 66*R* SiC crystal which has the rhombohedral space group *R*3*m*.

Theory

The determination of SiC polytypes is similar to that of ZnS polytypes because these two materials have similar structures: the stacking sequence to be determined in both cases is that of tetrahedra which consist of SiC_4 or ZnS_4 and share their corners. In this respect, the determination of a 66*R* SiC polytype is completely analogous to that of 66*R* ZnS which was mentioned in (I). In this section, the theory is briefly reviewed.

In the refinement of polytype structures of SiC, we can conveniently use the periodic intensity distribution function $S(h_1,h_2,h_3,h_4)$ instead of the usual structure factor $F(h_1,h_2,h_3,h_4)$ (Tokonami, 1966; Takeda, 1967). This is defined in the present notation by

$$S(h_1,h_2,h_3,h_4) = \frac{F(h_1,h_2,h_3,h_4)}{F_0(h_1,h_2,h_3,h_4)} M, \qquad (1)$$

where M is the number of SiC layers in the unit cell (M = 66 in the present case), h_1,h_2,h_3,h_4 are integers which designate reflections by the relation $\mathbf{h} = h_1\mathbf{a}^* + h_2\mathbf{b}^* + (h_3 + h_4/M)\mathbf{c}^*$ and $F_0(h_1,h_2,h_3,h_4)$ is the structure factor of the structure consisting of one SiC layer with the period M. $S(h_1,h_2,h_3,h_4)$ corresponds to the structure factor for the point atom with one electron located at the center of each SiC_4 tetrahedron. This is calculated from

$$S(h_1,h_2,h_3,h_4) = \sum_{\mu} \sum_{\nu=1}^{M} P^{\mu}(x_4^{\mu}) \times \exp\left\{2\pi i \sum_{j=1}^{4} h_j x_j^{\mu}\right\}, \qquad (2)$$

where the summation with respect to μ runs over the A, B, C sites; x_1^A, x_2^A, x_3^A ($\mu = A$) are the usual three-dimensional coordinates of the A site in the

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hexagonal unit cell: 0,0,0; x_1^B, x_2^B, x_3^B are those of the B site: $\frac{1}{3},-\frac{1}{3},0$; x_1^C, x_2^C, x_3^C are those of the C site: $-\frac{1}{3},\frac{1}{3},0$; and $x_4^\mu = (x_3^\mu + \nu)/M$ ($\mu = A, B, C$). [Note that, in the present method, we take $c = 2{\cdot}518$ Å which corresponds to the distance of one SiC layer (see I).] $P^\mu(x_4^\mu)$ represents the occupation probability of the μ (A, B or C) site at the νth ($1 \le \nu \le M$) layer perpendicular to the hexagonal c axis.

From the definition, $P^\mu(x_4^\mu)$ is the periodic function of x_4^μ with the period equal to one. Therefore, this can be expressed in terms of the Fourier series:

$$P^\mu(x_4^\mu) = \tfrac{1}{2}\sum_n [P_n^\mu \exp(2\pi i n x_4^\mu) + P_{-n}^\mu \times \exp(-2\pi i n x_4^\mu)], \quad (3)$$

where P_n^μ is the complex amplitude of the nth-order harmonics and P_{-n}^μ is its complex conjugate. In the method developed in (I), the sum of the squared weighted R factor $R_w^2 = \sum w(|S_o| - |S_c|)^2/\sum |S_o|^2$ and the squared penalty function $\mathrm{PF}^2 = \sum_{\mu\nu}[r(x_4^\mu)]^2/3M$ [where $r(x_4^\mu)$ has a value $2|P^\mu(x_4^\mu)|$ for $P^\mu(x_4^\mu) < 0$, $2|P^\mu(x_4^\mu) - 1|$ for $P^\mu(x_4^\mu) > 1$ and zero otherwise] are minimized, treating P_n^μ as variable parameters, by the least-squares method. In the case of the rhombohedral space group $R3m$, the following relations are derived from symmetry:

$$P^A(x_4^A) = P^B(x_4^A - \tfrac{1}{3}) = P^C(x_4^A + \tfrac{1}{3}). \quad (4)$$

This leads to

$$P_n^A = P_n^B \exp(-2\pi i n/3) = P_n^C \exp(2\pi i n/3) \quad (5)$$

and, in particular, $P_0^A = P_0^B = P_0^C$. Therefore, only P_n^A ($n = 0, 1, \ldots$) are independent. In addition, from the physical requirement of the SiC structure, the sum of the occupation probabilities of the A, B and C sites must be equal to one in each layer: $P^A(x_4^A) + P^B(x_4^A) + P^C(x_4^A) = 1$ for any x_4^A. This gives $P_0^A = \frac{1}{3}$ and

$$P_n^A[1 + \exp(2\pi i n/3) + \exp(-2\pi i n/3)] = 0 \quad (n \ge 1). \quad (6)$$

In particular, $P_{3m}^A = 0$ ($m = 1, 2, \ldots$).

In the present notation, the extinction rules of $66R$ SiC are $-h_1 + h_2 + h_4 \neq 0 \pmod 3$ for general reflections $h_1h_2h_3h_4$ and when $-h_1 + h_2 \neq 0 \pmod 3$, $h_4 \neq 0$. The first rule is derived from (2), (3), (5) and the second is explained by (2), (3) and (6). Therefore, the first rule is the extinction rule intrinsic to the space-group symmetry, while the second is due to the requirement that an atom occupies any one of the A, B, C sites in a layer perpendicular to the hexagonal c axis.

Experimental

The high-purity SiC crystals were synthesized by the reaction between the high-purity graphite crucible and molten silicon (Inoue, Inomata & Tanaka, 1974) because the impurities play an important role in the phenomenon of polytypism and the stacking faults. Silicon powder (>99·999% pure) was used as starting material. The graphite crucible (nominal ash component less than 20 p.p.m.) charged with the silicon powder was heated at 2773 K for 2 h by an electric resistance furnace in a pure argon atmosphere (the impurity of N_2 content was less than 5 p.p.m.). This method made the long-period polytypes grow more predominantly than the sublimation method, the so-called Lely method (Lely, 1955).

A new polytype of SiC, $66R$, was found among other long-period ones which grew in the crucible. Its shape was hexagonal columnar and its length along the c axis was 0·2 mm; it was pale green in transmitted light.

X-ray precession and Weissenberg photographs confirmed that this crystal did not show any evidence of stacking faults and that it was of entirely $66R$ type. A sample for intensity-data collection was polished into an ellipsoid 0·1 mm in diameter using diamond paste and immersed several times in liquid nitrogen to reduce the secondary extinction. X-ray diffraction data were collected on a Rigaku four-circle diffractometer with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å, monochromatized by a graphite monochromator so arranged that the incident and reflected rays at both the monochromator and the specimen all lie in a plane). The 2θ–ω scanning mode was employed for the intensity measurements where $2\theta \le 55{\cdot}0°$ and $\overline{66} \le h_4 \le 66$. 270 non-zero reflections were collected from six rows equivalent to $100h_4$ and $110h_4$ through the corrections of Lorentz and polarization effects (Whittaker, 1953), and then a set of 46 independent non-zero reflections was obtained by averaging these equivalent reflections.

Structure refinement

The structure refinement can be carried out by taking P_n^A ($n \neq 3m$; $m = 1, 2, \ldots$) as parameters and taking the relation (5) into account. However, further simplification is possible in the present case. From (2) and (5), the contributions of the A, B, and C sublattices (consisting of the A, B, C sites) to the reflections allowed by the extinction rule due to the Bravais lattice, that is, to the reflections $h_1h_2h_3h_4$ fulfilling $-h_1 + h_2 + h_4 = 0 \pmod 3$, are the same. Therefore we need calculate only the contribution from the A sublattice to $S(h_1,h_2,h_3,h_4)$. As shown by Tokonami (1966), the following relation must be fulfilled in SiC:

$$\sum_{h_4=1}^{M} |S(1,0,0,h_4)|^2 = |S(1,1,1,0)|^2 = M^2. \quad (7)$$

Furthermore, $S(h_1,h_2,h_3,h_4)$ are periodic in reciprocal space. Their periods are unity for h_1,h_2,h_3 and M for h_4.

From these facts and the relations derived from the symmetry of the space group, only $S(1,0,0,h_4)$ ($h_4 = 1, 2, \ldots, M$) are independent. Therefore, $S(1,0,0,h_4)$ ($h_4 = 1, 2, \ldots, M$) are scaled to fulfill the relation

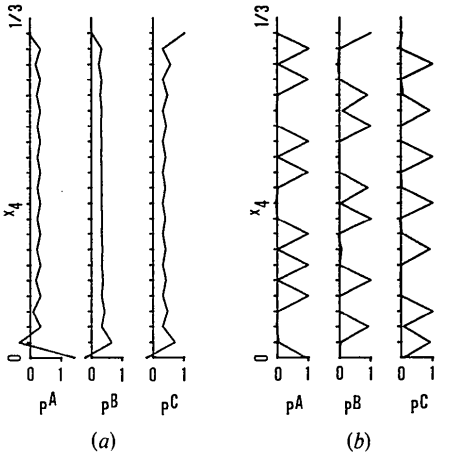
$$\sum_{h_4=1}^{M} |S(1,0,0,h_4)|^2 = M^2, \qquad (8)$$

and only these reflections are used in the analysis.

Fixing the scale factor at unity, the refinement was initiated from the starting point where all parameters were equal to $0{\cdot}05 + i0{\cdot}05$ except for $P_0^A = \frac{1}{3}$ and $P_{3m}^A = 0$ ($m = 1, 2, \ldots$). The weighted R factor and the penalty function smoothly converged from 0·70 and 0·15 to 0·032 and 0·036 after 26 cycles. The conventional R factors for $S(1,0,0,h_4)$ of the initial and final states were 0·68 and 0·031. The occupation probabilities of these two states are illustrated in Fig. 1. From the final result, the structure of $66R$ SiC can be easily recognized as the structure with the Zhdanov symbol $[23233333]_3$. The final parameters are shown in Table 1 together with the parameters of the $[23233333]_3$ structure. This stacking gives an R factor of 0·078. Observed and calculated $S(h_1,h_2,h_3,h_4)$ are listed in Table 2.

Table 1. *The final parameters, and the parameters for the* $[23233333]_3$ *stacking in the* $66R$ SiC *polytype*

	Final parameters	Parameters for $[23233333]_3$ stacking
P_0^A	0·3333	0·3333
P_1^A	0·0056 + *i*0·0046	0·0063 + *i*0·0055
P_2^A	−0·0071 − *i*0·0313	−0·0040 − *i*0·0279
P_4^A	−0·0146 + *i*0·0076	−0·0131 + *i*0·0038
P_5^A	−0·0471 − *i*0·0266	−0·0432 − *i*0·0197
P_7^A	−0·0062 + *i*0·0504	−0·0126 + *i*0·0431
P_8^A	−0·0697 + *i*0·0364	−0·0563 + *i*0·0361
P_{10}^A	0·1095 + *i*0·1355	0·1159 + *i*0·1338
P_{11}^A	0·0040 − *i*0·1142	− *i*0·1049
P_{13}^A	−0·0574 + *i*0·0008	−0·0500 + *i*0·0071
P_{14}^A	0·1037 + *i*0·0625	0·0936 + *i*0·0601
P_{16}^A	0·0017 − *i*0·0054	0·0024 − *i*0·0053
P_{17}^A	0·1399 − *i*0·0588	0·1326 − *i*0·0605
P_{19}^A	−0·0185 − *i*0·0186	−0·0126 − *i*0·0197
P_{20}^A	0·0269 − *i*0·2370	0·0344 − *i*0·2395
P_{22}^A	0·2758 + *i*0·0034	0·3030
P_{23}^A	0·1345 + *i*0·0922	0·1186 + *i*0·1028
P_{25}^A	−0·0242 + *i*0·0224	−0·0149 + *i*0·0233
P_{26}^A	−0·0756 + *i*0·0157	−0·0657 + *i*0·0192
P_{28}^A	−0·0002 + *i*0·0090	0·0034 + *i*0·0075
P_{29}^A	−0·0399 + *i*0·1418	−0·0380 + *i*0·1295
P_{31}^A	−0·1005 + *i*0·0070	−0·0859 − *i*0·0123
P_{32}^A	0·2341 + *i*0·2741	0·2528 + *i*0·2918



(*a*) (*b*)

Fig. 1. Occupation probabilities of $66R$ SiC. (*a*) The starting point with $P_n^A = 0{\cdot}05 + i0{\cdot}05$, except for $P_0^A = \frac{1}{3}$. (*b*) The final result. This shows the stacking sequence *ACBCABACABCBACABCBACAB*.... This structure is represented by the Zhdanov symbol $[23233333]_3$.

Table 2. *Observed and calculated* $|S(1,0,0,h_4)|$ ($\times 10/3$) *of* $66R$ SiC

(*a*) Observed values. (*b*) Calculated values for the final result. (*c*) Calculated values for the $[23233333]_3$ stacking. (*d*) Observed values after the absorption and secondary-extinction corrections.

h_4	(*a*)	(*b*)	(*c*)	(*d*)
−32	119	119	127	124
−29	51	49	45	48
−26	27	26	23	25
−23	57	54	52	54
−20	79	79	80	78
−17	53	50	48	50
−14	42	40	37	40
−11	40	38	35	37
−8	26	26	22	25
−5	19	18	16	18
−2	11	11	9	10
1	3	2	3	2
4	6	6	5	5
7	18	17	15	16
10	59	57	59	58
13	20	19	17	18
16	1	2	2	1
19	9	7	8	8
22	91	91	100	96
25	12	11	9	11
28	3	3	3	3
31	35	33	29	33

Secondary extinction

One of the remarkable experimental results obtained from the sample used in the analysis is that the first term of (7) is much larger than the second term (see Table 3). This may suggest that the secondary extinction is very large because the observed intensity of 1110 is stronger than that of any $100h_4$ reflections and strong reflections are affected by secondary extinction. Furthermore, as shown in Table 2, observed values of $S(1,0,0,h_4)$ for strong reflections are systematically less than those of $[23233333]_3$ stacking. Therefore, the absorption and secondary-extinction corrections were made by using a program written [by

Table 3. *The check of* $\sum_{h_3=1}^{M}|S_o(1,0,0h_4)|^2 = |S_o(1,1,1,0)|^2$ *for the two cases before and after the absorption and secondary-extinction corrections*

The observed S value is scaled so that the left-hand side of this equation is equal to M^2.

	Left-hand side	Right-hand side
Before corrections	4356	1566
After corrections	4356	4261

one of us (AY)] on the basis of new transfer equations (Kato, 1976). After the correction, we have $R = 0{\cdot}053$ for the stacking mentioned above and (7) is approximately fulfilled (see Table 3). The result after the correction is also listed in Table 2. The systematic error is improved in this case. This result shows that the secondary-extinction effect is large under the present experimental conditions and the mosaic structure of SiC is hardly affected on immersion in liquid nitrogen.

Convergence test

As mentioned before, the least-squares program smoothly converged from the starting point with $P_n^A = 0{\cdot}05 + i0{\cdot}05$ for $n \neq 3m$ ($m = 1, 2,\ldots$) and $P_0^A = \frac{1}{3}$ and a reasonable stacking sequence of $66R$ SiC was obtained. To confirm that this smooth convergence is independent of the starting point and that the final result is a unique solution of the present problem, a similar calculation was made from a different starting point with $P_n^A = 0{\cdot}05 - i0{\cdot}05$ for $n = 3m + 1$, $P_n^A = -0{\cdot}05 + i0{\cdot}05$ for $n = 3m + 2$ and $P_0^A = \frac{1}{3}$. After 31 cycles, the R factor reduced to 0·029, which is comparable with 0·031 in the previous calculation. The initial and final occupation probabilities are shown in Fig. 2. This final result is equivalent to the previous one: if the origin is shifted by $x_4 = 9/66$, Fig. 2(*b*) is superposed on Fig. 1(*b*). Thus we obtained the same stacking sequence from different initial states.

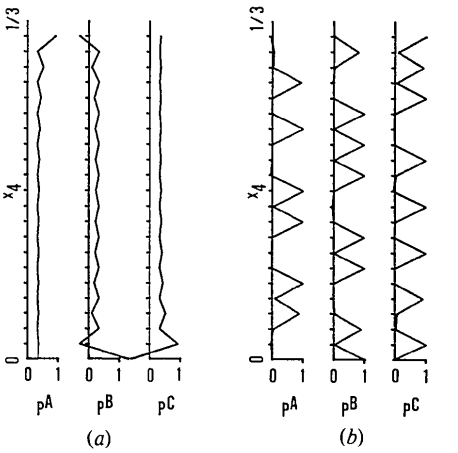


Fig. 2. Occupation probabilities of $66R$ SiC obtained from a different starting point. (*a*) The starting point which has $P_n^A = 0{\cdot}05 - i0{\cdot}05$ for $n = 3m + 1$ and $P_n^A = -0{\cdot}05 + i0{\cdot}05$ for $n = 3m + 2$ and $P_0^A = \frac{1}{3}$. (*b*) The final result. From (*b*), the stacking sequence $BCBACABCBACABCBABCACBC\ldots$ is obtained. This is represented by the Zhdanov symbol $|33332323|_3$, which is equivalent to the symbol $|23233333|_3$ obtained from Fig. 1.

Conclusion

The present study determined the stacking sequence of the $66R$ SiC polytype by applying the method of modulated structure analysis described in (I). The stacking is represented by the Zhdanov symbol $[23233333]_3$. From the convergence check in the present analysis and the analyses of $21H$ SiC and $66R$ ZnS in (I), we conclude that the method developed in (I) can be used for any other polytypes of SiC or ZnS.

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