Unit cell and space group of orthorhombic SiB₆.

Unit cell and space group of orthorhombic SiB_6. By ROBERT F. ADAMSKY, *Basic Research Branch, Research and Development Division, The Carborundum Company, Niagara Falls, New York, U.S.A.*

The original study of the silicon–boron system was carried out by Moissan & Stock (1900), who reported synthesis of two compounds, SiB_3 and SiB_6, the former occurring as black rhombic plates, and the latter as black, irregular crystals. A number of subsequent papers by other authors indicated inability to duplicate this synthesis, however, Samsonov & Latyscheva (1955) claimed the preparation of SiB_3, and reported some of its physical properties. Although Samsonov and Latyscheva at the time were unable to prepare SiB_6, Zhuravlev (1956) later reported on the crystal structure of SiB_6, using SiB_6 powder obtained from these authors. The SiB_6 was apparently prepared in the same manner as SiB_3. Zhuravlev (1956) reports that SiB_6 is cubic with $a_0 = 4.142$ Å, that it has a calculated density of 2.18 g.cm.$^{-3}$, and is isostructural with CaB_6. Recently Gurevich, Epel'baum & Ormont (1957) have questioned the conclusions of Samsonov & Latyscheva (1955) regarding the characterization of SiB_3, and pointed out errors in the X-ray data. However, the latter authors, to our knowledge, have not as yet commented on the criticism, or explained the differences in experimental conditions which led to the formation of SiB_6, rather than the originally reported single phase of SiB_3.

The silicon-boron system was under study in these laboratories prior to our knowledge of the work of the Russian authors, and Cline (1958a, b) has prepared single crystals of a new form of SiB_6 by fusion of the elements. When prepared from a melt containing excess silicon, the compound crystallizes as large (up to 2·0 mm.), black, opaque crystals, often with well developed faces. Goniometric measurements indicate that the crystals are orthorhombic, with prominent forms {010}, {111}, and {110}. The average of five independent chemical analyses shows the compound to have the composition boron $69.5 \pm 0.5\%$, and silicon $29.8 \pm 0.5\%$, compared to the respective theoretical values of 69.8 and 30.2%. No deviation from stoichiometry is indicated, within experimental error. The density, measured with a pycnometer, is 2.43 g.cm.$^{-3}$.

The unit-cell dimensions of SiB_6 were measured from Weissenberg photographs taken about the b and c axes. The crystal of SiB_6 which was used had been ground into a sphere of 0·50 mm. diameter by the method of Bond (1951). The cell dimensions are:

$$a_0 = 14.392_0 \pm 0.0010, \quad b_0 = 18.267_3 \pm 0.0015,$$
$$c_0 = 9.885_2 \pm 0.0010 \text{ Å}.$$

The constants were measured using a method of moderate precision similar to that of Christ (1956), using high purity silver as a calibrating substance. Narrow powder patterns of well-annealed silver were recorded on each side of the Weissenberg patterns for SiB_6, and the precise values of θ for silver, calculated by Christ (1956) from the data of Straumanis & Ievins (1940), were used to obtain corrections for film shrinkage and departure of the camera radius from an assumed value. The apparent spacings obtained were corrected for eccentricity and absorption errors by the method of Bradley & Jay (1932). The wave lengths used are: $\lambda(Cu\,K\beta_1) = 1.39217$, $\lambda(Cu\,K\alpha_1) = 1.54050$, $\lambda(Cu\,K\alpha_2) = 1.54434$, $\lambda(Cu\,K\alpha) = 1.5418$ Å (Bragg, 1947).

The accuracy of the method was checked by measuring the lattice constant of a single crystal of NaCl grown from water solution. A value for a_0 of $5.639_4 \pm 0.0010$ Å was obtained, in good agreement with the Siegbahn value of 5.63937 Å, and Van Bergen's (1941) value of 5.63960 Å.

Systematic absences were observed for $0kl$ with $k+l$ odd, and for $h0l$ with $h+l$ odd, indicating probable space groups $Pnn2$ and $Pnnm$. The latter space group is preferred on the basis of the morphological evidence. Tests for pyroelectricity were negative. Assuming 40 molecules per unit cell, the calculated density is 2.39 g.cm.$^{-3}$.

The structure of the orthorhombic modification of SiB_6 is currently under investigation. Considering the space group $Pnnm$, an approximate structure can be postulated which resembles that of B_4C (Clark & Hoard, 1943) in that groups of twelve boron atoms arranged at the vertices of an icosahedron are bonded to other similar groups, and to groups of two silicon atoms which take the place of the linear chains of three carbon atoms in B_4C. Diffraction intensities are presently being measured by counter techniques, and details of the structure will be reported later.

In view of the reported cubic modification of SiB_6 (Zhuravlev, 1956), and the possible existence of SiB_3, we have examined by optical and X-ray methods, numerous crystals from many different preparations, without finding evidence of cubic SiB_6 or a tetragonal SiB_3 phase (Samsonov & Latyscheva, 1955). However, very small crystals of two phases other than the SiB_6 reported above have been found. Examination of the single crystals shows one phase, which occurs as black, irregular, twinned crystals, to be orthorhombic, and the other phase, which occurs as black rhombic plates, to be hexagonal. The chemical compositions of these phases are not known, and their characterization is, as yet, incomplete.

References

BOND, W. L. (1951). *Rev. Sci. Instrum.* **22**, 344.

BRADLEY, A. J. & JAY, A. H. (1932). *Proc. Phys. Soc. A*, **44**, 536.

BRAGG, W. L. (1947). *J. Sci. Instrum.* **24**, 27.

CHRIST, C. L. (1956). *Amer. Min.* **41**, 569.

CLARK, H. K. & HOARD, J. L. (1943). *J. Amer. Chem. Soc.* **65**, 2115.

CLINE, C. F. (1958a). *Nature, Lond.* **181**, 476.

CLINE, C. F. (1958b). Thesis, Niagara University.

GUREVICH, M. A., EPEL'BAUM, V. A. & ORMONT, B. F. (1957). *Zhur. Neorg. Khim.* **2**, 206.

MOISSAN, A. & STOCK, A. (1900). *C. R. Acad. Sci. Paris*, **131**, 139.

SAMSONOV, G. V. & LATYSCHEVA, V. P. (1955). *Doklady Akad. Nauk. SSSR.* **105**, 499.

STRAUMANIS, M. & IEVINS, A. (1940). Die Präzisions-bestimmung von Gitterkonstanten nach der asymmetrischen Methode. Julius Springer, Berlin (reprinted

by Edwards Brothers, Inc. Ann Arbor, Michigan, 1948).
VAN BERGEN, H. (1941). Ann. Phys. 39, 553.
ZHURAVLEV, N. N. (1956). Kristallografiya, 1, 666.

On the crystallography of calclacite, Ca(CH₃COO)Cl.5 H₂O.

On the crystallography of calclacite, Ca(CH_3COO)Cl.5 H_2O. By R. VAN TASSEL, *Institut royal des Sciences naturelles de Belgique, Brussels, Belgium*

The mineral name calclacite has been given, by the author, to a silky, acicular efflorescence, occurring on fossils and limestones in wooden museum cases. The chemical composition corresponds to Ca(CH_3COO)Cl.5 H_2O. The needles show a thickness of only 0·03–0·16 mm. and occasionally reach 4 cm. in length. The substance has also been observed on pottery sherds (Frondel, 1951; Gettens, 1957).

The 'natural' efflorescence is, as shown by its X-ray diffraction powder pattern, identical with the synthetic monoclinic calcium acetate chloride pentahydrate, described by Handl (1861) and Rammelsberg (1882), but is crystallographically different from the salt of same composition, previously prepared and examined by the author. Identity between the former substances was established by comparison with material from a large (4½ g.), {010} flattened crystal, labelled 'essigsaurer Kalk–Chlorcalcium', prepared, before 1880, by von Foullon in von Hauer's laboratory, Vienna. The availability of well developed synthetic calclacite crystals, 2 to 3 mm. long and 0·5 mm. thick, permitted further investigation. Miss E. West, Freer Gallery of Art, Washington, prepared them starting from an equimolecular solution of $CaCl_2$ and Ca(CH_3COO)₂ evaporated at room temperature.

Optical goniometer measurements revealed the forms {001}, {110}, {120}, {130}, {010} and {210}. The last form, observed on four faces, is new for the substance. For the obtuse angle β the value of 116° 42′ (mean of 5 measurements) was found, which is in good agreement with 116° 49′ (Handl, 1861) and 116° 59′ (Rammelsberg, 1882). The elongation direction lies along the c axis. The crystals usually show good (010) faces; the other prism faces are narrow and, as well as the top face, of rather poor quality for goniometer readings.

X-ray rotation photographs round the three crystal axes, using the morphological angle β for the a-axis, were taken. Weissenberg photographs were obtained with the elongation direction c as rotation axis, in normal-

beam setting for the zero layer and in equi-inclination setting for the first layer. The following absolute parameters were observed:

$$a = 11·51, \quad b = 13·72, \quad c = 6·82 \text{ Å}.$$

The monoclinic symmetry and the morphological angle β were confirmed. The ratio $a_0:b_0:c_0$ is 0·839:1:0·496, where $a_0:b_0$ is in good agreement with the values 0·8395 (Handl) and 0·856 (Rammelsberg). The Weissenberg photographs showed no restriction for the hkl reflections, but systematic absences were observed for h00 when h is odd and for 0k0 when k is odd; hence the space group is $P2_1/a$.

Density determinations were based on following specimens:

1) 'natural' efflorescence: > 1·48, < 1·59 g.cm.⁻³, measured by flotation (Van Tassel, 1945), 2) large crystal, prepared by von Foullon: 1·487 g.cm.⁻³, measured with hydrostatic balance, 3) crystals, prepared by E. West: 1·52 g.cm.⁻³, measured with Berman's precision torsion balance. The densities provided by the synthetic substances are to be considered as too small, as microscopic examination showed the presence of solution inclusions. The volume of the unit cell is 962 Å³. Using the experimental density of 1·52, it is found that the number of molecules in the cell is 3·9 (molecular weight Ca(CH_3COO)Cl.5 H_2O = 224·6). There are thus 4 molecules per unit cell, as required for the general position in $P2_1/a$. The calculated density is 1·55 g.cm.⁻³.

The powder data, obtained with a Debye–Scherrer camera of 5·73 cm. diameter and with filtered Fe-radiation, are given for identification purposes. The reflections satisfy the equation:

$$\sin^2 \theta_{Cu} = 0·005621h^2 + 0·003156k^2 + 0·01601l^2 - 0·008523hl.$$

The lines in Table 1 have been indexed on this basis. The optic axial plane is (100), with the c crystallo-

Table 1. *Powder lines*

d (Å)	I	hkl	d (Å)	I	hkl	d (Å)	I	hkl
8·27	s	110	3·00	w	222	2·04	m	510, 003, 052, 41$\bar{1}$
6·87	m	020	2·94	vw	012, 22$\bar{1}$	1·907	vw	360, 15$\bar{2}$
6·15	w	001, 111	2·65	w	23$\bar{1}$	1·876	vw	450, 530, 171, 601
4·86	vw	210, 121	2·43	s	340	1·842	w	270, 10$\bar{3}$
4·16	m	221, 220	2·30	m	060	1·704	w	460, 600
3·67	w	031	2·22	w	33$\bar{1}$	1·560	vw	470, 35$\bar{2}$
3·24	s	112, 212	2·14	w	113	1·486	w	024
3·06	w	002						

(Visually estimated intensities: s = strong; m = medium; w = weak; vw = very weak.)