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MORPHOLOGICAL AND STRUCTURAL CRYSTALLOGRAPHY AND OPTICAL PROPERTIES OF SILICON CARBIDE (SiC)*

PART I: MORPHOLOGICAL CRYSTALLOGRAPHY AND ETCHING FIGURES

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ABSTRACT

The morphological crystallography of β -SiC (cubic), and of five modifications or "types" of α -SiC (hexagonal), two of them new, is given in detail. Each of the α -SiC types is characterized by its own series of crystal forms, those of types I, IV and VI being typical for crystals based on rhombohedral lattices, while those of types II and III are characteristic of hexagonal lattices. Each α -SiC type must be referred to its own axial ratio, all of which, however, are rationally related, and the crystal forms common to two or more of the types are those whose indices are equivalent when referred to the greatest common divisor axial ratio. Two or more of the hexagonal modifications often coalesce in such a

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manner that c and a axes are common and the basal pinacoids form the plane of contact. Two methods of twinning were noted. In the more common case it was impossible to distinguish between two possible laws: twinning axis perpendicular to a common first order pyramid, or twinning plane parallel to a very rare first order pyramid. The second twinning arrangement, involving only type I crystals, obeys the law: twinning axis, the c axis. Crystal measurements made on β -SiC for the first time indicate the hextetrahedral class of the isometric system. Beta SiC is commonly intergrown with α -SiC in such a manner that tetrahedron faces of the former are in contact with or parallel to basal pinacoids of the latter.

Etching figures obtained on crystals of the α -SiC types by the use of Cl_2 at 1000°C . and by fused borax indicate that α -SiC, types I, IV and VI are ditrigonal-pyramidal, and that types II and III are dihexagonal-pyramidal. Etching phenomena reveal that purely morphological criteria are inadequate for the distinction between upper and lower basal pinacoids.

INTRODUCTION

Many studies have been made of the morphology and structure of silicon carbide, and of its physical properties, including density and indices of refraction, but there has been no attempt to correlate the data for the many observed modifications, nor to seek the relationships among them. Moreover, in addition to the lack of consistency and the incompleteness of the literature on the subject, little work has been done on crystals of known chemical analysis. For these reasons it seemed advisable to undertake a detailed study of the morphological and structural crystallography, and the optical constants of this substance.

The investigation has been carried out in the Laboratories of Norton Company, with the exception of the x-ray determinations which were made in the Mineralogical Laboratory at the University of Michigan. Although silicon carbide manufactured by the Norton Company under the trade name "cristolon" supplied most of the material for the study, commercial SiC manufactured by all the American and most of the important foreign producers was included.

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MORPHOLOGICAL CRYSTALLOGRAPHY

REVIEW OF LITERATURE

Frazier (1893) examined platy crystals of SiC , the yellow-green of which showed a distinct rhombohedral-like development while the blue were apparently hexagonal holohedral. The axial ratio and most of the crystal forms observed by Frazier as well as by subsequent investigators are contained in Table 1, while forms which must be considered uncertain are listed in Table 2. The one twin observed was said to obey the law: twinning plane, the unit rhombohedron (now designated by the letter r).

Becke (1895) studied poorly developed tabular crystals. He also described twins similar to that observed by Frazier, but recognized two possible laws: (1) twinning axis normal to the unit trigonal pyramid (now designated r), or (2) twinning plane the form $(10\bar{1}4)$ (now represented by E). Becke believed the first possibility to be more likely since it is a more common twinning law.

Negri (1902) measured almost a hundred SiC crystals, some of which were apparently hexagonal holohedral, while others appeared to be rhombohedral. He, however, referred them all to the hexagonal-scalenohedral class. A later investigation which was to have included the results of etching experiments, and a discussion of 22 other rare and very rare forms was unfortunately never published.*

Baumhauer (1912), studying 20 small tabular SiC crystals, divided them into three groups, or "types," each having its own characteristic suite of forms, but referred them all to the same axial ratio. Some forms were common to two types, but only the base was common to all three. Crystals of the first type clearly showed a rhombohedral-like development and were considered hexagonal-scalenohedral, while those of types II and III were apparently holohedral and said to be dihexagonal-dipyramidal. Crystals of the different types were adjacent to and irregularly intergrown with one another, and in two cases there was a coalescence of types I and II in such a manner that, although each crystal was apparently single and homogeneous, all the faces adjacent to one base were those of type I while all faces adjacent to the other base belonged to type II. The plane of contact between the two types was parallel to both basal pinacoids. The yellow crystals were found to be type I, the green, type II, while all three types were represented by the dark blue and black SiC .

Baumhauer (1915) described additional cases of coalescences of the SiC

* Personal communication from Professor A. Pelloux, Director, Institute di Mineralogia, Genoa, Italy, August 26, 1939.

types. Evidence for hemimorphism was afforded by the distribution of iridescent coatings on the various crystal faces, so Baumhauer considered type I ditrigonal-pyramidal. Certain triangular markings discussed more fully later led him to conclude that type II also belonged to the same class. Type III was considered dihexagonal-pyramidal. Two modes of twinning were reported: twinning plane the first order prism, and twinning plane the basal pinacoid.

Weigel (1916) observed many crystals of hexagonal SiC whose twinning plane was said to be that of a pyramid.

Espig (1921) confirmed Baumhauer's observations of SiC types and coalescences, and twinning parallel to the base. Crystals of type I were said to be yellow-green, while those of type II were blue.

The crystal of cubic SiC studied by Braekken (1930) was reported to be octahedral with poor skeletal faces, but apparently no goniometric measurements were attempted.

Peacock and Schroeder (1934) studied thin tabular crystals all of which proved to be type II. The indices of the forms of all the known SiC types were simplified to the greatest possible extent by referring each type to its own individual axial ratio, namely, that resulting from the *x*-ray studies of Ott (1925*a*, 1925*b*, 1926).

Appended to the above article, Peacock (1934) has described SiC crystals in the collection at Harvard University. The forms listed in Table 1 under type I were observed.

Cortelezzi and Schroeder (1934) studied type II crystals, some or all of which were apparently the same as those studied by Peacock and Schroeder.

The Handbook of Chemistry and Physics (1943) and Wyckoff (1931) refer to the three modifications of SiC mentioned above as SiC I, II and III. Cubic SiC is designated SiC IV, and the hexagonal modification with 51 formula weights per cell as described by Ott (1928) is noted as SiC V.

Table 1, which correlates the crystal forms observed by the different authors, is divided by heavy vertical lines into four major sections. The earlier investigators referred all crystals to the same *c*:*a* ratio, but did not distinguish definite crystal types. Later Baumhauer and Espig each recognized three definite types but referred all to an axial ratio twice that of the earlier writers. Peacock and Schroeder, Peacock, and Cortelezzi and Schroeder recognized the three types but referred each to its own unique axial ratio. Finally, the present writer has distinguished five crystal types each with its own *c* value and has for the first time definitely differentiated between upper and lower forms by etching methods.

There is some doubt as to the number of types observed by the early investigators and the proper correlation of forms later found to be com-

TABLE 1. CORRELATION OF ESTABLISHED FORMS ON α -SiC

Frazier (1893)	Becke (1895)	Negri (1902)	Baumhauer (1912), (1915)	Espig (1921)	Peacock and Schroeder (1934), Peacock (1934)	Cortezzi and Schroeder (1934)	Thibault	Calculated angle to base	α -SiC Type	
$c=1.2264$ base — 1 10/7 5/2 10 — 10/11 5/4 2 5	$c=1.2243^*$ (0001) OR — (10 $\bar{1}$ 1) R ? (10.0.10.7) 10/7R (5052) 5/2R (10.0.10.1) 10R — — (20 $\bar{2}$ 1) 2R ? (5051) 5R	$c=1.2266$ (111) (23.23.7) (100); (22 $\bar{1}$) ? (17.17.13); (911) (778) (11.11.19) — (31.1.1); (773) (14.1.1) (51 $\bar{1}$); (11 $\bar{1}$) ? (11.4.4)	$c=2.4532$ OR (111)(0001) -5/13R (166)(5.0.5.13) -1/2R (011) (1012) -5/7R (144) (5057) -5/4R (233) (5054) -5R (322) (5051) — 5/11R (722) (5.0.5.11) 5/8R (611) (5.0.5.8) R (100) (1011) 5/2R (411) (5052)	$c=2.4538$ (0001); (0001) — (10 $\bar{1}$ 2)?; (1012) (5057); (5057) (5054); (5054) (5051); (5051) — (5.0.5.11) (5058); (5058) (1011); (1011) (5052); (5052)	$c=12.2660$ c , 0(0001) m , -1/13 (1.0.1.13) r , -1/10 (1.0.1.10) f , -1/7 (1017) g , -1/4 (1014) z , -1 (1011) k , +1/14 (1.0.1.14) h , +1/11 (1.0.1.11) i , +1/8 (1018) x , +1/5 (1015) e , +1/2 (1012)	— — — — — — — — — — — —	$c=12.267_5$ c (0001); \bar{c} (0001) M (1.0.1.13) r (1.0.1.10) f (1017); \bar{f} (0117) g (1014); \bar{g} (0114) z (1011); \bar{z} (0111) — h (0.1.1.11); \bar{h} (1.0.1.14) i (0118); \bar{i} (1.0.1.11) x (0115); \bar{x} (1015) e (0112); \bar{e} (1012) b (1.1.2.15)	0°00' 47°27½' 54°47' 63°42' 74°14' 85°57½' 45°20' 52°10' 60°32½' 70°33½' 81°58' 58°33½'	I	
base first order prism 4/5 1 ? 4/3 2 ? 4	(0001) OR (1010) ∞ R — (10 $\bar{1}$ 1) R ? (4043) 4/3R (20 $\bar{2}$ 1) 2R ? (4041) 4R	(111) (211) ? (13.1.1); (331) (100); (221) ? (11.1.1); (775) ? (51 $\bar{1}$); (11 $\bar{1}$) ? (311); (557)	$c=2.4532$ \pm OP (111) (0001); (111) (0001) ∞ P (211) (1010) \pm 2/5P (311) (2025); (177) (2025) \pm 1/2P (411) (1012); (011) (1012) \pm 2/3P (711) (2023); (155) (2023) \pm P (100) (1011); (122) (1011) \pm 2P (511) (2021); (111) (2021)	$c=2.4538$ (0001); (0001) (1010) — (1012); (1012) (2023); (2023) (1011); (1011) (2021); (2021)	$c=4.9064$ c , 0 (0001) a , ∞ (1010) — r , 1/4 (1014) s , 1/3 (1013) x , 1/2 (1012) y , 1 (1011)	$c=4.9065$ c , 0 (0001) a , ∞ (1010) — r , 1/4 (1014) s , 1/3 (1013) x , 1/2 (1012) y , 1 (1011)	$c=4.9070$ c (0001); \bar{c} (0001) m (1010) n^* (1015); \bar{n} (1015) r (1014); \bar{r} (1014) s (1013); \bar{s} (1013) x (1012); \bar{x} (1012) y (1011); \bar{y} (1011) b (1126)	0°00' 90°00' 48°34½' 54°47' 62°06' 70°33½' 79°59½' 58°33½'	II	
?	?	(111) (211) ? (25.1.1); (17.17.7) — (11.1.1); (775) ? (19.5.5); (11.11.13)	$c=2.4532$ \pm OP (111) (0001); (111) (0001) ∞ P (211) (1010) \pm 4/9P (17.5.5) (4049)?; (1.13.13) (4049) \pm 2/3P (711) (2023); (155) (2023) \pm 4/3P (11.1.1) (4043); (577) (4043)	$c=2.4538$ (0001); (0001) (1010) — (4049) (2023); (2023) (4043); (4043)	$c=3.2709^*$ — — — — —	— — — — —	$c=3.2713$ c (0001); \bar{c} (0001) m (1010) — d^* (1013) s (1012); \bar{s} (1012) l^* (1011); \bar{l} (1011) b (1124)	0°00' 90°00' — 51°32½' 62°06' 75°10½' 58°33½'	III	
				$c=2.4538^*$ (7075); (7075) (7072); (7072) — (7.0.7.10); (7.0.7.10) (7074); (7074) (7071)				$c=17.174_5$ c (0001); \bar{c} (0001) N (0.1.1.11); \bar{N} (1.0.1.11) G (0118); \bar{G} (1018) L (0115) K (0112); \bar{K} (1012) — O (0.1.1.19) Q (0.1.1.16) P (0.1.1.13) H (1.0.1.10); \bar{H} (0.1.1.10) I (1014); \bar{I} (0117) J (1011); \bar{J} (0111)	0°00' 60°59' 68°02' 75°51' 84°14½' 46°13½' 51°06' 56°45' 63°14½' 70°33½' 78°36' 87°07'	IV
				$c=2.4538^*$ (11.0.11.5) ?			No morphological data available. Type established by Ott (1928) from x-ray study.		V	
							$c=26.989$ c (0001) C (1.0.1.28) r (1.0.1.22) u (1.0.1.16); \bar{u} (0.1.1.16) t (1.0.1.13); \bar{t} (0.1.1.13) q (1.0.1.10); \bar{q} (0.1.1.10) p (1017); \bar{p} (0117) o (1014); \bar{o} (0114) j (1011); \bar{j} (0111) D (0.1.1.26) B (0.1.1.23); \bar{B} (1.0.1.23) A (1.0.1.20) w (0.1.1.17); \bar{w} (1.0.1.17) x (0.1.1.11); \bar{x} (1.0.1.11) v (0115); \bar{v} (1015)	0°00' 48°03½' 54°47' 62°49½' 67°21½' 72°12½' 77°20½' 82°41' 88°09½' 50°09½' 53°34½' 57°18½' 61°23' 70°33½' 80°53'	VI	

*Calculated from twinning angles.

* Types IV and VI not recognized as distinct types by Espig.

* Calculated from previous data. No type III crystals observed by these authors.

* Letters assigned by Peacock and Schroeder although they did not observe these forms.

TABLE 2. UNCERTAIN FORMS ON α -SiC

Angle to Base		Letter	Symbol	(when) $c =$	Observed by	α -SiC type	Times Observed
Observed	Calculated						
?	15°49'*	—	1/5	1.2264	Frazier (1893)	?	?
?	81°32½'*	—	19/4	1.2264	Frazier (1893)	?	?
35°20'	35°18½'	E**	(1014)	2.4532	{ Baumhauer (1915)	I	1
43°20½'	43°21½'	—	(1013)	2.4532	Espig (1921)	?	1
?	57°34½'	—	(5059)	2.4538	Baumhauer (1915)	III	1
			(5059)		Espig (1921)	?	2
?	87°58½'*	—	(10.0.10.1)	2.4538	Espig (1921)	I?	1
84°55'	84°57½'	—	(2021)	4.9070	Thibault	II	1
70°29'	70°33½'	x	(1017)	17.174 ₅	Thibault	IV	1
50°16½'	50°09½'	D	(0.1.1.26)	26.989	Thibault	VI	1
48°24'	48°03½'	C	(1.0.1.28)	26.989	Thibault	-VI	1
54°49'	54°47'	r	(1.0.1.22)	26.989	Thibault	VI	1

* Calculated from symbols and axial ratios given by the authors.

** Letter assigned by the writer to facilitate reference to the form in connection with twinning.

mon to two types. This is indicated by question marks in Table 1. Except in one case Espig gave no observed angles for the forms which he listed, and, from the data which he presented, the writer was not able to gain a clear conception of the combination of forms or types on many of the crystals which he described. For example, although the indices given for several forms would indicate that Espig observed faces belonging to the new modification now designated α -SiC, type IV, these faces did not always occur in the proper sequence and faces of forms belonging to other hexagonal SiC modifications were interspersed in an irregular manner. The same may be said of (11.0. $\bar{1}$ 1.5) which is equivalent to one of the forms of the new modification, type VI. Espig apparently recognized only modifications I, II and III, and did not explain the presence of these faces which did not belong to the simple arithmetical series of forms of the first three types. Although these forms might be considered questionable, they are included in Table 1 for the purpose of correlation with equivalent forms now definitely established.

ALPHA SiC

Introduction. Commercial abrasive silicon carbide consists very largely of hexagonal or α -SiC crystals in all states of perfection, intergrowths and aggregates of subhedral crystals and dense crystalline masses. Usually small amounts of cubic or β -SiC and certain impurities are also present.

Euhedral crystals are most frequently tabular parallel to the base. In such a case one basal pinacoid is usually well developed while the other is poorly developed or absent altogether, but this is not universal. Less commonly the individuals are thick tabular to equant, and rarely, elongated parallel to the c axis. Crystals showing skeletal growth with prisms and pyramids accompanied by many horizontal striae and re-entrant angles are very common.

About a hundred and fifty crystals were completely measured during the course of this study, and, in addition, certain zones on about five hundred more were investigated. A one-circle goniometer was used almost exclusively.

Type I. This type is apparently the second most common of the α -SiC modifications. As indicated by Tables 3 and 4, and Fig. 1, the crystals are rhombohedral-like in development as evidenced by the different series of forms characteristic of alternate first order trigonal pyramid zones. One very small black crystal contained five faces of the new form \bar{b} . In this case, as well as with individuals of types II and III and 24 minute crystals of undetermined type examined under the stereoscopic microscope, all faces of the second order pyramid occurred adjacent to only one of the basal pinacoids which etching showed to be the lower form.

As will be discussed in the section devoted to etching figures, type I SiC is hemimorphic, belonging to the ditrigonal-pyramidal class of the hexagonal system. Previous investigators apparently distinguished between upper and lower forms from a consideration of the crystal habit. For example, Becke (1895) retained the larger and more perfectly developed base as the upper form and stated that the lower trigonal pyramids were larger and more numerous, while Peacock (1934) spoke of hemimorphism as evident in the very poor development of the lower trigonal pyramids.

The present study of a larger number of crystals has indicated that morphological criteria for the distinction between upper and lower forms are inadequate. While as a whole the upper first order pyramids, especially those least inclined to the basal pinacoid, were found to be more numerous than the corresponding lower forms, and the upper basal pinacoid larger and more perfectly developed than the lower, several individual crystals violated these generalizations. Thus etching experiments, or possible electrical tests such as for pyroelectricity, are necessary for the reliable distinction between upper and lower forms, and, since it does not appear that any of the previous investigators used such methods for separating these forms, it seems likely that their distinctions between them as indicated in Table 1 were often incorrect, except when faces of both upper and corresponding lower forms occurred on the same crystal. In the present work all distinctions have been made on the basis of differential etching of the basal pinacoids. Form \bar{b} is probably good morphological evidence of hemimorphism, but this form is only present very rarely.

Table 3 contains the morphological data for type I. The axial ratio on which the calculated values and indices are based is that which is indicated by the x -ray study, and gives the greatest simplification of the form indices. Within the limits of error of the measurements, it was found to be rationally related to the very precisely determined $c:a$ value of type II crystals by a factor of $2\frac{1}{2}$, as indicated in Table 8. Table 4 contains an angle table for two-circle goniometry. Insofar as possible, the presentation of the crystallographic data follows the procedure adopted for the new edition of Dana's *System of Mineralogy* as outlined by Wolfe (1941).

Type II. As observed by the previous investigators, crystals of type II were found to be by far the most abundant. The type has been studied in greater detail and the axial ratio more precisely determined than is true of the other types, and it therefore serves as a standard of comparison.

Table 5 gives the morphological data for type II crystals as determined on the one-circle goniometer. Partial data from two-circle measurements

TABLE 3. MORPHOLOGICAL DATA, TYPE I SiC

Form	No. Times Observed	Quality	Angle between Form and Base			
			Measured Range	Weighted Average	Calculated Value	
$c\bar{c}$	0001	22	A-C	—	—	0°00'
M	1.0.1.13	1	C	47°30'	47°30'	47°27½'
r	1.0.1.10	2	A-B	54°46'	54°46'	54°47'
$f\bar{f}$	1017	13	A-C	63°37' - 63°45'	63°42½'	63°42'
$g\bar{g}$	1014	7	A-C	74°11' - 74°19'	74°14½'	74°14'
$z\bar{z}$	1011	9	A-C	85°51' - 86°02'	85°57½'	85°57½'
\bar{k}	0.1.1.14	1	C	45°10'	45°10'	45°20'
$h\bar{h}$	0.1.1.11	5	B-C	52°10' - 52°13'	52°11'	52°10'
$i\bar{i}$	0118	12	A-C	60°30' - 60°40'	60°33'	60°32½'
$x\bar{x}$	0115	6	A-C	70°30½' - 70°35'	70°33'	70°33½'
$e\bar{e}$	0112	5	B-C	81°52' - 82°00'	81°56'	81°58'
\bar{b}	1.1.2.15	5	D-E	58°32½' - 58°36½'	58°34½'	58°33½'

TABLE 4. α -SiC, TYPE I, ANGLE TABLEHexagonal— R ; ditrigonal pyramidal— $3m$

$$a:c = 1:12.267_5$$

$$p_0:r_0 = 14.165_3:1$$

$$\alpha = 13^\circ 54\frac{1}{2}'$$

$$\lambda = 119^\circ 30\frac{1}{2}'$$

Lower	Upper		ϕ	ρ	A_1	A_2
\bar{c}	c	0001	—	0°00'	90°00'	90°00'
	M	1.0.1.13	+30°00'	47°27½'	50°21'	90°00'
	r	1.0.1.10	+30°00'	54°47'	44°58'	90°00'
\bar{f}	f	1017	+30°00'	63°42'	39°04'	90°00'
\bar{g}	g	1014	+30°00'	74°14'	33°33'	90°00'
\bar{z}	z	1011	+30°00'	85°57½'	30°15'	90°00'
\bar{k}		0.1.1.14	-30°00'	45°20'	90°00'	51°59'
\bar{h}	h	0.1.1.11	-30°00'	52°10'	90°00'	46°50½'
\bar{i}	i	0118	-30°00'	60°32½'	90°00'	41°03½'
\bar{x}	x	0115	-30°00'	70°33½'	90°00'	35°15'
\bar{e}	e	0112	-30°00'	81°58'	90°00'	30°57½'
\bar{b}		1.1.2.15	0°00'	58°33½'	64°45'	64°45'

on two crystals showing form \bar{b} , one of which is illustrated by Fig. 2, are included in Table 6. This shows that \bar{b} is a second order pyramid since the ϕ value is 30° from that of the other pyramids which were found to be first order forms.

TABLE 5. MORPHOLOGICAL DATA
TYPE II SiC

Form	No. Times Observed	Quality	Angle between Form and Base		
			Measured Range	Weighted Average	Calculated Values
$c-\bar{c}$ 0001	67	A-B	—	—	0°00'
m 1010	26	A-B	89°56' -90°01½'	90°00'	90°00'
$n-\bar{n}$ 1015	23	C-D	48°27' -48°40½'	48°33½'	48°34½'
$r-\bar{r}$ 1014	17	A-B	54°45' -54°53'	54°47'	54°47'
$s-\bar{s}$ 1013	56	A-B	62°03' -62°08'	62°06'	62°06'
$x-\bar{x}$ 1012	34	A-B	70°29½' -70°35½'	70°33½'	70°33½'
$y-\bar{y}$ 1011	31	A-B	79°57½' -80°02½'	79°59½'	79°59½'
\bar{b} 1126	5	C-E	58°10' -58°57'	58°37'	58°33½'

TABLE 6. PARTIAL MORPHOLOGICAL DATA, TWO-CIRCLE GONIOMETRY,
TYPE II SiC

Form	No. Times Observed	Quality	Observed, Weighted Averages		Calculated	
			ϕ	ρ	ϕ	ρ
\bar{b} 1126	5	C-E	-0°02'*	58°32'	0°00'	58°33½'

* Zone of first order pyramids (+30°00') used as reference.

Etching experiments on a large number of type II individuals likewise proved conclusively that, although this type is hemimorphic, morphological criteria were wholly inadequate to distinguish upper from lower basal pinacoids, except in the rare case when \bar{b} was present.

Although Negri's careful measurements of silicon carbide left little to be desired, axial ratios were calculated from the best observations made on type II crystals during the present investigation. These are contained in Table 7 where a comparison is afforded with the results of Negri and of Espig when the proper transformations have been made. The axial ratio retained, 4.9070, is that which gives the greatest simplification of form indices and the one indicated by x -ray studies.

Table 7 includes measurements on both green and blue black crystals. In order to ascertain whether axial ratios calculated from measurements on green SiC differed from similar calculations on the blue black, $c:a$

TABLE 7. ACCURATE MEASUREMENTS, TYPE II SiC

Form	Excellent Signals		Good Signals		Weighted Average	$c:a$	$c:a$ from Negri (1902)	$c:a$ from Espig (1921)
	Number	Average	Number	Average				
$r-\bar{r}$	5	54°46'03"	12	54°47'25"	54°46'48"	4.9070 ₄	4.9064 ₈	—
$s-\bar{s}$	24	62°06'15"	32	62°05'43"	62°06'01"	4.9069 ₆	4.9070 ₄	—
$x-\bar{x}$	11	70°33'38"	23	70°33'19"	70°33'28"	4.9068 ₈	4.9066 ₄	4.9074 ₈
$y-\bar{y}$	7	79°59'09"	24	79°59'40"	79°59'29"	4.9071 ₆	4.9074 ₄	—
				Weighted Average		4.9070	4.9069	

TABLE 8. OBSERVED AND CALCULATED AXIAL RATIOS, α -SiC TYPES

α -SiC type	Quality and Number of Observed Faces					Observed $c:a$	$c:a$ Calculated from Type II Observed Value	Per Cent Difference
	Excellent	Good	Fair	Poor	Very Poor			
II	47	91	—	—	—	4.9070	—	—
II, green	22	52	—	—	—	4.9073	4.9070	+ .006
II, blue-black	25	39	—	—	—	4.9066	4.9070	- .008
I	11	30	20	—	—	12.2667	12.267 ₅	- .007
III	4	7	11	2	2	3.2713	3.2713	none
IV	1	10	10	3	0	17.1897	17.174 ₅	+ .089
VI	3	22	14	6	2	26.982	26.989	- .026
I (from Negri)	(total of 428 of all qualities)					12.2697	12.267 ₅	+ .018
III (from Negri)	(total of 15 of all qualities)					3.2708	3.2713	- .015

values were determined for each of these two varieties. These are included in Table 8. Although the ratios differ by seven units in the fourth decimal place, this is well within the probable limit of error for the number of angles measured and the rather high $c:a$ value.

TABLE 9. ALPHA SiC, TYPE II ANGLE TABLE
Hexagonal— P ; dihexagonal pyramidal— $6mm$.
 $a:c=1:4.9070$ $p_0:r_0=5.6661:1$

Lower	Upper		ϕ	ρ	M	A_2
\bar{c}	c	0001	—	0°00'	90°00'	90°00'
	m	1010	+30°00'	90°00'	60°00'	90°00'
\bar{n}	n	1015	+30°00'	48°34½'	67°59'	90°00'
\bar{r}	r	1014	+30°00'	54°47'	65°53½'	90°00'
\bar{s}	s	1013	+30°00'	62°06'	63°46½'	90°00'
\bar{x}	x	1012	+30°00'	70°33½'	61°52'	90°00'
\bar{y}	y	1011	+30°00'	79°59½'	60°30'	90°00'
\bar{b}		1126	0°00'	58°33½'	90°00'	64°45'

An angle table for two-circle goniometry is given in Table 9.

Type III. The third most common form of α -SiC is designated type III. Although more numerous in previous investigations, only two crystals were found in the course of the present study. The larger, black in color, is illustrated by Fig. 3; the other, about 1½ mm. in diameter, contained five faces of the form \bar{b} . Table 10 gives the morphological data, and Table 11 an angle table for the type. The axial ratio indicated by x -ray study yields the greatest simplification of form indices. Crystal measurement shows it to be 3.2713, which is precisely two thirds of the c value determined for type II crystals.

Type IV. Two entirely new types of hexagonal SiC were observed during the course of this study. One, represented by a single large yellow-green crystal, is designated α -SiC, type IV, and is illustrated by Fig. 4.

When this crystal was measured on the goniometer, it was immediately evident that it did not belong to any of the SiC types previously mentioned. Although, like type I, the specimen showed rhombohedral-like face development, it was characterized by an entirely different suite of trigonal pyramids only one of which was apparently equivalent to a type I form. An axial ratio was sought which would simplify the indices of the forms to the greatest extent and at the same time yield simple arithmetical series characteristic of crystals with rhombohedral lattices. When these conditions were fulfilled, the observed $c:a$ value was found to be 17.1897, a ratio which was later substantiated by x -ray study and

which, within the limits of error of the measurements, is $3\frac{1}{2}$ times that precisely determined for type II crystals.

TABLE 10. MORPHOLOGICAL DATA
TYPE III SiC

Form	No. Times Observed	Quality	Angle between Form and Base			
			Measured Range	Weighted Average	Calculated Value	
<i>c</i>	0001	1	A	—	—	0°00'
\bar{c}	0001	1	A	—	—	0°00'
<i>m</i>	1010	5	A-B	89°57' -90°00 $\frac{1}{2}$ '	89°59 $\frac{1}{2}$ '	90°00'
<i>d</i>	1013	5	C-E	50°53' -51°34'	51°29'	51°32 $\frac{1}{2}$ '
<i>s</i>	1012	6	A-C	62°05' -62°08'	62°07'	62°06'
\bar{s}	1012	5	A-D	62°04 $\frac{1}{2}$ ' -62°11'	62°07'	62°06'
<i>l</i>	1011	5	B-C	75°06' -75°12'	75°10'	75°10 $\frac{1}{2}$ '
\bar{l}	1011	3	A-C	75°09 $\frac{1}{2}$ ' -75°11'	75°10 $\frac{1}{2}$ '	75°10 $\frac{1}{2}$ '
\bar{b}	1124	5	D-E	58°32' -58°35 $\frac{1}{2}$ '	58°33'	58°33 $\frac{1}{2}$ '

TABLE 11. α -SiC, TYPE III, ANGLE TABLE
Hexagonal—*P*; dihexagonal pyramidal—*6mm*.
 $a:c=1:3.2713$ $\rho_0:r_0=3.7774:1$

Lower	Upper		ϕ	ρ	M	A ₂
\bar{c}	<i>c</i>	0001	—	0°00'	90°00'	90°00'
	<i>m</i>	1010	+30°00'	90°00'	60°00'	90°00'
	<i>d</i>	1013	+30°00'	51°32 $\frac{1}{2}$ '	66°57'	90°00'
	<i>s</i>	1012	+30°00'	62°06'	63°46 $\frac{1}{2}$ '	90°00'
	<i>l</i>	1011	+30°00'	75°10 $\frac{1}{2}$ '	61°05 $\frac{1}{2}$ '	90°00'
\bar{b}		1124	0°00'	58°33 $\frac{1}{2}$ '	90°00'	64°45'

Table 12 gives the morphological data and Table 13 an angle table for the type.

Type V. Type V SiC is reserved for the modification with 51 formula weights per unit cell which has been reported by Ott (1928) on the basis of *x*-ray measurements. A morphological study of the crystal could not be made by Ott because all pyramids had been broken from the thin tabular piece. No crystal of this type was encountered during the present study, but in view of the new types IV and VI with rather high *c:a* values and large number of formula weights per unit cell, type V is not at all improbable.

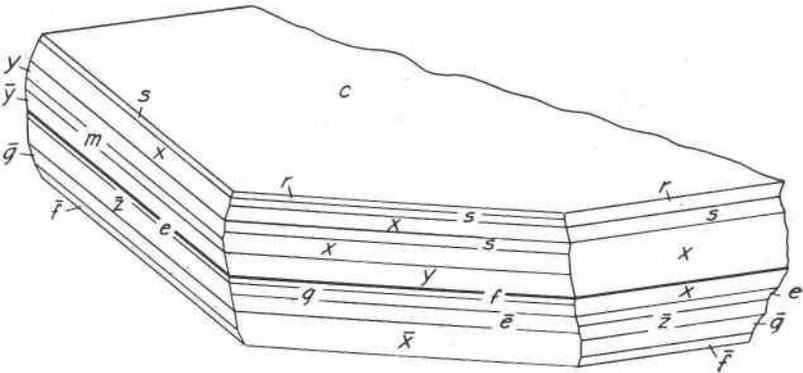
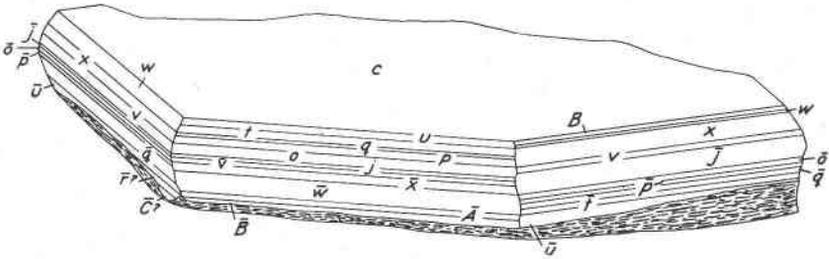
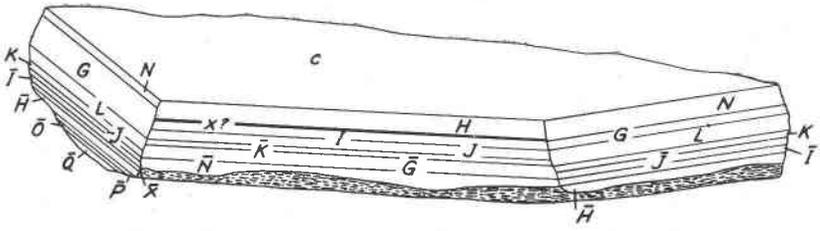


FIG. 4 (top). Alpha SiC, type IV.

FIG. 5 (center). Alpha SiC, type VI.

FIG. 6 (bottom). Coalescence of alpha SiC, type II (above), with type I (below).

TABLE 12. MORPHOLOGICAL DATA
TYPE IV SiC

Form	No. Times Observed	Quality	Angle between Form and Base		
			Measured Range	Weighted Average	Calculated Value
c 0001	1	A	—	—	
\bar{c} 0001	1	C	—	—	0°00'
\bar{Q} 0.1.1.19	1	D	46°13½'	46°13½'	46°13½'
\bar{O} 0.1.1.16	1	C	51°04½'	51°04½'	51°06'
\bar{P} 0.1.1.13	1	B	56°46'	56°46'	56°45'
\bar{H} 1.0.1.10	1	B	63°19'	63°19'	63°14½'
\bar{H} 0.1.1.10	2	C	63°03' - 63°15½'	63°09½'	
\bar{x} 0117	1	C	70°41'	70°41'	70°33½'
\bar{I} 1014	1	C	78°41'	78°41'	78°36'
\bar{I} 0114	2	C-D	78°32' - 79°03'	78°47½'	
\bar{J} 1011	1	B	87°11'	87°11'	87°07'
\bar{J} 0111	2	C-D	87°16' - 87°26'	87°21'	
\bar{N} 0.1.1.11	2	B	61°03' - 61°09½'	61°06½'	60°59'
\bar{N} 1.0.1.11	2	B	60°54½'	60°54½'	
\bar{G} 0118	2	B-C	67°59' - 68°06'	68°02½'	68°02'
\bar{G} 1018	1	B	67°51½'	67°51½'	
\bar{L} 0115	2	A-B	75°51½' - 75°52'	75°52'	75°51'
\bar{K} 0112	2	C	83°44' - 83°57'	83°50½'	
\bar{K} 1012	1	B	84°12½'	84°12½'	84°14½'

TABLE 13. α -SiC, TYPE IV, ANGLE TABLE

Hexagonal—R; ditrigonal pyramidal—3m

$a:c=1:17.174_5$

$\alpha=9^\circ 58'$

$p_0:r_0=19.831_4:1$

$\lambda=119^\circ 45'$

Lower	Upper		ϕ	ρ	A ₁	A ₂
\bar{c}	c	0001	—	0°00'	90°00'	90°00'
\bar{Q}		1.0.1.19	+30°00'	46°13½'	51°17½'	90°00'
\bar{O}		1.0.1.16	+30°00'	51°06'	47°37½'	90°00'
\bar{P}		1.0.1.13	+30°00'	56°45'	43°35½'	90°00'
\bar{H}	H	1.0.1.10	+30°00'	63°14½'	39°21'	90°00'
\bar{x}		1017	+30°00'	70°33½'	35°15'	90°00'
\bar{I}	I	1014	+30°00'	78°36'	31°54'	90°00'
\bar{J}	J	1011	+30°00'	87°07'	30°07½'	90°00'
\bar{N}	N	0.1.1.11	-30°00'	60°59'	90°00'	40°46½'
\bar{G}	G	0118	-30°00'	68°02'	90°00'	36°34'
	L	0115	-30°00'	75°51'	90°00'	32°53'
	K	0112	-30°00'	84°14½'	90°00'	30°30'

Type VI. Figure 5 illustrates a large black SiC crystal showing rhombohedral-like face development with different series of forms in alternate trigonal pyramid zones. These series, however, were entirely unlike those of any of the other α -SiC types, only the basal pinacoid and the first order pyramids r and $x\bar{x}$ being equivalent to forms found on the other types.

Again an axial ratio was sought which would offer the greatest simplification of form indices, yield simple arithmetical series of forms characteristic of crystals with rhombohedral lattices and at the same time be rationally related to the observed $c:a$ value for type II crystals. A ratio $5\frac{1}{2}$ times that of type II was found to satisfy these requirements; later the ratio was substantiated by x -ray study. Table 8 indicates that, within the limits of error of the measurements, the axial ratio is truly rationally related to that of type II.

TABLE 14. MORPHOLOGICAL DATA, TYPE VI SiC

Form	No. Times Observed	Quality	Angle between Form and Base		
			Measured Range	Weighted Average	Calculated Value
c 0001	1	A	—	—	0°00'
C 1.0.1.28	2	B	48°00' -48°02½'	48°01½'	48°03½'
r 1.0.1.22	2	A-B	54°42' -54°46'	54°44'	54°47'
u 1.0.1.16	3	B-C	62°48' -62°51'	62°49½'	62°49½'
\bar{u} 0.1.1.16	2	B	62°45' -62°47½'	62°46½'	
l 1.0.1.13	2	B-D	66°54' -67°24'	67°14'	67°21½'
\bar{l} 0.1.1.13	1	B	67°24'	67°24'	
q 1.0.1.10	3	C-E	71°44½' -72°20'	72°14'	72°12½'
\bar{q} 0.1.1.10	2	A-B	72°12½' -72°14'	72°13½'	
p 1017	1	C	77°20'	77°20'	77°20½'
\bar{p} 0117	2	B-C	77°17½' -77°23'	77°20½'	
o 1014	1	B	82°43'	82°43'	82°41'
\bar{o} 0114	2	B	82°42' -82°44'	82°43'	
j 1011	1	B	88°10½'	88°10½'	88°09½'
\bar{j} 0111	2	A-D	87°47' -88°11'	88°04'	
D 0.1.1.26	1	B	50°09'	50°09'	50°09½'
B 0.1.1.23	2	C-E	53°28½' -53°33'	53°32'	53°34½'
\bar{B} 1.0.1.23	3	C-D	53°38' -53°40½'	53°39'	
A 1.0.1.20	2	D	57°18½' -57°20½'	57°19½'	57°18½'
w 0.1.1.17	3	B-C	61°22½' -61°23'	61°22½'	61°23'
\bar{w} 1.0.1.17	3	B-C	61°18½' -61°30½'	61°24'	
x 0.1.1.11	3	B-D	70°33' -70°37'	70°34'	70°33½'
\bar{x} 1.0.1.11	1	B	70°33½'	70°33½'	
v 0115	2	C	80°51½' -80°55½'	80°53½'	80°53'
\bar{v} 1015	1	C	80°52'	80°52'	

TABLE 15. α -SiC, TYPE VI, ANGLE TABLE
 Hexagonal— R ; ditrigonal pyramidal— $3m$
 $a:c=1:26.989$ $\alpha=6^{\circ}21\frac{1}{2}'$
 $p_0:r_0=31.164:1$ $\lambda=119^{\circ}54'$

Lower	Upper		ϕ	ρ	A_1	A_2
	\bar{c}	0001	—	0°00'	90°00'	90°00'
	\bar{C}	1.0. $\bar{1}$.28	+30°00'	48°03 $\frac{1}{2}'$	49°54'	90°00'
	\bar{r}	1.0. $\bar{1}$.22	+30°00'	54°47'	44°58'	90°00'
\bar{u}	\bar{u}	1.0. $\bar{1}$.16	+30°00'	62°49 $\frac{1}{2}'$	39°36 $\frac{1}{2}'$	90°00'
\bar{l}	\bar{l}	1.0. $\bar{1}$.13	+30°00'	67°21 $\frac{1}{2}'$	36°56 $\frac{1}{2}'$	90°00'
\bar{q}	\bar{q}	1.0. $\bar{1}$.10	+30°00'	72°12 $\frac{1}{2}'$	34°27'	90°00'
\bar{p}	\bar{p}	10 $\bar{1}$ 7	+30°00'	77°20 $\frac{1}{2}'$	32°20'	90°00'
\bar{o}	\bar{o}	10 $\bar{1}$ 4	+30°00'	82°41'	30°48'	90°00'
\bar{j}	\bar{j}	10 $\bar{1}$ 1	+30°00'	88°09 $\frac{1}{2}'$	30°03'	90°00'
	\bar{D}	0.1. $\bar{1}$.26	-30°00'	50°09 $\frac{1}{2}'$	90°00'	48°19 $\frac{1}{2}'$
\bar{B}	\bar{B}	0.1. $\bar{1}$.23	-30°00'	53°34 $\frac{1}{2}'$	90°00'	45°49 $\frac{1}{2}'$
\bar{A}		0.1. $\bar{1}$.20	-30°00'	57°18 $\frac{1}{2}'$	90°00'	43°12 $\frac{1}{2}'$
\bar{w}	\bar{w}	0.1. $\bar{1}$.17	-30°00'	61°23'	90°00'	40°31'
\bar{x}	\bar{x}	0.1. $\bar{1}$.11	-30°00'	70°33 $\frac{1}{2}'$	90°00'	35°15'
\bar{v}	\bar{v}	0115	-30°00'	80°53'	90°00'	31°14'

Table 14 gives the morphological data for type VI, while an angle table is included in Table 15.

Relationship of Types. It will be even more evident after the x -ray and optical data have been considered that the types are not merely different habits of hexagonal SiC, nor do they, on the other hand, represent modifications with entirely separate physical and optical properties, such as shown by the usual polymorphic substances of which calcite and aragonite may be taken as examples. In view of these relationships all the hexagonal modifications are now referred to as α -SiC, the types being designated by Roman numerals. Following Baumhauer, the phenomenon is called "polytypism" the adjective being "polytypic" and each one of the different modifications a "type." On the other hand, the cubic modification differs in crystal system and optical properties as would be expected of the usual dimorphic substances, sphalerite and wurtzite, for example, and is here designated β -SiC.

Although the axial ratios to which each of the types has been referred afford the greatest simplification of first order pyramid forms, this is not the case with the second order pyramid \bar{b} . If the greatest common divisor of the accepted $c:a$ ratios of the various types, 0.8178, be chosen as the axial ratio of all the modifications and Bravais indices then calculated from it, the relationships among the types and among the various forms are evident in the remarkable manner indicated in Table 16. Here

in the vertical columns are the upper forms of the various α -SiC types and the Bravais indices calculated from $c=0.8178$. This new method of notation shows that in the case of the first order pyramids the first and third or the second and third numerals of the indices are exactly the number of formula weights in the unit cells of the respective SiC types, and that the only forms which are common to two or more modifications are those forms whose indices are equivalent when referred to this greatest common divisor $c:a$ value. The table also shows that the greatest simplification of the second order pyramid is obtained by this treatment. These relationships would seem to indicate that 0.8178 is the "axial ratio" of one "molecule" of SiC which is common to all the α -SiC types.

COALESCENCE OF TYPES

The crystals thus far considered contained forms which were consistent throughout with one of the SiC types, but this was not usually the case. Figure 6 illustrates a broken but otherwise well-developed individual which actually consists of two portions; all the faces adjacent to the upper base are those of type II, while those adjacent to the lower base belong to type I. In this crystal the contact between the two types is clearly a plane which is parallel to the basal pinacoids; it is indicated on the figure by the heavy line. The outcrop of this contact on the fractured portion of the crystal is marked by a fine striation. Figure 6 thus indicates a coalescence of types I and II with common c and a axes such that the resulting mass is indistinguishable under the stereoscopic microscope from a crystal composed entirely of one type. It should be pointed out that in one zone face x is common to both types involved in the coalescence. This is possible since the form is one of those occurring in both SiC types.

Other examples found during the course of this study, in addition to the numerous cases cited by Baumhauer (1915) clearly indicate that any combination of types may coalesce in the manner described and illustrated above. It would undoubtedly be found that SiC crystals which show multitudes of small re-entrant angles and striae consist of thin plates of several of the types, or oscillations between two or more of them.

Ungemach (1935*b*) has introduced the term *syntaxie* to describe the coalescence of polytypic substances as illustrated above with the SiC types. The best English equivalent is probably "syntaxis," the adjective being "syntaxic."

In addition to this intimate and special method of contact between the various types, there are others. Crystals which are of one type throughout, for example, may appear adjacent to individuals entirely of another type, either as parallel growths or as intergrowths with no common planes, or as indicated below, twinning may involve two or more types.

TABLE 16. CORRELATION OF FORMS ON α -SiC TYPES. INDICES REFERRED TO $c:a=0.8178$
 α -SiC TYPES

I	IV	VI	II	III
c 0001	c 0001	c 0001	c 0001	c 0001
M 15.0. $\overline{15}$.13		C 33.0. $\overline{33}$.28	m 60 $\overline{60}$ (10 $\overline{10}$)	m 40 $\overline{40}$ (10 $\overline{10}$)
r 15.0. $\overline{15}$.10 (30 $\overline{32}$)	*	r 33.0. $\overline{33}$.22 (30 $\overline{32}$)	n 60 $\overline{65}$	d 40 $\overline{43}$
f 15.0. $\overline{15}$.7	N 0.21. $\overline{21}$.11	u 33.0. $\overline{33}$.16		
g 15.0. $\overline{15}$.4	G 0.21. $\overline{21}$.8	t 33.0. $\overline{33}$.13		
z 15.0. $\overline{15}$.1	L 0.21. $\overline{21}$.5	q 33.0. $\overline{33}$.10		
	K 0.21. $\overline{21}$.2	p 33.0. $\overline{33}$.7		
		o 33.0. $\overline{33}$.4		
k 0.15. $\overline{15}$.14	Q 21.0. $\overline{21}$.19	j 33.0. $\overline{33}$.1		
h 0.15. $\overline{15}$.11	O 21.0. $\overline{21}$.16	D 0.33. $\overline{33}$.26		
i 0.15. $\overline{15}$.8	P 21.0. $\overline{21}$.13	B 0.33. $\overline{33}$.23		
	H 21.0. $\overline{21}$.10	A 0.33. $\overline{33}$.20		
		w 0.33. $\overline{33}$.17		
x 0.15. $\overline{15}$.5 (03 $\overline{31}$)	x 21.0. $\overline{21}$.7 (30 $\overline{31}$)	x 0.33. $\overline{33}$.11 (03 $\overline{31}$)	s 60 $\overline{63}$ (20 $\overline{21}$)	s 40 $\overline{42}$ (20 $\overline{21}$)
e 0.15. $\overline{15}$.2	I 21.0. $\overline{21}$.4 J 21.0. $\overline{21}$.1	v 0.33. $\overline{33}$.5	x 60 $\overline{62}$ (30 $\overline{31}$) = (03 $\overline{31}$)	l 40 $\overline{41}$
b 11 $\overline{21}$	*	*	y 60 $\overline{61}$	b 11 $\overline{21}$

* Not observed but of possible occurrence from theoretical considerations.

TWINNING

The most readily observed and probably the most frequent twinning arrangement involving α -SiC is that reported upon by previous investigators, namely, that in which the basal pinacoids of the twinned individuals are inclined to each other an average of about $70^{\circ}36'$ (obtuse angle as measured on the goniometer). The lines of contact between the individuals, which are usually tabular, are at the same time parallel to edges of the basal pinacoids of each of the portions involved in the twin. In certain areas on some lumps of crude SiC this type of twinning affects almost all of the crystals. Here repeated twinings and parallel growths are common.

In an attempt to distinguish between the two possible twinning arrangements suggested by Becke, careful determinations of the obtuse angle between the basal pinacoids were made on fifty twins of this nature chosen at random. The only twins accepted for measurement were those whose basal pinacoids adjacent to the obtuse angle afforded signals which were single and of excellent quality.

In spite of the fact that each angle is probably accurate to within $\pm 1'$, it is of particular interest to note that the observed twinning angle varied from $70^{\circ}25'$ to $70^{\circ}44'$, a range of $19'$, and that the maximum number of observations at any one angular value was 6. For comparison, the angles between the pyramids s or \bar{s} and the nearest basal pinacoid of type II crystals were also measured in fifty cases at random. In spite of the lower expected accuracy of the individual readings, they varied from $62^{\circ}03'$ to $62^{\circ}08'$, or a range of only $5'$, with 26 of the angles at the one value of $62^{\circ}06'$. Eighty-eight per cent of the angles fell within $\pm 1'$ of the average, while with the case of the twins only 30% fell within this limit. These data indicate that this type of twinning in α -SiC is to be classed with parallel growths as an arrangement of individuals according to a law which is only approximately satisfied. It also explains why Becke's value for the axial ratio of SiC differs greatly from that of all other investigators (see Table 1). His value was calculated from twinning angles, while all other axial ratios were determined from interfacial angles on single crystals.

The average of the fifty observed twinning angles is $70^{\circ}35'55''$; this compares with $70^{\circ}33'10''$, the weighted average of published values on eight crystals. If the twinning satisfied the law: twinning axis perpendicular to the form r , as suggested by previous investigators, the calculated twinning angle would be $70^{\circ}26'24''$, which is lower than all but one of the fifty twins included in the study mentioned above. If the twinning plane were the possible form E (see Table 2), the calculated angle would be

$70^{\circ}37'02''$. The closer accord with the latter value might suggest this twinning law, but it is difficult to believe that the twinning is related to the complex plane E in preference to the simpler and very fundamental plane r .

In the following section on cubic SiC it will be shown that in one crystal of this substance there exist two very thin plates of α -SiC which are parallel to adjacent faces of the positive and negative tetrahedrons. These two α -SiC plates are thus inclined to one another $70^{\circ}31\frac{3}{4}'$, the octahedral angle. Since cubic SiC may be a low-temperature form which, according to Tone (1938), reverts to hexagonal SiC at an elevated temperature, it is possible that the octahedral angle might be preserved should any α -SiC twin have grown from inclusions of α -SiC in the cubic modification as described above. This possibility should be investigated experimentally before any opinion is expressed concerning the twinning law involving the individuals described above.

Eight twins were examined in detail for hexagonal SiC types involved. The most common twin of the nature described above contained individuals of type II as illustrated by Fig. 7. In one case types I and II were twinned, and in three cases individuals of type II were twinned with syntaxial intergrowths of types I and II.

Another twinning arrangement was observed which involved only type I α -SiC. It is illustrated by the clinographic projection, Fig. 8, as well as by the diagram of etching figures, Fig. 10. It will be shown in the section devoted to etching that the twinning law represented here is: twinning axis, the c crystallographic axis. Although only two examples of this twinning law were encountered during the study, it is probable that it is more common in the more complex syntaxial intergrowths accompanied by highly striated faces. It is also probable that the twinings described by Baumhauer and by Espig as: twinning plane parallel to the base, were in reality twinned around the c axis since these authors apparently made no experiments which were capable of distinguishing between the two possibilities. Certainly in the course of etching over a hundred α -SiC crystals during the present study nothing was observed which would indicate that the basal pinacoid was a twinning plane.

BETA SiC

Practically all samples of sized commercial silicon carbide contain less than about five per cent of particles which are either entirely isotropic, or are partially isotropic containing lamellae of anisotropic material, as is fully described in the section on optical properties.

Examination of a "pig" of SiC from the usual resistance type furnace of intermittent operation revealed a concentration of this isotropic con-

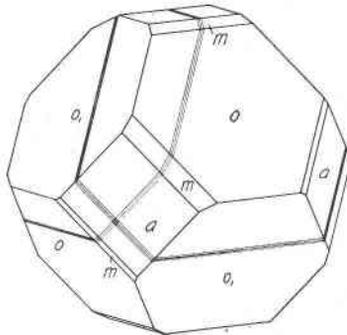
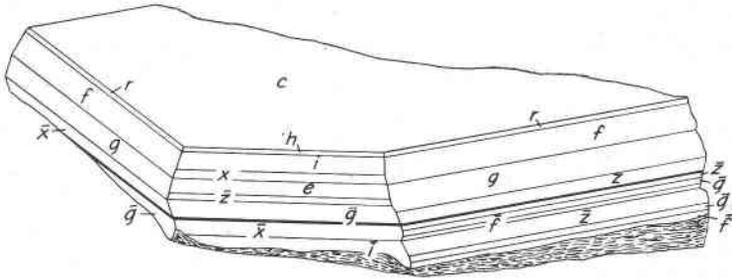
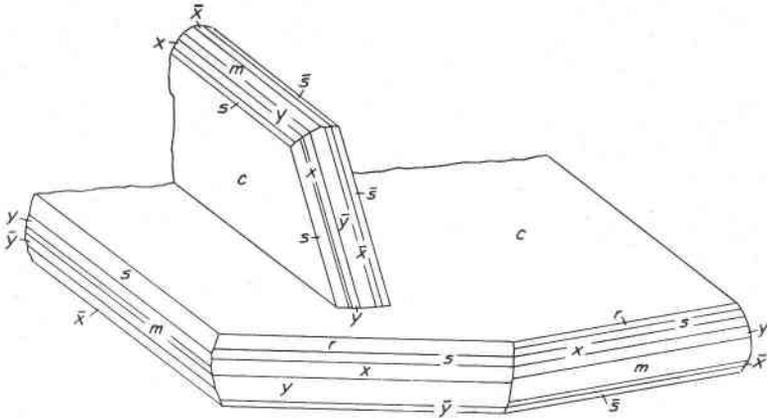


FIG. 7 (top). Most common twinning arrangement of alpha SiC. Type II twinned with type II.

FIG. 8 (center). Alpha SiC, type I, twinned with type I. Twinning axis: c crystallographic axis.

FIG. 9 (bottom). Beta (cubic) SiC. Striations indicate outcrops of included plates of alpha SiC.

stituent in the zones containing very finely crystalline SiC and "firesand." These occur between the area of closely intergrown larger crystals and masses of α -SiC toward the hotter core of the furnace, and the cooler zone of partially converted to unconverted material toward the outside of the "pig." Even in the fine crystalline and "firesand" zones, however, the isotropic substance was a very minor constituent, most of the material being α -SiC with small amounts of carbon and other impurities.

Most of the isotropic substance was present as tiny irregular to rounded individuals less than $\frac{1}{2}$ mm. in size, sometimes occurring alone, but more often in the form of very finely granular aggregates showing multitudes of minute crystal faces, or associated with single or twinned crystals or aggregates of α -SiC.

Several essentially isotropic individuals were sufficiently well developed for measurement on the one-circle goniometer. One of these crystals, illustrated by Fig. 9, although only 0.27 mm. in its largest diameter, was exceptionally well developed and only slightly distorted. Transparent, olive green in color, it was practically complete and showed no apparent point of attachment to other crystals. The forms observed under the high power of a stereoscopic microscope were six faces of the cube, four each of the positive and negative tetrahedrons, and ten, possibly eleven, of a positive trigonal tristetrahedron which goniometric measurements proved to be the form $m(113)$. No faces of a corresponding negative trigonal tristetrahedron were present.

Other combinations of forms observed were: positive and negative tetrahedrons distorted by elongation parallel to one of the binary axes; a large cube face with smaller positive and negative tetrahedrons; a pseudo-hexagonal combination of cube and positive and negative tetrahedrons.

Table 17 gives the results of goniometric measurements on the four cubic crystals. Because of the extremely small size of the crystals, and hence of the faces, most of the signals were weak and broad. No signal could be obtained from some of the smallest faces although they could be seen under the high powers of a stereoscopic microscope. In spite of the poor signals obtained from these minute faces, the agreement between observed and calculated values is very satisfactory. The presence of ten, possibly eleven, faces of the positive trigonal tristetrahedron $m(113)$ with a complete absence of the corresponding negative form, and the absence of tetartohedral forms would indicate the hextetrahedral class of the isometric system.

The cubic crystal illustrated by Fig. 9, in common with most of the isotropic substance in commercial SiC, contained lamellae of anisotropic material identified as thin basal plates of α -SiC. There were two such

lamellae in this crystal. The outcrops of these on the surface of the crystal were marked by striae which are indicated on the figure. One lamella was parallel to a face of the positive tetrahedron; the second, penetrating the first, was parallel to a face of the negative tetrahedron, the two thus being inclined to each other at about $70^{\circ}32'$. It is important to

TABLE 17. MORPHOLOGICAL DATA, β -SiC

Angle	Number of Readings on Different Angles	Measured Range	Average	Calculated Value
$a(001) \wedge o(111)$ or $a(001) \wedge o_1(\bar{1}11)$	17	$54^{\circ}19' - 55^{\circ}13'$	$54^{\circ}45\frac{1}{4}'$	$54^{\circ}44\frac{1}{4}'$
$o(111) \wedge o_1(111)$	13	$70^{\circ}20' - 70^{\circ}44'$	$70^{\circ}31\frac{1}{2}'$	$70^{\circ}31\frac{3}{4}'$
$a(001) \wedge m(113)$	6	$25^{\circ}00' - 25^{\circ}25'$	$25^{\circ}14\frac{1}{2}'$	$25^{\circ}14\frac{1}{4}'$
$o(111) \wedge m(113)$	7	$29^{\circ}15' - 29^{\circ}33'$	$29^{\circ}27\frac{1}{2}'$	$29^{\circ}29\frac{3}{4}'$

note that within the cubic crystal there were two tabular crystals of α -SiC intergrown in the same manner as the most common α -SiC twins and with similar inclination angle, and that the basal pinacoids of the included α -SiC plates were parallel to tetrahedron faces. The same relationships were observed on associations of the cubic substance and macroscopic crystals of α -SiC. In all cases tetrahedron faces of the cubic material were in contact with basal pinacoids of α -SiC.

Because of these facts and the additional relationships pointed out in the section on x-ray crystallography, there is little doubt that this cubic substance is an entirely different modification of SiC which will be designated β -SiC. A sufficient amount of this material could not be isolated for complete chemical analysis, but a spectroscopic analysis of a sample containing over 50% of the cubic substance, with the remainder α -SiC, was made by Dr. W. J. O'Leary and Mr. W. M. Hazel of the Norton Chippawa laboratories. A large amount of Si, a very small amount of Al and a trace of Mg were found. Because of the use of carbon electrodes the detection of this element in the sample tested was not possible.

In the relationships pointed out above, one of the four diagonal axes of trigonal symmetry in β -SiC is parallel to the c axis of α -SiC. It is not mere coincidence that both of these axes are polar, but an indication of the close structural similarity of the two modifications. The relationships also explain why α -SiC crystals twinned according to the most common law are symmetrical to a plane bisecting the acute re-entrant angle.

ETCHING FIGURES

REVIEW OF LITERATURE

Becke (1895), using a melt of NaNO_3 and Na_2CO_3 to etch SiC crystals, observed that the larger and more perfectly developed base, which he designated the upper basal pinacoid, always remained bright after etching, but contained very small six-sided etching figures having three longer sides alternating with three shorter. At the same time, the lower basal pinacoid was attacked to a greater extent and showed no etching figures. No observations concerning the results of etching on pyramid or prism faces were recorded. As a result of these observations and the evidence from crystal morphology, Becke placed SiC in the ditrigonal-pyramidal class of the hexagonal system, a determination accepted by Groth (1906). Individuals which Becke considered to be twinned on the normal to the form now designated r were symmetrical to a plane bisecting the acute re-entrant angle.

Baumhauer (1915), repeating Becke's etching experiments, was unable to obtain any clear etching figures on any of his newly discovered three types, but did observe that the basal pinacoids were differentially attacked. On a crystal of type II which he had not etched, Baumhauer observed white spots containing equilateral triangles, or two equilateral triangles one turned 60° with respect to the other. This led him to believe that type II was also ditrigonal-pyramidal.

Weigel (1916), using a melt of K_2CO_3 and KNO_3 (2:1) on a type II crystal, observed equilateral hexagons on one basal pinacoid while the other base was quite evenly dulled. Pyramids and the prism in one zone showed modified triangles which were symmetrical to a vertical plane, but which indicated the absence of a horizontal plane of symmetry. Using borax at 1000°C ., Weigel obtained equilateral hexagons on both basal pinacoids of a type II crystal and bisymmetrical rectangular etches on prism faces.

Espig (1921), using a melt of KOH, NaNO_3 and Na_2CO_3 as the etching medium, obtained a six-sided cavity with three longer sides alternating with three shorter on one base of a type I crystal and an equilateral hexagon on one base of a type II crystal. Espig referred type I to the ditrigonal-pyramidal, and type II to the dihexagonal-pyramidal class of the hexagonal system.

Although the etching experiments carried out by these investigators suggest the classes accepted by Espig, the class of type I has not been proven from these data. Moreover, Weigel's description of bisymmetrical etches on the prism of a type II crystal affords contradictory evidence for the dihexagonal-pyramidal class.

ETCHINGS BY FUSION METHODS

Because of the incomplete and inconsistent nature of the published data, a thorough study of etching was undertaken in order to determine the crystal class of each of the available SiC modifications, and the laws governing the twinning.

Crystals of types I and II were etched by all the media described in the literature. In every case, except with the use of borax, results similar to those reported by Espig were obtained, and no figures could be observed on any of the pyramids or prisms.

In order to ascertain whether, as stated by Becke, the larger and more perfectly developed base were the least attacked by a $\text{NaNO}_3\text{-Na}_2\text{CO}_3$ fusion, twelve crystals of undetermined type were selected for study. In each case one base was exceptionally large and perfectly developed, while the other base was very small and imperfect. Ten of the crystals yielded the expected result upon etching, but two were exactly opposite. Apparently Becke's generalization was based on too few observations, for it is impossible to correctly determine which is the upper and which the lower base without carefully etching each crystal, or detecting polarity by some electrical method.

Excellent etches were obtained by employing a borax fusion at red heat for a duration of 1-2 hours. Iron crucibles were used throughout this study since they were found to have sufficient life if carefully treated. Within the area defined by the dotted lines, Figure 10 shows in a diagrammatic manner the etches observed on type I α -SiC. Only mature figures of definite forms are included in the diagram which does not attempt to indicate the relative size or frequency of the etches, nor the size or shape of the crystal faces. The shape and distribution of the figures indicate three vertical planes of symmetry bisecting the first order pyramids, and a vertical axis of three-fold symmetry. The absence of a horizontal plane and center of symmetry is indicated by differential etching of the bases as well as by entirely differently shaped figures on similar pyramids at opposite ends of the crystal.

Figure 10 shows the etching figures obtained by the use of borax on the type I twin illustrated by Fig. 8. In Figure 10, the heavy lines between certain crystal faces indicate the position of the prism which, however, does not occur in type I; the dotted line indicates the position of the composition plane of the twin. Since type I SiC has a vertical axis of three-fold symmetry and lacks a center of symmetry, the twinning law could be either: (1) twinning plane (0001), or (2) twinning axis parallel to the c crystallographic axis. Neither morphological nor x -ray study is capable of answering the question, but a study of the etching arrangement indicates that the latter is the correct twinning law.

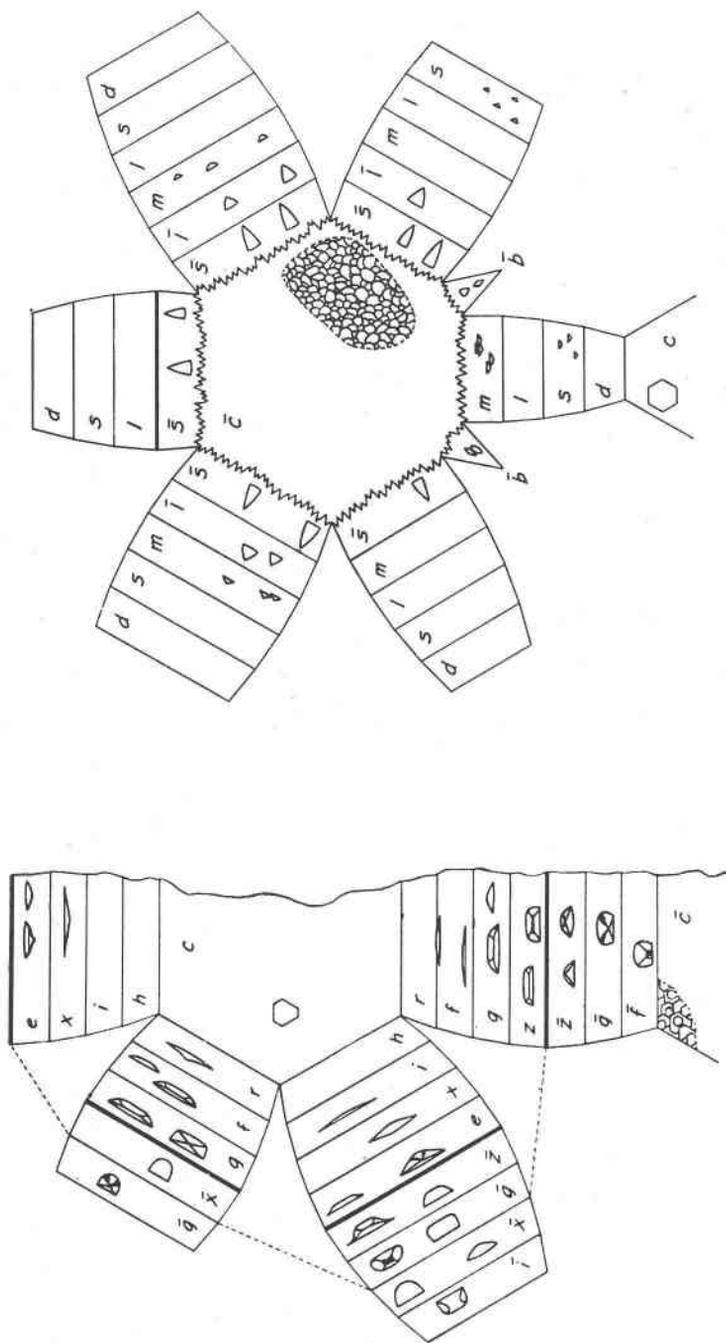


FIG. 10. Etching figures obtained by fused borax on the alpha SiC, type I, twin illustrated by Fig. 8. Dotted line indicates composition plane of twin.

FIG. 11. Etching figures obtained on alpha SiC, type III, by Cl₂ at 1000° C.

Except that the hexagons formed on the one basal pinacoid were equilateral, the etching figures developed by fused borax on α -SiC, type II, were very similar in general appearance to those on type I. A vertical axis of six-fold symmetry and at least three vertical planes of symmetry were present, while a horizontal plane and center of symmetry were absent. The prism faces *m* contained etches devoid of a horizontal plane of symmetry although some of them, especially when not fully mature, were nearly the bisymmetrical rectangles reported by Weigel.

Because of the small number of type III crystals available, none was etched with borax.

Small portions chipped from α -SiC, types IV and VI, were etched by the borax method. The etching figures were very similar to those obtained on type I and the same symmetry elements are indicated.

Twenty-four examples of individuals twinned according to the most common method were etched by the Na_2CO_3 - NaNO_3 fusion method. Green and black crystals from several sources, both domestic and foreign, were included, but in all cases the twinned individuals were symmetrical to a plane bisecting the acute re-entrant angle, as observed by Becke.

ETCHINGS BY CHLORINE

Moissan (1893) stated that SiC was completely decomposed by a current of Cl_2 at about 1200°C . The substance is progressively attacked with volatilization of Si as SiCl_4 , leaving a carbon pseudomorph which may also be removed by reaction with O_2 or air at elevated temperatures forming CO_2 . It was found that a partial chlorination of suitable SiC crystals followed by a removal of the carbon by burning in air produced excellent well-defined etching figures very different in appearance from those formed by the borax fusion.

In the apparatus used for the etching, Cl_2 from the usual pressure cylinder was forced through a bubble tower partially filled with concentrated H_2SO_4 , into a fused silica tube of about one inch diameter, exit being made by rubber tubing to the outdoors. A gas-tight joint in one end of the fused silica tube permitted insertion of a fused silica boat containing the crystals to be etched. An electric furnace, cylindrical in shape with the upper half removable, entirely enclosed the central portion of the silica tube and permitted the enclosed boat with contents to reach a maximum temperature of 1000 – 1050°C ., at which temperature the etching experiments with Cl_2 were carried out. When chlorination of the crystals was judged sufficient, the Cl_2 was replaced by compressed air which removed the carbon remaining from the chlorination. In all the experiments the apparatus was operated by Mr. F. M. Fellows.

Figure 11 illustrates diagrammatically the type of etches obtained by

the Cl_2 method. In every case, whether with $\alpha\text{-SiC}$, types I, II or III, all of which were etched by this method, one basal pinacoid was very badly attacked, usually with the formation of isolated or grouped etch hillocks of modified conical shape. These were largely confined to the edges of the basal pinacoid so that when the crystal was viewed from the side, the contact between the base and the adjacent pyramid was saw-toothed as indicated in Fig. 11. The other basal pinacoid was in all cases only slightly attacked, and contained very well-defined etching figures similar to those produced by borax.

First order pyramids adjacent to the lower base contained well-defined triangles with apices pointing toward the upper base, while corresponding upper first order pyramids showed no etching figures, or, at most, tiny poorly-defined triangles with apices pointing in the same direction. Etches obtained on prism faces indicated the absence of a horizontal plane of symmetry.

Several crystals containing the second order pyramid, \bar{b} , were etched by the Cl_2 method, but only in the case of the type III crystal, Fig. 11, were any well-defined etches observed on these extremely minute faces. The etches observed in this case were symmetrical to a vertical plane.

Seven large crystals of types I and II were sawed in half parallel to the c axis. One-half of each crystal was etched with Cl_2 . The second half of four crystals was etched with borax, and the second half of the remaining three was etched with the $\text{Na}_2\text{CO}_3\text{-NaNO}_3$ melt. The basal pinacoid attacked to the greatest extent by the Cl_2 was also attacked most by the other etching media, and has arbitrarily been chosen the lower base in the present study.

Because of the extremely small size of all available crystals of $\beta\text{-SiC}$, no attempts were made to obtain etching figures on them.

The etching figures developed on $\alpha\text{-SiC}$, types I, IV and VI, both by fused borax and by Cl_2 at 1000°C ., admit of but one interpretation as to crystal class, namely, ditrigonal-pyramidal, or $3m$ of the hexagonal system, while types II and III are to be referred to the dihexagonal-pyramidal, or $6mm$ class of the same system.

(To be continued)