

bond. This distance is similar to some of the oxygen-oxygen separations found by Beevers, McDonald, Robertson & Stern (1952) in sucrose. Infrared spectra confirm this long O-O distance (Mann & Marrinan, 1958). β -D-glucose crystals show a band at 3540 cm.^{-1} , which is to be compared with a band at 3570 cm.^{-1} in sucrose and approximately 3620 cm.^{-1} for unbonded OH groups in dilute solution in carbon tetrachloride. The observed frequency in β -D-glucose must be due to an OH group, which interacts only weakly with its environment and it is concluded that O_4 and its associated hydrogen constitute this group.

The above co-ordinates were used to compute structure factors and the value of $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ was calculated for all three zones using a temperature factor of $\exp(-1.5 \sin^2 \theta/\lambda^2)$. The values obtained were

$$R(hk0) = 0.21, R(0kl) = 0.22, R(h0l) = 0.26$$

for all observed reflections.

It is intended to carry out three-dimensional refinement and full details of the crystallographic analysis will be published when the work is complete.

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A new form of boron silicide, B_4Si . By VLADO I. MATKOVICH, *Research Laboratories, Allis-Chalmers Manufacturing Company Milwaukee, Wisconsin, U.S.A.*

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There has been much interest in compound formation in the boron-silicon system since the original work of Moissan & Stock (1900). Two phases only have been reported, namely B_3Si and B_6Si . The latter is well established (Cline, 1959), and while our work on the boron silicides was in progress, structural data for orthorhombic B_6Si were reported (Cline, 1958; Adamsky, 1958). A cubic form of B_6Si has also been suggested (Zhuravlev, 1956). The reported tetragonal B_3Si (Samsonov & Latysheva, 1955) has been questioned (Gurevich, Epel'baum & Ormont, 1957).

The investigation of the silicon-boron system has been conducted in this laboratory for some time and samples for this investigation were obtained from E. Colton. Samples were made from mixtures of silicon and amorphous boron or from silicon melts at temperatures ranging from 1350 to 1850 °C. Excess silicon was removed by treatment with a mixture of nitric and hydrofluoric acids.

At least four different crystalline forms were found, two of which were identified, namely, B_6Si and a new form, B_4Si . The former has been obtained as powder and crystals, the data on which agree very well with earlier work (Cline, 1958; Adamsky, 1958; Cline, 1959).

Purification of samples for chemical analysis was difficult because $HF-HNO_3$ acid mixture slowly decomposes B_4Si . Furthermore, some negligible quantity of B_6Si is also always present in the sample. Because B_6Si is not attacked by the acid mixture, purification results in enrichment of B_6Si . Some amount of boron nitride appears also to be formed during purification. Samples for analysis contained, therefore, either some metallic silicon or, when silicon was completely removed, some

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B_3Si and BN. The boron to silicon ratio was therefore found to vary between 3.7 and 4.3. The following is a chemical analysis of such a sample.

Silicon	36.6%	Aluminum	0.3%
Boron	60.2	Iron	0.2
Magnesium	0.2	Calcium	0.2
Nitrogen	0.6	Moisture	0.3
Oxygen	0.5		

A more detailed report on the preparation and purification of B_4Si will appear later.

The specific gravity of B_4Si , measured by heavy liquids method is 2.47 g.cm.^{-3} .

Table 1. Powder diffraction data for B_4Si
(Cr $K\alpha$ radiation)

hkl	d (Å)	I/I_0	hkl	d (Å)	I/I_0
101	4.985	20	027	1.516	1
012	4.147	30	131	1.510	30
110	3.159	20	223	1.485	1
104	2.745	90	312	1.480	20
021	2.674	100	306	1.384	10
202	2.518	1	401	1.361	1
015	2.308	5	315	1.3059	2
006	2.120	1	119	1.2925	1
024	2.076	1	226	1.2689	1
211	2.043	20	321	1.2518	1
116	1.762	20	1,0,10	1.2410	2
107	1.724	10	232	1.2342	1
303	1.677	10	045	1.2070	3
125	1.606	50	410	1.1962	3
220	1.582	30	324	1.1700	5
018	1.527	5			

B_4Si crystals were examined by rotation and Weissenberg X-ray methods and dimensions corrected by measurement of X-ray powder photographs. The crystals are found to be rhombohedral with the following hexagonal unit cell.

$$a = 6.330 \text{ and } c = 12.736 \text{ \AA}.$$

Since the compound appears to be isomorphous with B_4C , the $R\bar{3}m$ space group is assigned. However, on the basis of systematic absences, any of the following space groups is possible: $R\bar{3}m$, $R3m$, $R32$, $R\bar{3}$, and $R3$. The rhombohedral unit cell contains three B_4Si molecules. Specific gravity as well as chemical analysis rule out the possibility of this new form of boron silicide being B_3Si .

X-ray powder diffraction lines for B_4Si , shown in Table 1, were obtained by use of $Cr K\alpha$ radiation with a 14 cm. camera.

B_4Si appears to be thermodynamically unstable under long heating in air. For example, after heating for about 100 hr. at 1370 °C., B_4Si is converted completely into orthorhombic B_6Si . This change may prove interesting from a structural viewpoint as a similarity between B_6Si and B_4C is indicated by Adamsky (1958).

The specific gravity of 2.47 g.cm.⁻³ as found for B_4Si is slightly lower than the value of 2.52 g.cm.⁻³ obtained by Moissan (1900) for B_3Si . In view of the difficulty experienced in removing excess silicon from reaction products, the author believes that what Moissan called B_3Si , probably was B_4Si .

Crystals of another orthorhombic and tetragonal form were also found. However, their chemical formulas have not been established.

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Some new intermetallic compounds of beryllium.*

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Two new classes of compounds are reported here (M_3Be and MBe_{20}), together with additional compounds of the M_2Be_{17} and MBe_{13} types. The X-ray data are based on powder diffraction patterns using $Cu K\alpha$ radiation. The lattice parameters were calculated from relatively low Bragg angles, i.e., in the forward reflection region.

(1) M_3Be

The compound Mo_3Be was prepared and found to be isomorphous with Mo_3Si (Templeton & Dauben, 1950), which is cubic. The preparation contained free molybdenum, in addition to Mo_3Be . No other beryllides were observed in this preparation.

(2) M_2Be_{17}

Compounds of the form M_2Be_{17} were found in the Hf-Be, Nb-Be, Ti-Be, Ta-Be, and Zr-Be systems, but not in the Cr-Be, Mo-Be, Re-Be, V-Be, or W-Be systems. Nb_2Be_{17} (Sands, Zalkin & Krikorian, 1959) and Zr_2Be_{17} (Zalkin, Bedford & Sands, 1959) are reported as isomorphous having rhombohedral symmetry. Their hexagonal unit cells are given as triply primitive. Based on a comparison of powder patterns, all of the M_2Be_{17} compounds mentioned here were found to be isomorphous. The lattice parameters of Hf_2Be_{17} , Ta_2Be_{17} , and Ti_2Be_{17} shown in Table 1 are based on the hexagonal unit cell.

* The work was performed in part under contracts with the U.S. Air Force, and is continuing under contracts with both the U.S.A.F. and the U.S. Atomic Energy Commission.

Table 1. Structures of some intermetallic compounds of beryllium

Compound	Structure	Lattice constants
Mo_3Be	Cubic- O_h^3	$a = 4.89 \text{ \AA}$
Hf_2Be_{17}	Hexagonal	$a = 7.50$ $c = 10.94$
Ta_2Be_{17}	Hexagonal	$a = 7.39$ $c = 10.76$
Ti_2Be_{17}	Hexagonal	$a = 7.34$ $c = 10.73$
$LaBe_{13}$	Cubic- O_h^3	$a = 10.44$
$MoBe_{20}^*$	Cubic- O_h^3 or T_h^4	$a = 11.64$
$ReBe_{20}^*$	Cubic- O_h^3 or T_h^4	$a = 11.54$
WBe_{20}^*	Cubic- O_h^3 or T_h^4	$a = 11.64$

* Assigned empirical formulas and space groups are tentative pending further investigation.

(3) MBe_{13}

The compound $LaBe_{13}$ was prepared and found to be isomorphous with $ZrBe_{13}$, which has a face-centered cubic $NaZn_{13}$ type structure (Baenziger & Rundle, 1949). Structural data are given in Table 1.

(4) ' MBe_{20} '

Compounds having the approximate composition of MBe_{20} were observed in Mo-Be, Re-Be, and W-Be systems. The compounds are mutually isomorphous, being cubic and having systematic absences characteristic of both O_h^3 and T_h^4 space groups. No intensity calculations