A NEW HEXAGONAL POLYMORPH OF SILICON CARBIDE, 19H*†

L. S. Ramsdell and R. S. Mitchell,
University of Michigan, Ann Arbor, Michigan

Abstract

Morphological and structural details of silicon carbide type 19*H* are given. The crystal has a structure represented by the zigzag sequence 22232323. The space group is *P3m*. The unit cell dimensions are $a_0=3.073$ kX and $c_0=47.75_3$ kX; $Z=19$.

Weissenberg photographs of silicon carbide modification 19*H* were first made in 1950. These were of very poor quality and only indicated that the crystal under investigation was an intergrowth of 6*H*, 15*R* and some other type which was not clear. The crystal was laid aside until 1952 when an intensive reinvestigation of a number of questionable crystals was undertaken using the Buerger precession and Laue methods. Excellent Buerger precession films were obtained of this modification as well as other previously unknown rhombohedral types consisting of many layers, e.g., 141*R*, 168*R*, 192*R*. Some of these will be reported in a forthcoming paper.

The existence of modification 19*H* was predicted by Ramsdell and Kohn (1952). They also predicted for its structure the zigzag sequence 22232323. It is assumed that the only numbers found in silicon carbide zigzag sequences are 2, 3 and 4 (Ramsdell and Kohn, 1952). No sequence involving the number 4 will complete a 19 layer hexagonal cell. The only possible way to complete this cell using 2 and 3 is the arrangement 22232323. The calculations for this sequence gave satisfactory agreement with the observed intensities of the films. Table 1 compares the calculated and observed intensities for this sequence. The observed intensities are an average of the results of a number of observers. The presence of intergrowths of 6*H* and 15*R* gave reflections which made the evaluation of the intensities of the 19*H* spots impossible in the case of $10\cdot 6$, $10\cdot 3$, and $10\cdot\overline{13}$. The presence of these "foreign" spots was also considered in evaluating the intensities of the other reflections listed in the table.

The 19*H* zigzag sequence 22232323 includes the 15*R* sequence 232323. As a consequence there should be a marked similarity in their reflections. This is most easily observed in the comparison of the intensities of the $10\cdot l$ reflections. On Weissenberg or precession films the rows of $10\cdot l$ reflections of all silicon carbide types coincide. Moreover, the *range* from $10\cdot 0$ to $10\cdot 19$ for 19*H* coincides exactly with the *range* $10\cdot 0$ to $10\cdot 15$ in

* Contribution from the Department of Mineralogy and Petrography, University of Michigan, No. 171.

† This investigation was made possible by assistance from the Office of Naval Research.

TABLE 1. COMPARISON OF OBSERVED AND CALCULATED INTENSITIES FOR SOME OF THE REFLECTIONS OF TYPE 19*H*

$(10\cdot l)$	$I_{calc.}$	$I_{obs.}$
$10\cdot 0$	1.7	*m*
1	12.6	*s*
2	0.5	*vw*
3	0.0	—
4	0.2	*vvw*
5	100.0	*vvs*
6	1.4	—
7	0.8	*w*
8	2.4	*m*
9	88.2	*vvs*
10	1.6	*vw*
11	0.9	*vw*
12	3.3	*m*
13	12.2	*s*
14	1.4	*vw*
15	1.0	*vw*
16	6.8	*ms*
17	3.3	*m*
18	0.8	*vw*
19	0.5	*vvw*
$10\cdot\bar{1}$	2.4	*m*
$\bar{2}$	14.5	*s*
$\bar{3}$	21.8	*s*
$\bar{4}$	3.8	*ms*
$\bar{5}$	4.0	*ms*
$\bar{6}$	39.8	*s*
$\bar{7}$	19.9	*s*
$\bar{8}$	2.1	*w*
$\bar{9}$	2.0	*w*
$\bar{10}$	72.4	*vs*
$\bar{11}$	1.3	*vw*
$\bar{12}$	0.3	*vvw*
$\bar{13}$	0.3	—
$\bar{14}$	28.6	*s*
$\bar{15}$	0.0	*a*
$\bar{16}$	0.0	*a*
$\bar{17}$	0.3	*vvw*
$\bar{18}$	3.7	*ms*
$\bar{19}$	0.3	*vvw*

15*R*. However, because of the rhombohedral extinctions of 15*R*, the only $10\cdot l$ reflections are those with $l=1$, 4, 7, etc. and $\bar{2}$, $\bar{5}$, $\bar{8}$, etc. The 19*H* reflections which do not approximately coincide with 15*R* positions are

either weak or absent. The 19*H* reflections which coincide most closely with 15*R* reflection positions are of stronger intensity, and, of these, those near very intense 15*R* reflection positions have the greatest intensity. For example, intensity calculations for 19*H* show $10\cdot5$ to be the strongest reflection. It is nearest in position to $10\cdot4$ for 15*R*, which likewise is the strongest 15*R* reflection. But the calculated intensity for $10\cdot\bar{5}$ of 19*H* is very low, and this corresponds to $10\cdot\bar{4}$, which is a missing reflection in the 15*R* lattice. Similar relationships are shown for other reflections in Table 2, in which the strongest 19*H* reflections are given.

TABLE 2. A COMPARISON OF THE INTENSITIES OF SOME 19*H* AND 15*R* REFLECTIONS

19*H*	$10\cdot17$–$10\cdot16$	$10\cdot13$–$10\cdot12$	$10\cdot9$	$10\cdot5$	$10\cdot1$	$10\cdot\bar{2}$–$10\cdot\bar{3}$	$10\cdot\bar{6}$–$10\cdot\bar{7}$	$10\cdot\bar{10}$	$10\cdot\bar{14}$	$10\cdot\bar{18}$
order	9	8	2	1	7	6	4	3	5	10
15*R*	$10\cdot13$	$10\cdot10$	$10\cdot7$	$10\cdot4$	$10\cdot1$	$10\cdot\bar{2}$	$10\cdot\bar{5}$	$10\cdot\bar{8}$	$10\cdot\bar{11}$	$10\cdot\bar{14}$
order	9	7	2	1	8	5	4	3	6	10

The 15*R* reflections which they approach are listed directly under them. The numbers under each of these indicate decreasing intensities. From these orders one can see the correlation of the intensities of the 19*H* reflections with the corresponding 15*R* reflections. In a few cases where two 19*H* reflections are both close to a 15*R* reflection position, the stronger of these was used in determining the order of intensity.

This structure has the space group *P3m*,* as in the 10*H* polymorph. The unit cell dimensions are $a_0=3.073$ kX,† $c_0=47.75_3$ kX, and $Z=19$. The zigzag sequence 22232323 results in the following atomic positions:

19 Si at 000, $002z$, $004z$, $008z$, $0011z$, $0015z$, $0017z$,
$\frac{1}{3}\,\frac{2}{3}\,1z$, $\frac{1}{3}\,\frac{2}{3}\,5z$, $\frac{1}{3}\,\frac{2}{3}\,7z$, $\frac{1}{3}\,\frac{2}{3}\,9z$,
$\frac{1}{3}\,\frac{2}{3}\,13z$, $\frac{1}{3}\,\frac{2}{3}\,16z$, $\frac{2}{3}\,\frac{1}{3}\,3z$, $\frac{2}{3}\,\frac{1}{3}\,6z$,
$\frac{2}{3}\,\frac{1}{3}\,10z$, $\frac{2}{3}\,\frac{1}{3}\,12z$, $\frac{2}{3}\,\frac{1}{3}\,14z$, $\frac{2}{3}\,\frac{1}{3}\,18z$.
19 C at $00p$, $002z+p$, $004z+p$, $008\,z+p$, $00\,11z+p$, $00\,15z+p$,
$00\,17z+p$, $\frac{1}{3}\,\frac{2}{3}\,1z+p$, $\frac{1}{3}\,\frac{2}{3}\,5z+p$, $\frac{1}{3}\,\frac{2}{3}\,7z+p$,
$\frac{1}{3}\,\frac{2}{3}\,9z+p$, $\frac{1}{3}\,\frac{2}{3}\,13z+p$, $\frac{1}{3}\,\frac{2}{3}\,16z+p$,
$\frac{2}{3}\,\frac{1}{3}\,3z+p$, $\frac{2}{3}\,\frac{1}{3}\,6\,z+p$, $\frac{2}{3}\,\frac{1}{3}\,10z+p$,
$\frac{2}{3}\,\frac{1}{3}\,12z+p$, $\frac{2}{3}\,\frac{1}{3}\,14z+p$, $\frac{2}{3}\,\frac{1}{3}\,18z+p$.
$z=1/19$, $p=3/76$

The crystal is dark blue in color. It is roughly 1 mm. in diameter and

* The hexagonal primitive lattice is designated as *P*, following the new *International Tables for X-ray Crystallography*.

† These dimensions are given in kX units to agree with the previously published values for the various SiC types.

TABLE 3. MORPHOLOGICAL DATA

Form	No. times observed	Quality	Observed	Calculated*
00·1	2	AC	0°00′	0°00′
10·0	3	DE	90°00′	90°00′
10·1	1	D	86°40′	86°49′
10·2	2	E	83°36′–83°50′	83°38′
10·3	2	CD	80°16′–80°25′	80°31′
10·4	1	D	77°34′	77°26′
10·5	2	CE	74°28′–74°31′	74°26′
10·6	1	E	71°26′	71°31′
10·7	0			68°41′
10·8	1	E	65°40′	65°58′
10·9	1	D	63°11′	63°22′
10·10	2	D	60°51′–60°54′	60°52′
10·11	0			58°29′
10·12	0			56°14′
10·13	3	DE	54°00′–54°34′	54°05′
10·14	0			52°02′
10·15	0			50°01′
10·16	0			48°16′
10·17	0			46°33′
10·18	0			44°54′
10·19	0			43°21′

* Calculated from the theoretical axial ratio for a 19 layer cell.

0.25 mm. thick. Table 3 gives the morphological data for those 19*H* faces measured on the crystal. The faces, which are confined to three pyramid zones, were in nearly every instance of very poor quality. No attempt was made to determine by etching which is the upper and which is the lower pinacoid (Thibault, 1944) and, thus, no distinction is made between the measured $10 \cdot l$ and $10 \cdot \bar{l}$ faces.

REFERENCES

RAMSDELL, L. S., AND KOHN, J. A. (1952), *Acta Cryst.*, **5**, 215.
THIBAULT, N. W. (1944), *Am. Mineral.*, **29**, 274–278.