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The Crystal Structure of SiB_6[1]

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The accurate and detailed structure of the compound SiB_6 has been determined by single-crystal X-ray diffraction. The final R value was 6.1% for 4225 reflections. The cell is orthorhombic with space group $Pnnm$ and a = 14.397(7) Å, b = 18.318(9) Å, c = 9.911(7) Å, and from the electron density appears to contain 43 silicon atoms and 238 boron atoms. The structure contains many features found in other structures of boron-rich phases, and obeys the crystal chemistry rules established for them. It contains interconnected icosahedra, icosihexahedra, as well as several isolated boron and silicon atoms. An unusual feature of this structure is the presence of icosihexahedra containing silicon atoms similar to those found previously in BeB_3. © 1986 Academic Press, Inc.

I. Introduction

Considerable work has been done in recent years on the elucidation of detailed structures and stoichiometries of a number of boron-rich phases. Many of these phases can be considered as derivatives of α- and β-rhombohedral boron, tetragonal boron, and boron carbide.

The binary boron–silicon system has also been studied extensively and a number of phases have been shown to exist.

The original work on the Si–B system was carried out by Moissan and Stock (*1*) who reported two compounds, SiB_3 and SiB_6. The existence of SiB_3 was confirmed by Samsonov and Latisheva (*2*) and by Knarr (*3*). A compound, with formula SiB_4 was also reported by several authors (*4–6*). It was later shown that, in fact, this phase has a wide homogeneity range ($SiB_{2.8-4.0}$) and corresponds more closely to SiB_3 than to SiB_4. Its structure derives from the B_4C-type (*4–7*). On the side of the phase diagram even richer in silicon a eutectic seems

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to be formed between the silicon solid solution and SiB_6 (*3, 4, 8*). In the boron-rich region of the phase diagram, a boron–silicon solid solution (*8–10*) exists and a compound SiB_x ($15 < x < 40$) has been postulated (*11*). The structure of the β-boron structure phase of composition $SiB_{\sim 36}$ was recently determined by Vlasse and Viala (*12*).

The compound SiB_6 was prepared again by Zhuravlev (*13*) who reported for it a cubic cell ($a = 4.14$ Å) having the cubic CaB_6 structure. However, diffraction studies on single crystals of this compound by several workers (*14–18*) indicated an orthorhombic unit cell with space group *Pnn*2 or *Pnnm*. Table I summarizes their results. Adamsky (*14*) had proposed a structure based on the B_4C type, but no further work was done to verify it.

Giese (*17*) reported a preliminary structure for SiB_6 on the basis of single crystal studies. This structure contained about 300 atoms in the unit cell and consisted principally of five polyhedra—four icosahedra and a triangulated polyhedron of 15 vertices and 26 faces (the icosihexahedron). No atomic coordinates were given by Giese; however, he did give the positions for the centers of the polyhedra. In addition, interstitial atoms were said to be present but without any specification of their coordinates. Furthermore the presence of carbon was suspected, but the amount and the location of carbon atoms was not at all clear. Since carbon may be an important impurity in previous studies of SiB_6 we have included this as a parameter in Table I. His *R* value was 0.20 and significant electron density was unaccounted for in the difference Fourier maps.

In order to completely elucidate the structure of this interesting boride and provide a detailed description of its structure, we decided to carry out the X-ray analysis of SiB_6.

II. Synthesis

Since Lugscheider *et al.* (*18*) have reported that SiB_6 has a rather broad homogeneity range we have studied single crystals prepared by two different methods.

Synthesis A. The SiB_6 synthesis used here has been described by Viala and Bouix (*9*). A homogeneous mixture of boron (Alfa, 99.7%) and silicon powder (Fluka, 99.9%) (0.6, 0.4 atomic comp.), was

TABLE I

LITERATURE VALUES FOR THE UNIT CELL PARAMETERS AND DENSITY OF SiB_6

V (10^{-24} cm^3)	Author	Lattice constants, Å			Measured density (g/cm^3)	Carbon atom %	Ref.
		a	*b*	*c*			
2598.8(7)	Adamsky (1958)[a]	14.392(1)	18.267(2)	9.885(1)	2.43	A[d]	*14*
2692.	Cline (1958)	14.60	18.40	10.02	2.45	A	*15*
2598.(6)	Cline (1959)[a]	14.39(1)	18.27(1)	9.88(1)	2.43	A	*16*
2575.0	Giese (1970)	14.346	18.226	9.848	2.490	8	*17*
2630.	Lugscheider (1979)[c]	14.440	18.322	9.39	?	1.5	*18*
2614.(4)	Present[c]	14.397(7)	18.318(9)	9.911(7)	2.42(1)	≤0.3	—
2634.(5)	Present[a]	14.458(9)	18.357(12)	9.923(7)	2.440(3)	~0.04	—

[a] Crystals grown from liquid silicon.

[b] For Si-rich side of phase, the parameters for the B-rich side were 0.3 to 0.5% smaller.

[c] Mixed powders, reacted at 1950°C.

[d] Sample A probably contains ~1 at.% carbon because the electrical resistivity is ~0.2 ohm cm (see Ref. (*16*)).

HF-heated in a boron nitride crucible at 1950°C for 1 hr under argon atmosphere. The resulting liquid was cooled from 1950 to 1400°C (50°C/min) to promote flux-growth from the melt. The HF heating was then turned off and SiB_6 single crystals were recovered from the solidified melt by leaching with $HF-HNO_3$ aqueous solution. The flotation density was found to be 2.42(1) g/cm^3.

Synthesis B. A mixture of silicon and boron powders containing 56 atom% boron and 44 atom% silicon was placed in a chemically vapor-deposited boron nitride crucible. This mixture was melted at 1900°C in a high-pressure furnace under blanketing argon at a pressure of 70 atm. A temperature of 1900°C was chosen in order to be above (*8*, *9*) the peritectic decomposition temperature of SiB_6 at 1860°C. The melt was slowly cooled at a rate of about 100°C/hr to room temperature. Crystals of SiB_6 were harvested from the solidified charge by dissolving the excess silicon with a mixture of HF and HNO_3 acids. From the Si–B phase diagram of Armas *et al.* (*8*) the SiB_6 crystals would have grown from solution at 1800°C and below. The pycnometric measurements of seven different crystals gave an average density of 2.440(3) g/cm^3. A microprobe chemical analysis gave a boron to silicon atom ratio of 5.73 ± 0.09.

III. Crystal Data

Two completely separate structure determinations were made. Two independent studies were started at about the same time. One by author M.V. on crystals grown by synthesis A, and one by authors M.G. and J.S.K. on crystals grown by synthesis B. Fortuitously the two studies turned out to be of crystals with very nearly the same composition, and there is little significant difference in the structural results. Thus we give the lattice constants, densities, and calculated numbers of atoms per unit cell for both studies. The actual atomic positions and interatomic distances are given from the study of author M.V. on a synthesis A sample since these data are more extensive and have smaller standard deviations in the atomic position parameters.

A preliminary study of the synthesis A sample using Weissenberg and precession methods indicated an orthorhombic symmetry. The systematic extinctions are compatible with the space group *Pnn*2 or *Pnnm*. This is in agreement with the previous studies. The space group retained for the analysis was *Pnnm* and was corroborated, post facto by the successful structure refinement. The cell parameters for synthesis A were refined from 30 high-angle 2θ values obtained on the diffractometer preliminary to the data collection (see Table I). These parameters, as well as the density, vary only slightly from those of previous studies. For the synthesis B sample the cell parameters were slightly different. They were determined using a powdered sample in a Guinier camera using powdered silicon as an internal standard.

The atomic contents of the unit cell can be calculated from the cell dimensions, the boron-to-silicon ratio, and the pycnometric density. The results are given in Table IIa for the two different syntheses. We have assumed natural abundances for the boron and silicon isotopes. We conclude that there are 289 ± 1 atoms in the unit cell from these data. If we count the total number of atoms in the unit cell from the X-ray measurements of the electron density then we obtain the results in Table IIb. The available lattice sites are 96.3% filled in synthesis A and 95.8% in synthesis B. The calculated X-ray densities are somewhat lower than the measured densities, and the number of boron atoms counted by X rays in Table IIb appears to be lower than the pycnometric number by about 3%. If so, these 3% are apparently not well localized in the

TABLE IIa

CONTENTS OF THE UNIT CELL DETERMINED FROM THE PYCNOMERIC DENSITY

Synthesis	Volume of unit cell (10^{-24} cm^3)	Atom ratio B/Si	Density (g/cm^3)	Cell contents B	Si	Total
A	2614.(4)	6.0(4)[a]	2.42(1)	246(4)	41(2)	287(2)
B	2634.(5)	5.73(9)[b]	2.440(3)	246(1)	43(1)	289(1)

[a] Assumed composition.

[b] Measured with electron-beam microprobe.

TABLE IIb

CONTENTS OF THE UNIT CELL DETERMINED FROM THE ELECTRON DENSITY

Synthesis	Cell contents B	Si	Total	Ratio B/Si	Total No. of sites	Calcd. density (g/cm^3)
A	238.47	42.65	281.12	5.59	292	2.397
B	237.22	42.66	279.66	5.56	292	2.371

unit cell. The number of silicon atoms from the two methods agree quite well.

The intensities for sample A were collected using a small crystal of approximate dimensions, 0.45 × 0.24 × 0.22 mm on a three-circle diffractometer (*19*) with molybdenum (λ = 0.71064 Å) radiation and a graphite monochromator. A $\theta/2\theta$ multiple scanning technique with a scan rate of 10°(2θ)/min was used. A total of 4814 independent reflections was obtained, after averaging two equivalent reflections, measured to $\theta_{\max} = 45°$. A total of 4224 of these had intensity $I > 4\sigma(I)$, and were considered observed. These intensities were corrected for Lorentz and polarization effects. No absorption correction was applied (μ = 5.6 cm^{-2}).

IV. Structure Determination and Refinement

The approximate structure was obtained by the application of the "Direct Methods" segment of the SHELXTL program (*20*). All five polyhedral groups were readily found by this method. During the course of the refinement for samples A and B certain polyhedral sites were found to be occupied by both boron and silicon (atoms B1 to B6 and Si1 to Si6). Their occupancies as well as their positions were refined independently with the restriction that the sum of the two occupancies is unity. The occupancies of several other atoms, both polyhedral (Si7, Si13) and interstitial (B7, Si9), were found to be partial. The refinement continued with anisotropic temperature factors and variable occupancy factors for the above-mentioned atoms using unit weights for all reflections and the SHELXTL system of programs (*20*). The final R value was 6.1% for 418 variable parameters and 4224 reflections. A final difference synthesis revealed no further significant electron density maxima.

Observed and calculated structure fac-

TABLE III

ATOMIC POSITION AND THERMAL PARAMETERS FOR SiB_6

Atom	Site	Polyh	Occup.	x	y	z	U_{eq}[a] (Å^2)
B(1)	8(h)	II	0.457(5)	0.3400(5)	0.1613(5)	0.1463(9)	0.0095(17)
Si(1)	8(h)	II	0.543(5)	0.3551(1)	0.1617(1)	0.1783(2)	0.0058(4)
B(2)	8(h)	15	0.606(6)	0.3553(5)	0.5526(4)	0.1077(7)	0.0109(14)
Si(2)	8(h)	15	0.394(6)	0.3410(2)	0.5564(1)	0.0995(3)	0.0061(5)
B(3)	8(h)	III	0.571(6)	0.4181(4)	0.1897(4)	0.6463(7)	0.0070(12)
Si(3)	8(h)	III	0.429(6)	0.4086(1)	0.1828(1)	0.6799(2)	0.0049(5)
B(4)	8(h)	15	0.756(5)	0.5469(1)	0.6251(3)	0.1065(5)	0.0053(8)
Si(4)	8(h)	15	0.244(5)	0.5551(3)	0.6195(3)	0.0952(5)	0.0101(10)
B(5)	8(h)	I	0.579(7)	0.0998(5)	0.4185(4)	0.6633(6)	0.0091(13)
Si(5)	8(h)	I	0.421(7)	0.1053(6)	0.4188(4)	0.6625(7)	0.0167(15)
B(6)	8(h)	I	0.590(7)	0.1489(6)	0.4649(4)	0.8334(10)	0.0149(16)
Si(6)	8(h)	I	0.410(7)	0.1398(2)	0.4731(1)	0.8448(2)	0.0085(6)
B(7)	4(g)	—	0.500(6)	0.2892(8)	0.4915(6)	0.5	0.0079(20)
B(8)	4(g)	II	1.0	0.1898(4)	0.1031(3)	0.0	0.0076(10)
B(9)	4(g)	II	1.0	0.3894(4)	0.1121(3)	0.0	0.0087(11)
B(10)	4(g)	II	1.0	0.3759(4)	0.2119(3)	0.0	0.0067(10)
B(11)	4(g)	IV	1.0	0.4858(4)	0.4098(3)	0.5	0.0068(9)
B(12)	4(g)	III	1.0	0.3442(4)	0.1968(3)	0.5	0.0077(10)
B(13)	4(g)	IV	1.0	0.5952(4)	0.4479(3)	0.5	0.0062(9)
B(14)	4(g)	III	1.0	0.4691(4)	0.3184(3)	0.5	0.0056(9)
B(15)	4(g)	III	1.0	0.5677(4)	0.2619(3)	0.5	0.0066(10)
B(16)	4(g)	II	1.0	0.1748(4)	0.1987(3)	0.0	0.0056(9)
B(17)	4(g)	III	1.0	0.4418(4)	0.1335(3)	0.5	0.0085(10)
B(18)	8(h)	I	1.0	0.3351(3)	0.3870(2)	0.8275(4)	0.0097(7)
B(19)	8(h)	IV	1.0	0.4116(2)	0.4703(2)	0.5914(4)	0.0057(6)
B(20)	8(h)	II	1.0	0.2167(3)	0.1529(2)	0.1498(4)	0.0065(6)
B(21)	8(h)	III	1.0	0.4950(2)	0.2687(2)	0.6508(3)	0.0057(6)
B(22)	8(h)	I	1.0	0.1288(3)	0.3614(2)	0.8316(4)	0.0089(7)
B(23)	8(h)	15	1.0	0.3520(3)	0.6510(2)	0.2066(4)	0.0098(7)
B(24)	8(h)	III	1.0	0.5386(3)	0.1795(2)	0.5910(4)	0.0077(7)
B(25)	8(h)	I	1.0	0.2455(3)	0.3174(2)	0.8293(4)	0.0080(7)
B(26)	8(h)	II	1.0	0.2684(2)	0.2376(2)	0.0902(4)	0.0066(6)
B(27)	8(h)	15	1.0	0.4654(3)	0.6884(2)	0.2052(4)	0.0088(7)
B(28)	8(h)	II	1.0	0.2903(2)	0.0735(2)	0.0921(4)	0.0065(6)
B(29)	8(h)	III	1.0	0.3748(3)	0.2798(2)	0.5920(4)	0.0076(7)
B(30)	8(h)	15	1.0	0.4489(3)	0.5933(2)	0.2089(5)	0.0130(9)
B(31)	8(h)	IV	1.0	0.5250(2)	0.4551(2)	0.6503(3)	0.0061(6)
B(32)	8(h)	I	1.0	0.2808(3)	0.4795(2)	0.8299(4)	0.0098(7)
B(33)	8(h)	I	1.0	0.1742(2)	0.3219(2)	0.6734(4)	0.0077(6)
B(34)	8(h)	I	1.0	0.2989(2)	0.3388(3)	0.6750(4)	0.0081(7)
B(35)	8(h)	I	1.0	0.2247(3)	0.4012(2)	0.5850(4)	0.0078(7)
B(36)	8(h)	I	1.0	0.3191(2)	0.4375(2)	0.6748(4)	0.0074(7)
B(37)	8(h)	I	1.0	0.2123(3)	0.4898(2)	0.6710(4)	0.0080(7)
B(38)	8(h)	I	1.0	0.2289(3)	0.4002(2)	0.9176(4)	0.0077(7)
Si(7)	4(g)	15	0.526(5)	0.4776(3)	0.5452(2)	0.0	0.0220(10)
Si(8)	4(g)	—	1.0	0.0128(2)	0.4370(1)	0.5	0.0490(11)
Si(9)	4(g)	—	0.460(4)	0.3517(2)	0.3818(1)	0.5	0.0041(6)
Si(10)	4(g)	—	1.0	0.0733(2)	0.5249(1)	0.0	0.0540(12)
Si(11)	4(g)	15	1.0	0.2858(1)	0.6620(1)	0.0	0.0153(4)
Si(12)	4(g)	15	1.0	0.5127(1)	0.7270(1)	0.0	0.0148(4)
Si(13)	8(h)	15	0.397(6)	0.3755(2)	0.7434(1)	0.1038(3)	0.0084(6)

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

tors are compared in a separate table.[3] The atomic, thermal and occupancy parameters are given in Table III, and the interatomic distances are presented in Table IV. The anisotropic thermal parameters will also be deposited in a separate table.[3]

V. Description and Discussion

A general view of the structure is shown in a projection on the (001) plane (Fig. 1). Other figures show detailed aspects of the atomic arrangement to facilitate discussion (Figs. 2 and 3).

The present analysis of the SiB_6 structure has revealed a new polyhedral arrangement for a boron-rich phase, central to which is the polyhedron containing 15 atoms and 26 triangular faces, the icosihexahedron M_{15} (see Fig. 2). The crystal structure of SiB_6 is basically a boron framework made up of M_{12} icosahedra and M_{15} icosihexahedra. The unit cell contains 18 M_{12} icosahedra [8 of M_{12}(I), 4 of M_{12}(II), 4 of M_{12}(III), and 2 of M_{12}(IV)], 4 M_{15} icosihexahedra, and 16 M_1

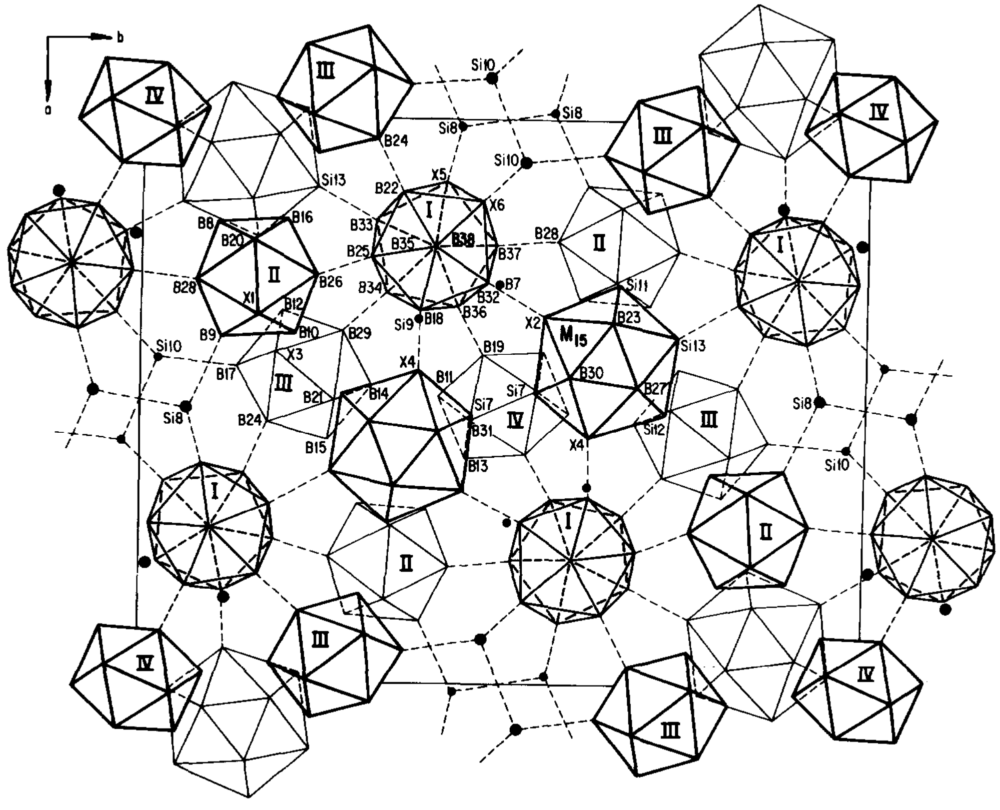

FIG. 1. Projection of the SiB_6 structure on the (001) plane. The heavy-lined polyhedra have centers at $z = 1.00$ and 0.00, the intermediate-lined polyhedra have centers at $z = 0.75$ and 0.25. The lightly lined ones have centers at $z = 0.50$.

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[3] See NAPS document No. 04348 for 10 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material. Remit \$1.50 for postage of any microfiche orders.

single-atom positions, not all filled. If full occupancy is assumed, the total number of atoms in the cell would be 292 (see Table IIb). The actual atom count depends on the occupancy of the various sites. The observed boron to silicon ratio found from the X-ray study is 5.59 = 238.47/42.65 for synthesis A and 5.56 for synthesis B. Both of these are in reasonable agreement with the phase diagram studies of Armas *et al.* (*8*) and Viala *et al.* (*9, 10*). For the sake of generality we shall use the formula SiB_6 in our discussion.

The three-dimensional boron–silicon skeleton seems to obey the general rules of crystal chemistry of boron-rich phases (*21*).

TABLE IVa

BONDS BETWEEN ATOMS WITHIN THE M_{12}(I) ICOSAHEDRON. ICOSAHEDRA CENTERED AT: 0.225, 0.402, ±0.250; 0.725, 0.098, ±0.250; 0.775, 0.598, ±0.250; 0.275, 0.902, ±0.250

Bond	Length (Å)	Number	Bond	Length (Å)	Number
Si(5)–Si(6)	2.121(6)	1 × .173	B(5)–Si(6)	2.135(6)	1 × .237
–B(6)	1.994(8)	1 × .248	–B(6)	2.016(8)	1 × .342
–B(22)	2.007(5)	1 × .421	–B(22)	2.013(8)	1 × .579
–B(33)	2.036(5)	1 × .421	–B(33)	2.071(8)	1 × .579
–B(35)	1.910(5)	1 × .421	–B(35)	1.984(8)	1 × .579
–B(37)	2.018(5)	1 × .421	–B(37)	2.082(8)	1 × .579
Si(6)–B(22)	2.056(7)	1 × .410	B(6)–B(22)	1.918(8)	1 × .590
–B(32)	2.039(6)	1 × .410	–B(32)	1.918(6)	1 × .590
–B(37)	2.037(6)	1 × .410	–B(37)	1.906(8)	1 × .590
–B(38)	1.987(6)	1 × .410	–B(38)	1.851(6)	1 × .590
B(18)–B(25)	1.814(6)	1			
–B(32)	1.866(7)	1			
–B(34)	1.826(6)	1			
–B(36)	1.789(6)	1			
–B(38)	1.787(6)	1			
B(22)–B(25)	1.864(6)	1			
–B(33)	1.846(6)	1			
–B(38)	1.819(6)	1			
B(25)–B(33)	1.857(6)	1			
–B(34)	1.756(5)	1			
–B(38)	1.767(6)	1			
B(32)–B(36)	1.805(7)	1			
–B(37)	1.868(7)	1			
–B(38)	1.850(7)	1			
B(33)–B(34)	1.822(5)	1			
–B(35)	1.846(6)	1			
B(34)–B(35)	1.801(6)	1			
–B(36)	1.831(6)	1			
B(35)–B(36)	1.755(5)	1			
–B(37)	1.842(6)	1			
B(36)–B(37)	1.812(6)	1			

TABLE IVb

BONDS BETWEEN ATOMS WITHIN THE M_{12}(II) ICOSAHEDRON. ICOSAHEDRA CENTERED AT: 0.282, 0.157, 0.000; 0.718, 0.843, 0.000; 0.782, 0.343, 0.500; 0.218, 0.657, 0.500

Bond	Length (Å)	Number	Bond	Length (Å)	Number
Si(1)–B(9)	2.048(4)	2 × 0.543	B(1)–B(9)	1.849(9)	2 × 0.457
–B(10)	2.014(4)	2 × 0.543	–B(10)	1.797(9)	2 × 0.457
–B(20)	2.019(5)	2 × 0.543	–B(20)	1.782(8)	2 × 0.457
–B(26)	2.061(4)	2 × 0.543	–B(26)	1.824(8)	2 × 0.457
–B(28)	2.052(4)	2 × 0.543	–B(28)	1.840(8)	2 × 0.457
B(8)–B(16)	1.764(8)	1			
–B(20)	1.785(5)	2			
–B(28)	1.795(6)	2			
B(9)–B(10)	1.838(8)	1			
–B(28)	1.830(6)	2			
B(10)–B(26)	1.848(7)	2			
B(16)–B(20)	1.809(5)	2			
–B(26)	1.767(6)	2			
B(20)–B(26)	1.819(5)	2			
–B(28)	1.888(5)	2			
B(26)–B(26)	1.788(8)	1			
B(28)–B(28)	1.826(8)	1			

TABLE IVc

BONDS BETWEEN ATOMS WITHIN THE M_{12}(III) ICOSAHEDRON. ICOSAHEDRA CENTERED AT: 0.046, 0.728, 0.000; 0.954, 0.272, 0.000; 0.454, 0.228, 0.500; 0.546, 0.772, 0.500

Bond	Length (Å)	Number	Bond	Length (Å)	Number
B(3)–B(12)	1.803(6)	2 × 0.429	Si(3)–B(12)	2.026(4)	2 × 0.571
–B(17)	1.811(6)	2 × 0.429	–B(17)	2.055(5)	2 × 0.571
–B(21)	1.823(6)	2 × 0.429	–B(21)	2.026(5)	2 × 0.571
–B(24)	1.826(6)	2 × 0.429	–B(24)	2.070(4)	2 × 0.571
–B(29)	1.845(6)	2 × 0.429	–B(29)	2.038(5)	2 × 0.571
B(12)–B(17)	1.821(8)	1			
–B(29)	1.827(6)	2			
B(14)–B(15)	1.757(8)	1			
–B(21)	1.789(5)	2			
–B(29)	1.782(6)	2			
B(15)–B(21)	1.829(5)	2			
–B(24)	1.808(6)	2			
B(17)–B(24)	1.862(7)	2			
B(21)–B(24)	1.849(5)	2			
–B(29)	1.837(5)	2			
B(24)–B(24)	1.804(8)	1			
B(29)–B(29)	1.824(8)	1			

TABLE IVd

BONDS BETWEEN ATOMS WITHIN THE M_{12}(IV) ICOSAHEDRON. ICOSAHEDRA CENTERED AT: 000 AND 1/2 1/2 1/2

Bond	Length (Å)	Number
B(11)–B(13)	1.723(8)	2
–B(19)	1.786(6)	4
–B(31)	1.796(7)	4
B(13)–B(19)	1.754(6)	4
–B(31)	1.805(7)	4
B(19)–B(19)	1.812(7)	2
–B(31)	1.744(7)	8
B(31)–B(31)	1.796(8)	2

However, a rather unusual coordination scheme seems to be present for the Si atoms at the centers of the hexagonal faces of the M_{15} polyhedron in Fig. 2. The same coordination scheme was found for Be atoms in BeB_3 by Mattes *et al.* (*22*). This M_{15} icosihexahedron is a rather bulky unit, with 9 of its 15 vertices totally or partially replaced by silicon atoms. This is reflected in the rather long average B–B distance of 1.852 Å. The average B–Si and Si–Si distances are 2.167 and 2.214 Å, respectively. These distances, which are averages weighted according to the frequency of occurrence, are given in Table V. The most interesting feature of this polyhedron is the

TABLE IVe

BONDS BETWEEN ATOMS WITHIN THE M_{15} ICOSIHEXAHEDRON. ICOSIHEXAHEDRA CENTERED AT: 0.424, 0.643, 0.000; 0.576, 0.357, 0.000; 0.924, 0.856, 0.500; 0.076, 0.143, 0.500

Bond	Length (Å)	Number	Bond	Length (Å)	Number
Si(2)–Si(2)	1.972(9)	1 × 0.155	B(2)–B(2)	2.135(9)	1 × 0.367
–Si(7)	2.208(9)	2 × 0.207	–B(23)	2.052(9)	2 × 0.606
–Si(11)	2.312(9)	2 × 0.394	–B(30)	1.838(8)	2 × 0.606
–B(2)	2.065(9)	1 × 0.478	–Si(7)	2.063(8)	2 × 0.319
–B(23)	2.038(9)	2 × 0.394	–Si(11)	2.481(8)	2 × 0.606
–B(30)	2.011(9)	2 × 0.394			
Si(4)–Si(4)	1.887(8)	1 × 0.060	B(4)–B(4)	2.111(9)	1 × 0.572
–Si(7)	1.997(8)	2 × 0.128	–B(27)	1.918(7)	2 × 0.756
–Si(12)	2.267(2)	2 × 0.244	–B(30)	1.833(7)	2 × 0.756
–B(4)	2.005(7)	1 × 0.368	–Si(7)	2.062(6)	2 × 0.398
–B(27)	2.109(6)	2 × 0.244	–Si(12)	2.200(6)	2 × 0.756
–B(30)	1.959(7)	2 × 0.244			
Si(7)–B(30)	2.288(5)	2 × 0.526			
Si(11)–Si(13)	2.225(5)	2 × 0.397			
–B(23)	2.268(5)	2 × 1.000			
Si(12)–Si(13)	2.247(4)	2 × 0.397			
–B(27)	2.258(5)	2 × 1.000			
Si(13)–Si(13)	2.058(6)	1 × 0.158			
–B(23)	2.004(5)	2 × 0.397			
–B(27)	1.924(5)	2 × 0.397			
B(23)–B(27)	1.771(6)	2 × 1.000			
–B(30)	1.750(6)	2 × 1.000			
B(27)–B(30)	1.759(6)	2 × 1.000			

TABLE IVf

BONDS BETWEEN POLYHEDRA

Polyhedra	Bond	Length (Å)	Number of bonds per unit cell
I–I	B(35)–B(35)	1.685(8)	4
I–I	B(38)–B(38)	1.633(8)	4
I–II	B(25)–B(26)	1.698(5)	8
I–II	B(28)–B(37)	1.722(5)	8
I–III	B(22)–B(24)	1.684(5)	8
I–III	B(29)–B(34)	1.743(6)	8
I–IV	B(19)–B(36)	1.679(5)	8
I–15	B(2)–B(32)	1.824(8)	8 × 0.606
I–15	Si(2)–B(32)	1.796(8)	8 × 0.394
I–15	B(4)–B(18)	1.834(7)	8 × 0.756
I–15	Si(4)–B(18)	1.761(6)	8 × 0.244
I–15	Si(13)–B(33)	1.748(5)	8 × 0.397
II–III	B(1)–B(3)	2.400(9)	8 × 0.261
II–III	B(1)–Si(3)	2.024(8)	8 × 0.196
II–III	Si(1)–B(3)	2.027(8)	8 × 0.310
II–III	Si(1)–Si(3)	1.649(3)	8 × 0.233
II–III	B(15)–B(16)	1.702(8)	4
II–IV	B(8)–B(13)	1.652(8)	4
II–15	B(10)–Si(12)	1.956(6)	4
II–15	B(20)–B(23)	1.734(6)	8
III–IV	B(11)–B(14)	1.691(8)	4
III–15	B(12)–Si(11)	1.977(6)	4
III–15	B(21)–B(27)	1.726(6)	8
IV–15	B(30)–B(31)	1.695(7)	8
15–15	Si(7)–Si(7)	1.776(7)	2 × 0.277

TABLE IVg

BONDS TO ISOLATED ATOMS

Bond	Length (Å)	Number of bonds per unit cell
Si(8)–B(5)	2.074(8)	8 × 0.579
–B(9)	1.991(6)	4
–Si(5)	2.116(4)	8 × 0.421
–Si(8))	2.337(5)	2
Si(10)–B(6)	2.263(8)	8 × 0.590
–B(17)	2.001(7)	4
–Si(6)	2.045(6)	8 × 0.410
–Si(10)	2.299(5)	2
B(7)–B(8)	2.067(8)	4 × 0.500
–B(13)	2.001(8)	4 × 0.500
–B(19)	2.019(8)	8 × 0.500
–B(28)	2.101(7)	8 × 0.500
–B(35)	2.076(7)	8 × 0.500
–B(36)	2.041(7)	8 × 0.500
–B(37)	2.025(7)	8 × 0.500
B(7)–Si(9)	2.202(7)	4 × 0.230
Si(9)–B(11)	1.996(7)	4 × 0.460
–B(14)	2.051(6)	4 × 0.460
–B(19)	2.048(5)	8 × 0.460
–B(29)	2.105(5)	8 × 0.460
–B(34)	2.051(5)	8 × 0.460
–B(35)	2.044(5)	8 × 0.460
–B(36)	2.065(6)	8 × 0.460

composite hexagonal faces (made of six trigonal faces) whose centers contain a silicon atom (Si7, Si11, Si12). This feature is unusual in polyhedra containing boron atoms, since they normally lead to pentagonal-shaped surfaces with the 6th bond perpendicular to the pentagon. The existence of this 6 + 1 bonding arrangement and of the M_{15} icosihexahedron itself is certainly due to the fact that the center atoms of the hexagonal pyramid are silicon and can participate in such a bonding scheme more easily than boron. The 7th bond is directed outwards along the pseudo-sixfold axis.

As shown in Fig. 2 the Si7 and Si13 sites are only partially occupied. From the par-

TABLE V

AVERAGE INTERATOMIC DISTANCES IN SiB_6

Unit[a]	B–B (Å)	B–Si (Å)	Si–Si (Å)
M_{12}(I)	1.849(12)	2.018(30)	2.121(6)
M_{12}(II)	1.816(7)	2.039(7)	—
M_{12}(III)	1.819(6)	2.043(8)	—
M_{12}(IV)	1.773(10)	—	—
M_{15}	1.852(42)	2.167(42)	2.214(60)
Si(8) and Si(10)	—	2.089(27)	2.170(39)
Interpolyhedral	1.731(11)	1.898(24)	1.678(45)

[a] For the polyhedral M units all of the distances listed are within the polyhedra.

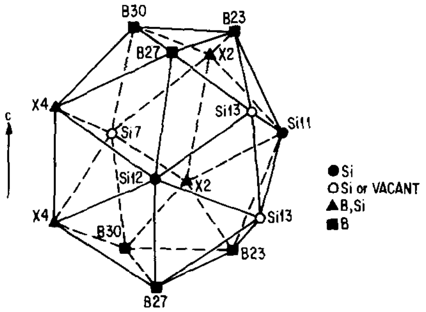

FIG. 2. Perspective drawing of the 26-hedron, the M_{15} icosihexahedron. The black atoms are fully occupied sites, the white atoms are only partially occupied.

tial occupancy it can be shown that only 8% of the M_{15} units have 15 atoms, while 33% have 14 atoms, 42% have 13 atoms, and 17% have 12 atoms. This latter 12-atom structural unit looks more like a doughnut or torus than a sphere. In the $B_{12}Be_3$ unit (22) the 15 sites were fully occupied. Thus Be appears to be more "comfortable" than Si with the M_{15} structure.

The M_{12} and M_{15} units are linked together by direct M–M interpolyhedral bonds and by bonds to two framework silicon atoms Si8 and Si10. This resultant three-dimensional boron–silicon skeleton provides a number of interstitial sites which are partially filled with two different interstitial atoms B7 and Si9.

There appear to be three possible interstitial sites around the M_{12}(I) icosahedron (see Fig. 1). The first is the B7 site between B32 and X2; the second is the Si9 site between B18 and X4; the third is the smaller-size vacant region between B33 and Si13. The notation X refers to a site which has a statistical mixture of B and Si atoms. The function of the interstitial atoms is probably to supply electrons to the electron-deficient boron framework.

The boron–silicon framework can be most easily described as the close packing of large rings (diam. ~9 Å) or pinwheels formed by the M_{12}(I) icosahedron acting as the hub with its pseudo-fivefold axis parallel to the hub axis and the *c*-axis of the cell. Attached at the end of each radial 6th bond is an M_{12} or M_{15} unit or a single M atoms. The periphery of the ring is made up then of three M_{15} units, two M_{12}(II), two M_{12}(III), one M_{12}(IV) units, and two single M atoms (Si8 and Si10) (see Fig. 1). These rings or centered tori are close-packed in the (001) plane to form layers (~5 Å thick). The stacking of these layers along the *c*-axis gives the three-dimensional framework and satisfies the 6th bond requirement of the remaining two atoms of the M_{12}(I) unit. The structure has the aspect of close-packed infinite cylinders along the (001) direction containing chains of M_{12}(I) icosahedra. This pinwheel configuration is somewhat reminiscent of the large B_{84} unit, in the form of a centered sphere, found in β-rhombohedral boron (*23, 24*). In the present structure the torus is open in one direction where two "missing" polyhedra are replaced by the atoms Si8 and Si10.

The polyhedra and single atoms making up the structure will now be discussed and compared in order to underline the unique-

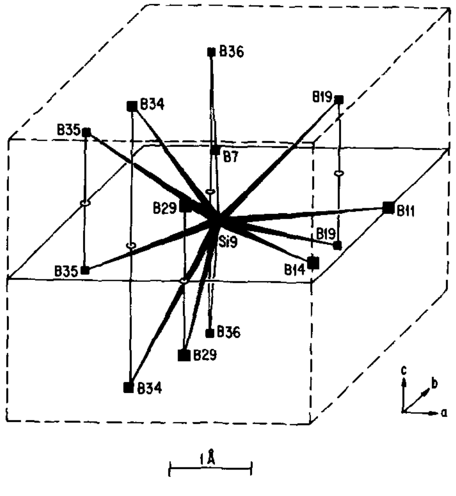

FIG. 3. Coordination of the Si(9) site. All of the 13 nearest neighbor centers are contained within a box, shown as a dashed outline, of size 3.8 × 4.1 × 3.5 Å. The horizontal plane through its center contains the centers of Si9, B7, B11, and B14.

ness of this structure. Five distinct polyhedra, two framework atoms, and two different interstitial atoms have been observed in SiB_6. As in the case with other boron-rich phases, the main polyhedral unit is the icosahedron, represented by four different types. The icosahedron M_{12}(I), with no symmetry, acts as the hub of the pinwheel unit. Two of its vertices are at times occupied by boron or silicon. The average interatomic distances are given in Table V. The M_{12}(II) and M_{12}(III) are very similar and are centered on a mirror plane. They form part of the torus. Their average B–B and B–Si distances are given in Table V. Two of their vertices are partially substituted by silicon. The M_{12}(IV) icosahedron is highly symmetric (2/*m*), contains only boron atoms, and is also part of the pinwheel ring. The average B–B distance is 1.773(10) Å. These distances are to be compared with the intraicosahedral B–B linkages of 1.80 Å in β-rhombohedral boron (*23, 24*), 1.799 Å in tetragonal boron (*25*), and 1.808 Å in YB_{66} (*26*). As can be seen, the average B–B distance in M_{12}(I) unit is much longer than the normally observed length. The lengthening of these bonds is certainly due to the partial substitution of two borons by silicon atoms. The B–B bonds in the M_{12}(II) and M_{12}(III) are only slightly longer than the normally observed bond lengths. The M_{12}(IV) icosahedron has normal B–B bond lengths, as is expected from an all-boron polyhedron.

The average B–Si distance in all the above polyhedra is quite normal and comparable to the 2.111 Å found in SiB_{36} (*12*) and 2.038 Å in SiB_3 (*7*). Equally, the average Si–Si distance is shorter than the 2.224 Å observed in $SiB_{\sim 36}$ and the 2.352 Å in elemental silicon. These shorter Si–Si bonds in SiB_6 could be the result of the partial occupation of some of the silicon sites by either boron or vacancies, allowing closer average approaches.

The weighted average of the boron–boron interpolyhedral distances is 1.731 Å. This is shorter, as has been customarily found, than the intrapolyhedral distance, and agrees fairly well with the 1.72 Å observed in β-rhombohedral boron (*23, 24*), the 1.726 Å in YB_{66} (*26*), and the 1.709 Å in α-AlB_{12} (*27*).

Of the four isolated, single atoms found in the structure two of them (Si8 and Si10) are part of the pinwheel ring in almost identical tetrahedral environments. The average distances to their boron and silicon neighbors are 2.089 and 2.170 Å, respectively. For the two interstitials (B7 and Si9) the average distance to the near neighbors is 2.055 and 2.062 Å, respectively. These have a coordination number of 13, and the local environment of Si9 is shown in Fig. 3. The environment of B7 is similar. The interstitial sites containing B(7) and Si(9) are possible candidates for occupation by other metal atoms. However, the relatively short bonding distances to these atoms would probably restrict substitution to atoms of small covalent radius. The Si(8) and Si(10) sites, due to their low coordination and their role of satisfying the bonding requirements of the M_{12}(I) unit, are not very likely to be substutited by other types of atoms with the exception of possibly carbon. The close-packed character of this framework provides only one other space for additional interstitial site. This site between B33 and Si13 on the $z = 0.5$ plane has four nearest neighbors (two of B33 and two of Si13) at 1.732 Å. Thus it is considerably smaller in diameter than the B7 and Si9 sites. The fractional occupancy was measured to be close to zero (i.e., ≤ 0.05).

It may also be possible to substitute some small impurity atoms such as Be in the partially occupied sites Si7 and Si13. There are, on the average, 7 of these sites vacant per unit cell. Large impurity ions such as transition metals might not enter such sites.

The lack of numerous interstitial sites of large dimensions in SiB_6 is in substantial contrast to β-rhombohedral boron (*12*) where many different kinds of atoms can be accommodated interstitially.

VI. Crystal Chemistry

A. Carbon Solutility

Since carbon is a common impurity in elemental boron there may well be carbon impurities in the samples of SiB_6 studied by various previous authors (see Table I). Giese (*17*) was particularly concerned about this. In order to determine whether carbon is actually soluble in SiB_6 we made up two samples of mixed, high-purity Si + B + C powders. The first was in the ratio 1 Si + 6B, with no carbon; the second was the same but with 1.1 atom% added carbon. These were both hot-pressed and reacted at 1840°C for 40 min. The lattice parameters of the two samples were measured and gave unit cell volumes of $2629 \pm 4 \times 10^{-24}$ cm^3 (undoped) and $2600 \pm 8 \times 10^{-24}$ cm^3 (with $c = 0.011$ atom fraction of carbon). The lattice shrinks as carbon is incorporated. The measured shrinkage rate is

$$S_{\mathrm{OBS}} = \frac{V}{V_0 C} = -1.1.$$

If we assume that the atoms in the SiB_6 lattice have very nearly the same atomic volumes as in their elemental forms (see Section VII), then the volume shrinkage expected for silicon being replaced by carbon is

$$S(\mathrm{Si}) = -1.58.$$

If carbon replaces only boron then the calculated value of S is

$$S(\mathrm{B}) = -0.18.$$

The experimental value is closer to the assumption that only Si is replaced by carbon, however some replacement of both is possible. Thus we find that carbon appears to be soluble in SiB_6, and may be responsible for the variations in the unit cell volume reported in Table I. On this basis Giese's sample probably had about 2 atom% carbon in it.

B. Atomic Volumes

The volume per atom for silicon and boron in elemental silicon and in α-boron at room temperature are

$$V_{\mathrm{Si}} = 20.0206 \times 10^{-24}\ \mathrm{cm}^3$$

$$V_{\mathrm{B}} = 7.2823 \times 10^{-24}\ \mathrm{cm}^3.$$

For synthesis B from Table IIa we would expect the volume of 43 ± 1 silicon and 247 ± 1 boron atoms to be

$$V_{\mathrm{TOT}} = 2660 \pm 27 \times 10^{-24}\ \mathrm{cm}^3.$$

This is equal to the measured cell volume to within the experimental error. Thus the packing of the atoms in SiB_6 is as dense as that in elemental Si and α-B. Note that if we had used the V_{B} of β-boron of 7.830×10^{-24} cm^3 the agreement would have been much worse. It is apparent that the space for interstitial impurities in SiB_6 is much less than that in β-B.

C. Phase Width

The width of the phase field in nominal SiB_6 is of some concern. Lugscheider *et al.* (*18*) have measured the unit cell volume of silicon-rich material as 2629.6×10^{-24} cm^3 while for boron-rich material it is 2599.9×10^{-24} cm^3. Presumably these samples all have the same, unknown carbon content. Since some of the lattice sites are occupied by either Si or B, we can expect a volume decrease as boron increasingly replaces Si. If there are a total of 289 atoms in a unit cell (see Table IIa) and n of these are silicon, the unit cell volume is approximately:

$$V_{\mathrm{CELL}} = nV_{\mathrm{Si}} + (289 - n)V_{\mathrm{B}}.$$

Then

$$\frac{\Delta V}{\Delta n} V_{\mathrm{Si}} - V_{\mathrm{B}} = 12.738 \times 10^{-24}\ \mathrm{cm}^3.$$

The ΔV value of 29.7×10^{-24} cm^3 found by Lugscheider *et al.* can be produced by a $\Delta n = 2.3$ atoms. This means that the phase width may extend from 246B and 43Si to 248.3B and 40.7Si, or from a B-to-Si ratio of 5.72 to 6.10. This is a much smaller chemical composition range than suggested by Lugscheider *et al.*

If we look at atom sites 1 through 6 in Table III, and ask how many Si atoms per unit cell might be replaced by B atoms in order to completely fill sites 1 through 6 with only B atoms we obtain $\Delta n = 19.5$. This is clearly much larger than observed. Thus the Si atoms are a necessary part of the icosahedra and icosihexahedra in SiB_6.

VII. Conclusions

1. The unit cell of SiB_6 is orthorhombic, *Pnnm* and contains about 290 atoms.
2. It is built up of a framework of 18 icosahedra, 4 icosihexahedra, and 8 single atoms. There are about four interstitial atoms per cell.
3. The atom packing is very dense with little room for interstitial impurities.
4. The width of the phase field is from approximately $SiB_{5.7}$ to $SiB_{6.1}$.
5. Carbon is soluble in SiB_6. It decreases the unit cell volume and probably replaces silicon.

Acknowledgments

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Note added in proof. The most recent work by Kieffer *et al.* (*28*) on the B–Si–C ternary system did not report any information on the extent of the SiB_6 phase field. However, it did show that SiB_6 is in equilibrium at 1840°C with both B_4C and SiC. Therefore, if a large excess of carbon is insoluble in SiB_6 it will precipitate out *both* B and Si, not just SiC. This is verified by the work of Feigelson and Kingery (*29*), who found that hot pressed SiB_6 exhibits both B_4C and SiC inclusions when exposed to a carbon monoxide atmosphere at high temperatures. Thus there is no evidence to suggest that excess carbon in SiB_6 will necessarily produce SiB_{6+x} at the boron saturation limit, and in fact it may produce almost no stoichiometric change at all.

The Si solid solubility in B_4C is at least 4.3 atom% (*1*), and Meerson *et al.* (*30*) claim that B_4C and B_4Si are mutually and completely soluble in each other. So one might expect some solubility of carbon in SiB_6. Experiments carried out at G.E. showed that the electrical conductivity of the SiB_6 containing (presumably) 1.1 atom% C is 8 times higher than that of the pure sample.

Further evidence for carbon solubility is the data of Giese (*17*) in Table I, which shows a unit cell volume even smaller than the 2600×10^{-24} cm^3 boron-rich limit. The sample studied by Giese (*17*) may have 2 to 8 atom% carbon in solution. A recent unpublished X-ray study by Feigelson *et al.* (*31*) indicates that up to 9 atom% carbon may be soluble in SiB_6.

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