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The Crystal Structure of $B_{2.89}Si$

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The crystal structure of the compound which has earlier been attributed the formulas B_3Si or B_4Si has been determined by two- and three-dimensional X-ray methods. The compound crystallizes in the space group $R\bar{3}m$, with $a = 6.319 \pm 0.005$ Å and $c = 12.713 \pm 0.010$ Å for the hexagonal cell. The structure can be described as a B_4C — structure where groups of two silicon atoms take the places of the chains of three carbon atoms, and where the remaining silicon atoms statistically substitute part of the boron atoms in the boron icosahedrons. The crystallographically determined composition is $B_{2.89}Si$, which is supported by chemical analyses and density measurements.

The original work on the silicon-boron system was carried out by Moissan and Stock[1], who reported two compounds, B_3Si and B_6Si. The compound B_6Si has recently been studied by Cline[2] and Adamsky[3] and is now relatively well-known. Its crystal structure has not yet been determined, but Adamsky reports to work on it and has proposed a configuration. The triboron silicide, which we have reason to refer to as $B_{2.89}Si$, has been extensively studied during the last few years, but the various authors do not agree about its composition and structure. Cline and Sands[4] report the composition B_4Si based on chemical and spectrographic analyses and indicate that it has structual features in common with B_4C. Colton[5] has analysed the compound and obtained a B/Si molar ratio 4.28, and states that it is slightly larger than the expected 4.00 due to the presence of B_6Si. Matkovich[6] has obtained B/Si molar ratios between 3.7 and 4.3 and concludes that the deviation from 4.00 is due to the presence of either silicon or, when silicon is completely removed, some B_6Si and BN. Knarr[7] reports the formula B_3Si based on phase-equilibrium studies. Although the hexagonal unit cell, which he has deduced, differs from the one given by all the other authors mentioned above, his X-ray data reveal that even in this case it is a question of the same compound. Rizzo and Bidwell[8] have analysed the compound very carefully and got a B/Si molar ratio 3.0. They propose that the compound is actually B_4Si, isomorphous with B_4C, with one additional silicon atom per rombohedral unit cell, *i.e.* $B_{12}Si_3 + Si$, an arrangement that is not in agreement with density data. In a recently published work Matkovich[9] has related the compound to other similar compounds and indicates that it is isomorphous with B_4C. It is evident that a crystal structure determination of this boron silicide would be of great value in order to establish its relationship with the B_4C structure[10,11] and the proposed B_6Si structure[3]. For this reason this work has been performed. The preliminary result has been published earlier[12].

EXPERIMENTAL

Preparation. The crystals of $B_{2.89}Si$ were prepared by melting a mixture of boron (10 %) and silicon (90 %) in a high frequency induction furnace in an argon atmosphere. Crucibles of boron nitride were used. This method usually gives beautiful crystals of this boron silicide embedded in the silicon phase. The excess silicon was dissolved in a nitric acid — fluoric acid mixture[1]. It is not possible to obtain it absolutely pure by this method, as there is always some B_6Si present.

Chemical analysis. Before the analysis the samples were boiled for differing times with HNO_3, which preferentially dissolves B_6Si, and then washed with hot KOH to remove the oxides surrounding the crystals[1]. These were afterwards dissolved in a Na_2CO_3—Na_2O_2-melt in a nickel crucible and analysed for silicon and boron by conventional methods. It is quite evident that the boiling with HNO_3 lowers the B/Si molar ratio. The following are typical figures:

Sample not boiled with HNO_3: B/Si molar ratio = 4.2.

Same sample boiled with HNO_3 for 42 hours: B/Si molar ratio = 3.2.

From our analyses it seems probable that the true B/Si molar ratio is approximately 3.0, and consequently that the analyses performed by Moissan and Stock[1] and Rizzo and Bidwell[8] are substantially correct.

X-Ray methods. In order to determine the cell-dimensions accurately, powder photographs of Guinier type were taken using CuKα radiation and with NaCl as a reference substance. Due regard was taken to film shrinkage by copying a scale on the films before development. The structural investigation was based on single crystal methods. Multiple-film equi-inclination Weissenberg photographs were taken with rotation about the hexagonal c-axis (layer lines 0—6) and the hexagonal a-axis (layer lines 0 and 1) using copper radiation. The reflexion intensities were estimated by visual comparison with standard scales. A subjective correction was made for variation in spot shape. No correction was made for absorption as very small crystals were used. The reflexion intensities were corrected using Lorenz- and polarisation factors.

DETERMINATION OF THE STRUCTURE

The cell dimensions were obtained from powder diffraction data by the method of least squares. $B_{2.89}Si$ is rombohedral. The dimensions of the hexagonal unit cell are the following:

$$a = 6.319 \pm 0.005 \text{ Å}$$
$$c = 12.713 \pm 0.010 \text{ Å}$$

Calculated and observed $\sin^2\Theta$-values are given in Table 1. Here and in the following the indices refer to the hexagonal cell.

In all photographs only reflexions from planes of the following type were observed:

$$-h + k + l = 3n$$

The following rule was obeyed by the intensities:

$$I_{hkl} = I_{kh\bar{l}}$$

Table 1. X-Ray powder diffraction data for $B_{2.89}Si$.

$h\ k\ l$	$10^4 \times \sin^2\Theta_{obs}$	$10^4 \times \sin^2\Theta_{calc}$
0 1 2	345	346
1 1 0	593	595
1 0 4	786	787
0 2 1	832	831
2 1 1	1426	1426
1 1 6	1920	1919
3 0 3, 0 3 3	2118	2117
1 2 5	2307	2308
2 2 0	2384	2381
1 3 1	2615	2616
3 1 2	2725	2727
3 0 6, 0 3 6	3110	3110

The same rule is found in simple rombohedral boron [13]. Of the three possible space groups, $R32$, $R3m$ and $R\bar{3}m$, only the centrosymmetric $R\bar{3}m$ was considered and was found to meet all demands of the data.

The density was found to be 2.44 g/cm^3 from a long series of determinations. We have not been able to reproduce the somewhat higher values mentioned in our preliminary report [12]. This, however, does not necessarily mean that these values are erroneous, but they may be interpreted as an indication of a homogeneity range of this boron silicide phase. This idea is supported by the fact that the values of the density of the compound in question in the litterature varies significantly. From the value 2.44 the number of molecules in the hexagonal unit cell is calculated to 10.67, *i.e.*, there are 3.57 molecules per rombohedral unit cell, if the formula is supposed to be B_3Si. This fact implies an unusual structure, provided that the assumption concerning the formula is correct.

From a Patterson projection on (001) it was concluded that the structure is similar to that of the compound B_4C. A three-dimensional Patterson synthesis showed that there are only two atoms in the 0,0,*z*-position, and that all the other atomic positions form icosahedrons in approximately the same way as in B_4C. The atoms in an icosahedron are of two different kinds, the atoms forming the top and bottom of the icosahedrons having higher electron density than the others.

These facts were interpreted in the following way. The structure is a B_4C-structure, where groups of two silicon atoms take the places of the chains of three carbon atoms. The rest of the silicon atoms are statistically substituting boron atoms in one of the two 18*h*-positions, in which the atoms forming the icosahedrons are placed.

This way of interpreting the symmetry of the three-dimensional Patterson synthesis affects the idea of the stoichiometry of the compound. Its formula could thus be given the following general expression:

$$B_{18}(B_{18-x}Si_x)Si_6$$

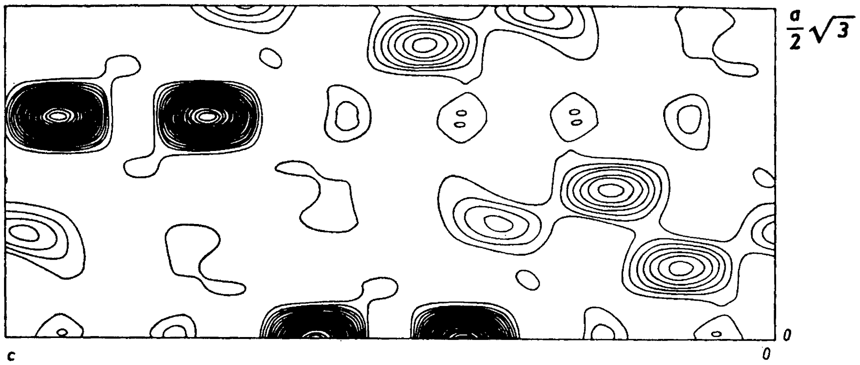

Fig. 1. Electron density, $\varrho(2x,x,z)$, on a mirror plane (120). The contours are at equal but arbitrary intervals.

Analytical data and density measurements indicate that x is in the neighbourhood of 5. If we at first restrict ourselves to whole numbers for x, the following formulas are possible:

$x = 3$	$B_{33}Si_9$
$x = 4$	$B_{32}Si_{10}$
$x = 5$	$B_{31}Si_{11}$
$x = 6$	$B_{30}Si_{12}$
$x = 7$	$B_{29}Si_{13}$

It was plausible to start with the formula $B_{31}Si_{11}$ in trying to account for observed X-ray data, as this formula gives a calculated density of 2.43, which is near the observed value of 2.44. Crystallographic calculations could now be based on parameters obtained from the three-dimensional Patterson synthesis mentioned above and structure factor signs obtained with the assumption of the formula $B_{31}Si_{11}$. This formula states that 5 of the 18 boron atoms in one of the two 18h positions (18h') are replaced by silicon atoms. This substitution implies the assigning to the atoms in 18h' an atomic form factor:

$$f = 5/18 f_{Si} + 13/18 f_B$$

This operation was easy to perform as the atomic form factors used were of the form [14]:

$$f_i = A_i \,.\, \exp\,(-a_i \sin^2\Theta) + B_i \,.\, \exp(-b_i \sin^2\Theta)$$

The electron density calculated in this way for the plane (120) is given in Fig. 1. The oval shape of the peaks is at least partly due to the fact that only reflexions with $l = 0-6$ are used in the Fourier synthesis. From the peaks in this plane, in fact all the parameter values for the structure are obtained. Their final values are given in Table 2. Here, and in the following, the atoms in the 18h position in which substitution occurs are denoted as Si,B-atoms.

Table 2. Atomic parameters for $B_{2.89}Si$.

Atom	Position	x	y	z
Si	6c	0	0	0.403_1
Si,B	18h'	0.107_5	-0.107_5	0.877_9
B	18h	0.158_0	-0.158_0	0.025_2

The final structure factors were then calculated. These and the observed values are given in Table 3. The structure factor disagreements,

$$R = \Sigma \,||F_{\text{calc}}| - |F_{\text{obs}}|| \,/\, \Sigma \,|F_{\text{obs}}|$$

of the final coordinates is $R_{hkl} = 9.45$ %, excluding those terms too week to be observed. Observed structure factors have been corrected for thermal

Table 3. Values of observed and calculated structure factors for $B_{2.89}Si$. See the text.

$h\,k\,l$	F_{obs}	F_{calc}	$h\,k\,l$	F_{obs}	F_{calc}
3 0 0	—	+ 1	1 4 3	—	− 5
6 0 0	32	+ 33	2 2 3	31	+ 41
3 3 0	77	+ 77	5 2 3	—	− 11
1 1 0	39	+ 47	2 5 3	—	+ 4
4 1 0	31	+ 27	1 0 4	89	− 92
4 4 0	58	+ 53	4 0 4	—	− 1
2 2 0	71	+ 72	1 3 4	25	− 19
5 2 0	26	+ 24	4 3 4	58	− 61
1 0 1	10	+ 10	1 6 4	—	+ 3
4 0 1	43	− 39	0 2 4	22	− 24
1 3 1	59	− 63	3 2 4	45	− 46
4 3 1	14	− 7	0 5 4	20	− 18
1 6 1	14	− 11	2 1 4	17	− 14
0 2 1	99	− 105	5 1 4	21	− 23
3 2 1	—	+ 4	2 4 4	53	− 48
0 5 1	37	− 37	2 0 5	—	− 2
2 1 1	41	− 39	5 0 5	67	+ 64
5 1 1	52	− 50	2 3 5	31	+ 32
2 4 1	16	− 14	0 1 5	30	+ 36
2 0 2	28	+ 25	3 1 5	42	+ 40
5 0 2	—	− 4	6 1 5	58	+ 59
2 3 2	21	+ 22	0 4 5	48	+ 43
0 1 2	46	+ 38	3 4 5	22	+ 14
3 1 2	62	+ 57	1 2 5	90	+ 87
6 1 2	—	− 3	4 2 5	—	− 11
0 4 2	27	− 39	1 5 5	29	+ 29
3 4 2	—	+ 10	0 0 6	33	− 32
1 2 2	6	− 8	3 0 6	99	− 92
4 2 2	—	− 10	6 0 6	25	+ 26
1 5 2	36	+ 38	0 3 6	10	+ 17
0 0 3	8	+ 7	3 3 6	41	− 39
3 0 3	66	+ 58	0 6 6	51	− 45
6 0 3	13	+ 14	1 1 6	41	− 47
0 3 3	17	− 17	4 1 6	29	− 35
3 3 3	23	− 30	1 4 6	41	− 36
0 6 3	75	+ 71	2 2 6	22	− 17
1 1 3	—	− 3	5 2 6	32	− 35
4 1 3	—	+ 8	2 5 6	32	− 25

Table 4. *R*-factors and calculated densities for various values of *x* in $B_{18}(B_{18-x}Si_x)Si_6$.

x	Formula	R-factor, %	Calc. density
3	$B_{33}Si_9$	12.63	2.303
4	$B_{32}Si_{10}$	10.44	2.368
4.80	$B_{2.89}Si$	—	2.420
5	$B_{31}Si_{11}$	9.45	2.433
6	$B_{30}Si_{12}$	10.29	2.499
7	$B_{29}Si_{13}$	12.78	2.564

vibration by the factor exp $[B(\sin\Theta/\lambda)^2]$ with $B = 1.13\times10^{-16}$ cm^2 determined by the method of least squares from the final structure factors. An isotropic temperature factor has been applied in spite of the fact that an anisotropic one would have been more satisfactory in this case.

The proposed structure is dependent on the assumption that the formula of the compound is $B_{31}Si_{11}$. It was, however, necessary to verify that the assumed stoichiometry gave the best agreement between observed and calculated intensity data. This has been done by calculating *R*-factors also for structures where the structure factors were based on the formula $B_{18}(B_{18-x}Si_x)Si_6$ with *x* equal to 3, 4, 6, and 7. The result is given together with the calculated densities in Table 4. From this table it is evident that the formula $B_{31}Si_{11}$ gives the best agreement.

This method of determining the composition, however, is not very good because of the fact that the value of the *R*-factor is not solely depending on the varying substitution in the 18*h*′ position. A better method is to calculate difference syntheses for various compositions and determine the true composition by observing when $\varrho_o - \varrho_c = 0$ at the atomic positions in question. By this method the composition was found to be $B_{2.89}Si$. As there is only a small difference between this composition and $B_{31}Si_{11}$ ($B_{2.82}Si$), no recalculation of structure factors was made.

The standard deviations of atomic coordinates were estimated according to Cruishank's method [15], and the standard deviations in bond lengths were readily calculated from these values. Calculated bond lengths and the standard deviations of these are given in Table 5.

The bond lengths given in Table 5 show that the Si—Si-distance is somewhat longer than the covalent radius sum, while the Si—B-distance and the Si,B—Si,B-distance between two icosahedrons are somewhat shorter than expected. Short bond lengths between icosahedrons are also noted in various forms of boron. [13,16]

Table 5. Bond lengths in $B_{2.89}Si$.

Si—Si	2.463 ± 0.012 Å	
B—B	1.844 ± 0.041 Å	
Si,B—Si,B	2.038 ± 0.018 Å	(within an icosahedron)
Si,B—Si,B	1.721 ± 0.036 Å	(between the icosahedrons)
Si—B	2.002 ± 0.029 Å	
Si,B—B_1	1.964 ± 0.040 Å	
Si,B—B_2	1.952 ± 0.033 Å	

DISCUSSION

The determination of the structure of a boron silicide phase with low boron content has shown that the material used had a composition $B_{2.89}Si$, not far from $B_{31}Si_{11}$. Whether there is a homogeneity range has not been determined, but does not seem improbable.

The structure of this phase has been found to be derivable from the B_4C-structure. This fact has earlier been proposed by several authors. However, it is obviously not quite correct to speak of isomorphism, as silicon atoms in $B_{2.89}Si$ not only correspond to carbon atoms in B_4C but also to part of the boron atoms.

It is interesting to compare the structure of $B_{2.89}Si$ to the structure, which has been hypothetically proposed [3] for B_6Si. This is supposed to be built up from icosahedrons of boron atoms and pairs of silicon atoms. The similarity between this structure and the one of $B_{2.89}Si$, determined in this work, is apparent.

In this connection, it seems justified to mention the principles for the building up of compounds belonging to this category (interstitial boron compounds) given by Matkovich [9]. According to his theory such compounds are built up of intact boron icosahedrons between which are situated groups of two or three atoms or single atoms. The present result seems to introduce a new principle. There seems to be no need for the boron icosahedron to be intact. Evidently, the boron atoms may be replaced by other atoms, which implies that more possibilities of configuration have to be considered than was earlier assumed. A determination of the atomic arrangement in these materials as well as in the compound $B_{11}C_4$, reported by Kranz [17], would be of considerable interest.

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