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X-ray crystallographic data on aluminum silicon carbide, α-Al_4SiC_4 and $Al_4Si_2C_5$

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Single-crystal and powder X-ray crystallographic data on α-Al_4SiC_4 and $Al_4Si_2C_5$ are given, and their respective space groups are $P6_3mc$ and $R\bar{3}m$. Powder X-ray diffraction lines are individually indexed in the 2θ-range from 5° to 110°. The unit cell dimensions obtained from a least-square computer program are $a = 3.2771$ Å (± 0.0001 Å), $c = 21.676$ Å (± 0.002) for α-Al_4SiC_4 and $a = 3.2512$ Å (± 0.0002 Å), $c = 40.1078$ Å (± 0.0027 Å) for $Al_4Si_2C_5$. In addition, it is proposed that the crystal structures of α-Al_4SiC_4 and $Al_4Si_2C_5$ may be formed by substituting SiC-layers for AlN-layers in the Al_5C_3N and $Al_6C_3N_2$ structures.

1. Introduction

X-ray powder diffraction data of α- and β-aluminium silicon carbides of Al_4SiC_4 was first given by Barczak [1] in 1961. Subsequently, a new unit cell dimension of α-Al_4SiC_4, different to that of Barczak, was proposed by Schneider [2] in 1978, who gave a new index based on the X-ray powder diffraction lines of α-Al_4SiC_4. Recently we have succeeded [3, 4] in synthesizing the pure phase of α-Al_4SiC_4 and $Al_4Si_2C_5$. The following is an attempt to interpret the crystallographic data obtained from the X-ray single-crystal method and the powder diffraction method for these crystals. The X-ray powder diffraction lines in the 2θ-range from 5° to 110° are given with their index, d-values and relative intensity distributions. Their space groups have been identified as $P6_3mc$ for α-Al_4SiC_4 and $R\bar{3}m$ for $Al_4Si_2C_5$ using X-ray single-crystal diffraction techniques. The unit cell dimensions obtained by the least-square computer program are also given as $a = 3.2771 \pm 0.0001$ Å, $c = 21.676 \pm 0.002$ Å for α-Al_4SiC_4 and $a = 3.2512 \pm 0.0002$ Å, $c = 40.1078 \pm 0.0027$ Å for the corresponding hexagonal lattice of $Al_4Si_2C_5$. The crystal structures of α-Al_4SiC_4 and $Al_4Si_2C_5$ are proposed as being similar to those of Al_5C_3N and $Al_6C_3N_2$, respectively. This is supported by the good agreement between observed and calculated relative intensity distributions of powder X-ray diffraction data on Al_4SiC_4 and $Al_4Si_2C_5$, respectively.

2. Synthesis of α-Al_4SiC_4 and $Al_4Si_2C_5$

Silicon carbide (Ibigawa Denko Co Ltd, β-type, particle size 3 µm, purity > 99.9%, oxygen content ≈ 0.2 wt%) and Al_4C_3 powder (Alfa Products Co, − 100 mesh) were used in the synthesis of aluminium silicon carbide. The amount of each powder used was in conformity with the compositions of Al_4SiC_4 and $Al_4Si_2C_5$. The ingredients were individually mixed in a polyethylene ball mill. The mixture of Al_4SiC_4 composition was packed into a graphite die (15 mm diameter) and heated by r.f. current up to 2000° C at a rate of 50° C min^{-1} in an argon atmosphere. The uniaxial pressure for hot-pressing was avoided in this procedure, because the specimen forms a melt at that temperature. After heating at 2000° C for a few minutes, the specimen was cooled to 1900° C at a rate of 5° C min^{-1}, then the electric power of furnace was turned off. The time constant calculated from the cooling curves was about 3 min.

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After cooling, α-Al_4SiC_4 specimen was recovered from the die. The weight loss observed was ~ 3% during the heating process.

The mixed ingredients of $Al_4Si_2C_5$ composition were packed into a graphite die and heated by r.f. current at a rate of 50° C min^{-1} up to 1970° C in an argon atmosphere. The specimen was maintained at that temperature for a few minutes and then cooled rapidly by turning off the electric power to the furnace. The time constant calculated from the recorded cooling curves was ~ 0.3 min. In the procedure mentioned above, the uniaxial hot-pressing process was avoided so as to prevent the extrusion of the specimen from die. After cooling, very small leaflet-like crystals of $Al_4Si_2C_5$ were found in the open hole of the specimen. The specimen consisted mainly of $Al_4Si_2C_5$ together with a small amount of α-Al_4SiC_4. $Al_4Si_2C_4$ crystals were synthesized only when the specimen was rapidly cooled from 1970° C to 24° C. If it was cooled slowly from 1970° C to 1900° C, the $Al_4Si_2C_4$ phase did not appear, α-Al_4SiC_4 and silicon carbide being formed instead.

3. X-ray single-crystal data

3.1. Single-crystal data of α-Al_4SiC_4

Small flake-like single crystals of α-Al_4SiC_4 grew mainly in the opening hole of the specimen or on its surface. These crystals bore polysynthetic twinning with (0 0 1) plane, appeared transparent, and were a yellow colour. The average size of the crystals was 0.2 mm diameter and 0.02 mm thick. A good crystal of 0.2 mm x 0.2 mm x 0.02 mm was selected by optical microscopy for X-ray single-crystal determination. The unit cell dimension and space group were revealed by the single-crystal method using a Weissenberg camera and a precession camera. As a result, the approximate unit cell constants were found to be $a = 3.27$ Å, $c = 21.63$ Å in the hexagonal lattice. The $(h\,o\,l)$ and $(h\,k\,2)$ reciprocal plane taken by the precession camera using Mo radiation are shown in Fig. 1. The condition limiting possible reflections are as follows:

$000l$: $l = 2n$

$hh\overline{2h}l$: $l = 2n$

$hkil$: if $h - k = 3n$, then $l = 2n$.

On the basis of the systematic extinctions, the possible space groups of this crystal are $P31c$, $P\bar{3}1c$, $P\bar{6}2c$, $P6_3mc$ or $P6_3/mmc$. However, the $(h\,k\,2)$ plane in Fig. 1 proves the existence of six-fold symmetry along the c-axis in this crystal. In addition, the existence of mirror symmetry perpendicular to [1 0 0] and parallel to [0 1 0] limits its space group to $P6_3mc$ or $P6_3/mmc$.

3.2. Single-crystal data of $Al_4Si_2C_5$

A very small plate-like crystal, yellow in colour, of $Al_4Si_2C_5$, 0.1 mm diameter and 0.02 mm thick, was picked up for X-ray investigation. The unit cell dimension and space group were determined by the X-ray moving camera technique with Mo radiation. It was consequently revealed that the

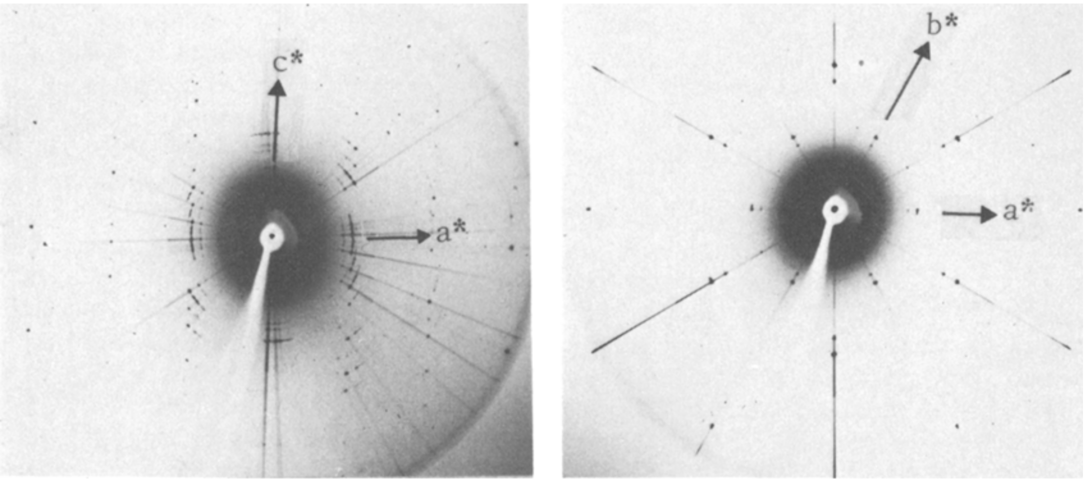

Figure 1 Precession photographs of α-Al_4SiC_4 taken by Mo radiation. The reciprocal planes of right, $(h\,0\,l)$, and left, $(h\,k\,2)$ are given.

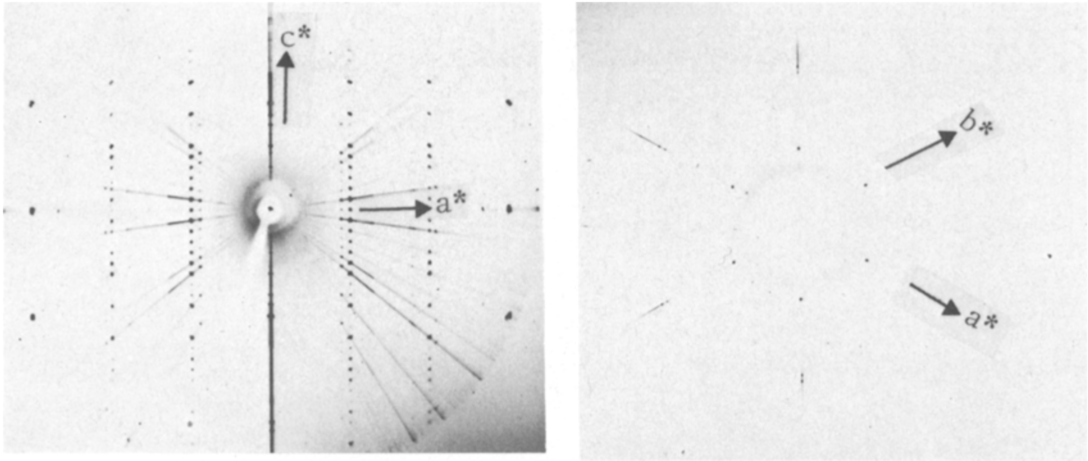

Figure 2 Precession photographs of $Al_4Si_2C_5$. Left, $(h\,0\,l)$, and right, $(h\,k\,0)$, planes are shown.

crystal lattice is intrinsically rhombohedral, with $a_0 = 13.50$ Å, $\alpha = 13.83°$, and it can be compared with a hexagonal lattice with $a = 3.25$ Å, $c = 40.11$ Å. The $(h\,o\,l)$ and $(h\,k\,o)$ reciprocal planes with the hexagonal index of this crystal are shown in Fig. 2. The conditions limiting possible reflections in the corresponding hexagonal axis are as follows:

$$hkil\colon\quad -h+k+l=3n$$

$$000l\colon\quad l=3n$$

$$hh\overline{2h}l\colon\quad l=3n$$

$$h\bar{h}0l\colon\quad h+l=3n.$$

Taking account of the systematic extinction rules mentioned above, the possible space groups of $Al_4Si_2C_5$ could be R3*m* and R3$\bar{m}$.

4. X-ray powder diffraction data

X-ray powder diffraction data for α-Al_4SiC_4 and $Al_4Si_2C_5$ were taken by Rigaku Geigerflex using Cu*K*α X-ray radiation with Ni-filter and scintillation counter detector scanning at $2\theta - 1°$ per 4 min. The X-ray reflections were collected in the range of 2θ from 5° to 110°, and then they were successfully indexed by taking account of the primary unit cell dimensions obtained from the single crystal X-ray method. Thus the calculated and observed planer spacings obtained, the observed 2θ, and their indexes are given in Tables I and II. Table I gives the data for α-Al_4SiC_4 and Table II those for $Al_4Si_2C_5$.

The unit cell dimensions were calculated by the least-square computer program. 31 reflections of α-Al_4SiC_4, which showed clear intensity peaks and were not superposed on other reflections, were selected for the least-square calculation. The refined unit cell dimensions are as follows:

$$a = 3.2771\ (\pm 0.0001)\,\text{Å}$$

TABLE I X-ray powder diffraction data of α-Al_4SiC_4

hkl	d_{calc}	d_{obs}	$2\theta_{\text{obs}}$
00 2	10.838	10.859	8.135
00 4	5.419	5.424	16.328
00 6	3.612	3.614	24.610
10 0	2.838	2.836	31.520
10 1	2.814	2.813	31.778
10 2	2.746	2.745	32.591
00 8	2.709	2.710	33.025
10 3	2.642	2.641	33.908
10 4	2.514	2.515	35.670
10 5	2.376	2.374	37.869
10 6	2.232	2.231	40.395
0010	2.168	2.168	41.625
10 7	2.092	2.092	43.210
10 8	1.960	1.960	46.291
10 9	1.836	1.836	49.613
1010	1.723	1.722	53.135
11 0	1.639	1.638	56.090
1012	1.524	1.524	60.720
20 1	1.416	1.416	65.900
20 4	1.373	1.373	68.270
20 5	1.349	1.349	69.65
20 6	1.321	1.321	71.340
1 1 10	1.307	1.307	72.208
20 9	1.223	1.223	78.080
2012	1.116	1.116	87.278
0020	1.084	1.084	90.600
21 1	1.071	1.071	91.938
21 4	1.052	1.052	94.125
21 6	1.028	1.028	97.00
21 9	0.980	0.980	103.62
30 0	0.946	0.946	109.02

TABLE II X-ray powder diffraction data of $Al_4Si_2C_5$

hkl	d_{calc}	d_{obs}	$2\theta_{obs}$
00 3	13.369	13.379	6.606
00 9	4.456	4.455	19.906
0012*	3.342	3.352	26.648
10 1	2.807	2.806	31.833
$10\bar{2}$	2.788	2.787	32.073
0015	2.674	2.672	33.485
$10\bar{5}$	2.656	2.656	33.710
10 7	2.527	2.527	35.494
$10\bar{8}$	2.455	2.454	36.571
1010	2.304	2.303	39.053
$10\overline{11}$	2.228	2.227	40.447
0018			
1013	2.080	2.080	43.476
1016	1.872	1.872	48.586
$10\overline{17}$	1.808	1.808	50.421
11 0	1.625	1.625	56.567
1022	1.530	1.530	60.442
$10\overline{23}$	1.483	1.483	62.603
$20\bar{1}$	1.407	1.406	66.450
20 2	1.404		
1115	1.389	1.388	67.410
20 5	1.387		
20 8	1.355	1.354	69.328
$10\overline{26}$	1.353		
$20\overline{10}$	1.328	1.328	70.881
2011	1.313	1.313	71.822
1118			
$20\overline{13}$	1.281	1.277	74.215
1028	1.277		
$20\overline{16}$	1.227	1.227	77.734
2017	1.209	1.209	79.157
$10\overline{32}$	1.145	1.145	84.549
$20\overline{22}$	1.114	1.114	87.465
0036			
2023	1.095	1.095	89.365
21 1	1.064	1.062	92.906
$21\bar{2}$	1.063		
$10\overline{35}$	1.061		
$21\bar{8}$	1.041	1.041	95.448
2026			
2110	1.028	1.028	
0039	1.028	1.028	96.979
2116	0.980	0.980	103.684
1040	0.945	0.945	109.261

* This reflection is affected by the presence of SiC as an impurity.

$$b = 21.676\ (\pm 0.002)\,\text{Å}$$

$$V = 201.60\ (\pm 0.002)\,\text{Å}^3,$$

where V is the unit cell volume, and the values in parenthesis indicate the standard deviations.

25 reflections of $Al_4Si_2C_5$ which were not overlapped were used for the calculation of the least-square refinement of unit cell dimensions. The results obtained with corresponding hexagonal lattices are as follows:

$$a = 3.2512\ (\pm 0.002)\,\text{Å}$$

$$c = 40.1078\ (\pm 0.0027)\,\text{Å}$$

$$V = 307.143\ (\pm 0.044)\,\text{Å}^3.$$

5. Discussion

There is some crystal chemical similarity between SiC [5] and AlN [6], i.e. (i) metal atoms M (Si or Al) are tetrahedrally co-ordinated with non-metal atoms X (C or N) and they form the four sp^3 tetrahedral bonds which are normally associated with the valence state of these elements; (ii) Wurtzite structure of SiC and AlN is formed by corner-sharing tetrahedra of MX_4; (iii) the size of each tetrahedra (SiC_4 and AlN_4) is almost the same. On the other hand, aluminium carbonitride is composed of three structural components of Al_2C_2, AlN and Al_2C layers [7]. These three hexagonal layers stack alternately along the [0001] direction forming hexagonal close packing. Al_5C_3N structure consists of successive layers of Al_2C, AlN and Al_2C_2, and $Al_6C_3N_2$ structure of AlN, Al_2C, AlN and Al_2C_2, respectively. If the SiC layers can be substituted for the AlN layers in aluminium carbonitride, the structure of aluminium silicon carbide will be formed. The very similar unit cell dimensions of aluminium carbonitride and aluminium silicon carbide suggest the validity of this assumption. The similarities of cell dimensions and space groups are shown in Table III.

Furthermore, in the case of Al_4SiC_4, the X-ray diffraction symmetry and extinction rules result from the following structural restrictions: (i) all atoms in the unit cell lie on three symmetrical axis of $[001]_{00}$, $[001]_{1/3,2/3}$ and $[001]_{2/3,1/3}$ in Niggli's notation, because of the existence of the 6_3 screw axis along the [0001] direction and the condition limiting possible reflections, i.e. $hkil$: if $h-k=3n$, then $l=2n$; (ii) the six-fold symmetry along [0001] indicates that the hexagonal packing layers are stacked along the [0001] direction; (iii) if a mirror plane perpendicular to [0001] exists in the structure of Al_2SiC_4, it violates the condition of close packing of MX_4 tetrahedron. Therefore, $P6_3mc$ appears more likely than $P6_3/mmc$ as the possible space group of Al_4SiC_4; (iv) as is evident from Fig. 1, among the $00l$ reflections, the strongest intensity was observed in $l = 10 \cdot n$, where n is an integral

TABLE III Similarity of the unit cell dimensions and space groups of aluminium carbonitride and aluminium silicon carbide

Formula	Z	Space group	Cell dimension		c/a	Mean layer distance
			a	c		
Al_4C_3AlN	2	$P6_3mc$	3.281	21.67	6.605	2.167
Al_4C_3SiC	2	$P6_3mc$	3.2771	21.676	6.614	2.168
$Al_4C_3(AlN)_2$	3	$R\bar{3}m$	3.248	40.03	12.33	2.224
$Al_4C_3(SiC)_2$	3	$R\bar{3}m$	3.2512	40.108	12.34	2.228

number. Therefore, the structure of α-Al_4SiC_4 is composed of ten layers of MX_4 in the unit cell.

In the case of $Al_4Si_2C_5$, eighteen layers of MX_4 are stacked in the unit cell along the c-axis direction because the strongest intensity was observed in $l = 18 \cdot n$ among the $0\,0\,0\,l$ reflections.

Taking this into account, the structural models of aluminium silicon carbide were developed from the aluminium carbonitride structure [8], i.e. the structural model of α-Al_4SiC_4 was induced from Al_5C_3N and $Al_4Si_2C_5$ from $Al_6C_3N_2$. The X-ray diffraction intensity distribution I_c of each structural model was calculated and then

TABLE IV Observed (I/I_0) and calculated (I/I_c) relative intensity distributions of X-ray powder diffraction on α-Al_4SiC_4

$h\,k\,l$	I/I_0	I/I_c
00 2	6	5.0
00 4	3	3.4
00 6	15	11.3
10 0	21	13.2
10 1	100	100.0
10 2	28	29.7
00 8	13	7.4
10 3	16	17.0
10 4	28	32.2
10 5	53	64.9
10 6	66	75.2
0010	71	54.6
10 7	5	6.3
10 8	5	5.3
10 9	35	39.0
1010	1	1.9
11 0	71	97.0
1012	26	29.7
20 1	5	8.6
20 4	4	6.5
20 5	7	10.8
20 6	8	12.8
1110	35	54.9
20 9	5	8.3
2012	5	9.4
21 4	2	2.8
21 6	5	5.7
21 9	5	4.4
30 0	7	16.9

TABLE V Observed (I/I_0) and calculated (I/I_c) relative intensity distributions of X-ray powder diffraction on $Al_4Si_2C_5$

$h\,k\,l$	I/I_0	I/I_c
00 3*	12	7.0
00 9*	10	3.7
0012*†	90	10.5
10 1	71	70.2
10 $\bar{2}$	59	59.4
0015*	27	6.3
10 $\bar{5}$	31	34.8
10 7	5	3.0
10 $\bar{8}$	41	60.4
1010	62	84.2
1011 0018*	100	88.1
1013	13	8.8
1016	25	30.5
10 $\overline{17}$	16	18.5
11 0	55	100.0
1022	11	14.8
10 $\overline{23}$	19	13.2
20 $\bar{1}$ 20 2	4	11.5
11 5 20 5	2	5.0
20 8 10 $\overline{26}$	11	17.0
20 $\overline{10}$	7	13.0
2011 1118	32	27.1
20 $\overline{13}$ 1028	4	10.4
20 $\overline{16}$	2	5.0
2017	2	4.0
10 $\overline{32}$	1	2.9
0036*	3	2.0
2023	3	4.7
21 1 21 $\bar{2}$ 10 $\overline{35}$	3	9.4
2110	4	6.9
2116	1	3.1
1040	4	7.4

* Reflections affected by preferred orientation.

† Reflection affected by the presence of graphite as an impurity.

TABLE VI Proposed co-ordinates of α-Al_4SiC_4 and $Al_4Si_2C_5$. Atoms in asymmetric units are given

Atoms	α-Al_4SiC_4			$Al_4Si_2C_5$		
	x	y	z	x	y	z
Si (1)	0.0	0.0	0.155	0.0	0.0	0.0850
Si (2)	–	–	–	0.6667	0.3333	0.2471
Al (1)	0.3333	0.6667	0.045	0.6667	0.3333	0.0244
Al (2)	0.3333	0.6667	0.261	0.6667	0.3333	0.1403
Al (3)	0.0	0.0	0.345	0.0	0.0	0.1911
Al (4)	0.3333	0.6667	0.455	0.0	0.0	0.3092
C (1)	0.0	0.0	0.0	0.0	0.0	0.0
C (2)	0.0	0.0	0.248	0.6667	0.3333	0.0740
C (3)	0.3333	0.6667	0.367	0.0	0.0	0.1351
C (4)	0.3333	0.6667	0.137	0.6667	0.3333	0.1975
C (5)	–	–	–	0.0	0.0	0.2597

compared with each observed intensity I_0. These comparisons are tabulated in Tables IV and V for α-Al_4SiC_4 and $Al_4Si_2C_5$, respectively. As is evident from the tables, there is good agreement between I_0 and I_c in both aluminium silicon carbides. Such good agreement gives the validity of these proposal structural models of α-Al_4SiC_4 and $Al_4Si_2C_5$. The observed intensity distribution of $00 0 l$ exceeded the calculated ones: this should be caused by the preferred orientation of the powder sample. The atomic co-ordinates of both aluminium silicon carbides thus obtained are given in Table VI. The details of the three-dimensional X-ray single-crystal structure analyses will be reported elsewhere.

6. Conclusions

From the symmetry of single crystals of α-Al_4SiC_4 and $Al_4Si_2C_5$ and a comparison of the relative intensity distributions between observed and calculated powder X-ray diffraction lines, we conclude that the crystal structures of α-Al_4SiC_4 and $Al_4Si_2C_5$ may be formed by substituting SiC layers for AlN layers in the structures of Al_5C_3N and $Al_6C_3N_2$, respectively, and that the space group of the former is $P6_3mc$ and the latter is $R\bar{3}m$.

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