

in Tables 1 and 2 are more than an order of magnitude lower than those previously quoted for Ca<sub>2</sub>IrO<sub>4</sub> and CaIrO<sub>3</sub>. We therefore believe the Ir—O bond length reported here to be more reliable than that determined in the earlier X-ray studies.

This work demonstrates that although absorption of neutrons is a significant problem when working with iridium compounds, the application of an absorption correction makes data refinement to a high standard possible.

We wish to thank SERC for financial support and Drs S. Hull and R. Smith, Rutherford–Appleton Laboratory, for advice and assistance.

#### References

- ATTFIELD, M. P., BATTLE, P. D., BOLLEN, S. K., KIM, S. H., POWELL, A. V. & WORKMAN, M. (1992). *J. Solid State Chem.* **96**, 344–359.
- BABEL, D., RUDORFF, W. & TSCHOPP, R. (1966). *Z. Anorg. Allg. Chem.* **347**, 282–288.
- BROWN, P. J. & MATTHEWMAN, J. C. (1987). Rutherford–Appleton Laboratory Report RAL-87-010.
- CHAMBERLAND, B. L. & PHILPOTTS, A. R. (1992). *J. Alloys Compd.* **82**, 355–363.
- DAVID, W. I. F., JOHNSON, M. W., KNOWLES, K. J., MORETON-SMITH, C. M., CROSBIE, G. D., CAMPBELL, E. P., GRAHAM, S. P. & LYALL, J. S. (1986). Rutherford–Appleton Laboratory Report RAL-86-102.
- FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
- HULL, S. & MAYERS, J. (1989). Rutherford–Appleton Laboratory Report RAL-89-118.
- RANDALL, J. J. & KATZ, L. (1959). *Acta Cryst.* **12**, 519–521.
- RANDALL, J. J. & WARD, R. (1959). *J. Am. Chem. Soc.* **81**, 2629–2631.
- RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.
- RODI, F. & BABEL, D. (1965). *Z. Anorg. Allg. Chem.* **336**, 17–23.
- SHANNON, R. D. & PREWITT, C. T. (1969). *Acta Cryst.* **B25**, 925–945.
- WILEY, J. B. & POEPELMEIER, K. R. (1991). *Mater. Res. Bull.* **26**, 1201–1210.

*Acta Cryst.* (1993). **C49**, 854–856

## Structure of a Synthetic Double-Layer Silicate, Rb<sub>2</sub>Cu<sub>2</sub>Si<sub>8</sub>O<sub>19</sub>

BY I. WATANABE AND A. KAWAHARA\*

*Department of Earth Sciences, Faculty of Science, Okayama University, Tsushima-Naka 1-1, Okayama 700, Japan*

(Received 30 January 1992; accepted 11 November 1992)

**Abstract.** Rb<sub>2</sub>Cu<sub>2</sub>Si<sub>8</sub>O<sub>19</sub>,  $M_r = 826.7$ , monoclinic,  $P2_1/m$ ,  $a = 11.450(2)$ ,  $b = 8.409(2)$ ,  $c = 9.847(1)$  Å,  $\beta = 95.28(1)^\circ$ ,  $V = 944.1(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.91$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 8.35$  mm<sup>-1</sup>,  $F(000) = 792$ ,  $T = 298$  K, final  $R = 0.045$  for 1411 independent reflections. The structure consists of staggered double sheets of SiO<sub>4</sub> tetrahedra. The sheets consist of six-membered rings. The doubling of sheets forms ten-membered rings viewed parallel to the  $c$  axis. These double sheets are linked by pairs of Cu atoms in four coordination sites. Rb atoms are located in the cavities of these ten-membered rings and have eight and ten nearest neighbours. The structure of this silicate is classified as Rb<sub>2</sub>Cu<sub>2</sub>{ $uB, 2_\infty$ }[<sup>4</sup>Si<sub>8</sub>O<sub>19</sub>] after the classification symbol of Liebau [*Structural Chemistry of Silicates* (1985), pp. 69–75, 121–126, 232, 250, 267. Berlin: Springer].

**Introduction.** This study was initiated with the purposes of exploring new phases of silicates and contri-

buting to the crystal chemistry of alkali copper silicates. Until now, two sodium copper silicates (Kawamura & Kawahara, 1976, 1977), a lithium copper silicate (Kawamura, Kawahara & Iiyama, 1978), a potassium copper silicate (Kawamura & Iiyama, 1981) and a caesium copper silicate (Heinrich & Gramlich, 1982) have been investigated. The hydrothermal synthesis of a series of rubidium copper silicates, Rb<sub>x</sub>Cu<sub>y</sub>Si<sub>p</sub>O<sub>q</sub>, was attempted and several new phases were obtained. The present paper reports the structure of one of the newly synthesized phases.

**Experimental.** Hydrothermal synthesis of the title compound was carried out with a test-tube-type apparatus (723–873 K, 700–2500 kg cm<sup>-2</sup>, 3 d) with reagent mixtures of CuSO<sub>4</sub>·5H<sub>2</sub>O, SiO<sub>2</sub> and Rb<sub>2</sub>CO<sub>3</sub>. Crystals of Rb<sub>2</sub>Cu<sub>2</sub>Si<sub>8</sub>O<sub>19</sub> were deep bluish and less than 0.1 mm in size. The size of the crystal is approximately proportional to the pressure value. The chemical composition of the product was determined by X-ray microprobe analysis. A crystal with dimensions 0.02 × 0.03 × 0.01 mm was used for

\* Author to whom correspondence should be addressed.

Table 1. Atomic positional parameters ( $\times 10^4$ ) and equivalent isotropic temperature factors with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ ( $\text{\AA}^2$ )
Cu	5185 (1)	4929 (2)	8499 (1)	1.31 (2)
Rb(1)	4422 (2)	7500	4740 (2)	3.02 (4)
Rb(2)	236 (1)	2500	8967 (1)	2.36 (3)
Si(1)	2839 (2)	689 (3)	6587 (2)	1.20 (6)
Si(2)	7414 (2)	4347 (3)	741 (2)	1.30 (6)
Si(3)	8890 (2)	663 (3)	5652 (2)	1.24 (5)
Si(4)	2236 (2)	626 (4)	1937 (2)	1.35 (6)
O(1)	7657 (10)	2500	1110 (10)	2.32 (27)
O(2)	5821 (5)	9729 (9)	3130 (6)	1.81 (16)
O(3)	6065 (5)	278 (9)	300 (6)	1.62 (16)
O(4)	7733 (6)	461 (8)	4640 (6)	1.56 (15)
O(5)	0	0	5000	3.00 (29)
O(6)	8787 (5)	9779 (9)	7086 (6)	1.95 (17)
O(7)	7882 (5)	9609 (8)	2075 (6)	1.51 (14)
O(8)	3464 (6)	5009 (11)	2476 (6)	2.41 (18)
O(9)	1760 (5)	5179 (10)	457 (5)	1.90 (16)
O(10)	927 (12)	7500	3994 (14)	4.11 (36)
O(11)	7438 (10)	7500	3906 (9)	1.93 (24)
O(12)	2142 (12)	2500	1619 (13)	3.79 (37)

data collection. The intensity data were collected on a Rigaku AFC-5R diffractometer with a generator operated by a rotating anode (40 kV, 200 mA) with graphite-monochromated Mo  $K\alpha$  radiation in the  $2\theta$ - $\omega$  scan mode. 3 standard reflections,  $\bar{1}2\bar{1}$ ,  $\bar{1}21$ ,  $\bar{1}\bar{1}2$ , were monitored every 150 reflections with a variation of 1.5%. 2434 reflections were collected up to  $2\theta = 60^\circ$  ( $0 \leq h \leq 16$ ,  $0 \leq k \leq 11$ ,  $-13 \leq l \leq 13$ ), of which 1411 were observed with  $I > 3\sigma(I)$ . Lorentz-polarization corrections were made but no absorption correction. The cell dimensions were refined from 25 reflections with  $27 < 2\theta < 44^\circ$ .

Preliminary film methods gave  $P2_1$  or  $P2_1/m$ . The existence of centres of symmetry was confirmed from Wilson statistics, so  $P2_1/m$  was obtained. The Cu atom was found from Patterson syntheses and the other atoms were located on the subsequent Fourier maps. Full-matrix least-squares refinement with anisotropic temperature factors, minimizing  $\sum w(\Delta F)^2$ , gave  $R = 0.045$ ,  $wR = 0.050$ ,  $w = 1/\sigma(F)^2$ ,  $S = 0.94$ , 149 parameters refined,  $(\Delta/\sigma)_{\text{max}} = 0.14$ ,  $(\Delta\rho)_{\text{max,min}} = 1.25, -1.02 \text{ e \AA}^{-3}$ .

Atomic scattering factors for neutral atoms were used throughout the calculations (from *International Tables for X-ray Crystallography*, 1974, Vol. IV). The final positional parameters and equivalent isotropic thermal factors are shown in Table 1.\* Calculations using the modified programs of UNICS (Sakurai, 1971) were carried out at the Data Processing Centre of Okayama University.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55777 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH1000]

**Discussion.** A stereographic figure using ORTEP (Johnson, 1965) of the structure of  $\text{Rb}_2\text{Cu}_2\text{Si}_8\text{O}_{19}$  is shown in Fig. 1. This is isostructural with  $\text{Cs}_2\text{Cu}_2\text{Si}_8\text{O}_{19}$  (Heinrich & Gramlich, 1982). The structure consists of staggered double sheets of  $\text{SiO}_4$  tetrahedra parallel to the *bc* plane. The sheets consist of six-membered rings. They are connected to each other through the apical O atoms of four  $\text{SiO}_4$  tetrahedra forming ten-membered rings parallel to the *ac* plane. The mode of linkage of the double sheets is illustrated in Fig. 2. The double sheets are interconnected by  $\text{Cu}_2\text{O}_6$  units. In these units, Cu atoms have square-planar coordinations with two squares sharing an edge.

The  $\text{SiO}_4$  double sheets can be expressed as  $\text{Rb}_2\text{Cu}_2\{uB_2\}_\infty\{^4\text{Si}_8\text{O}_{19}\}$  after the classification symbol of Liebau (1985). Here, the symbol *uB* stands for 'unbranched' and superscript 2 represents 'two-dimensional framework'. The superscript 4 on Si corresponds to the number of tetrahedra within one

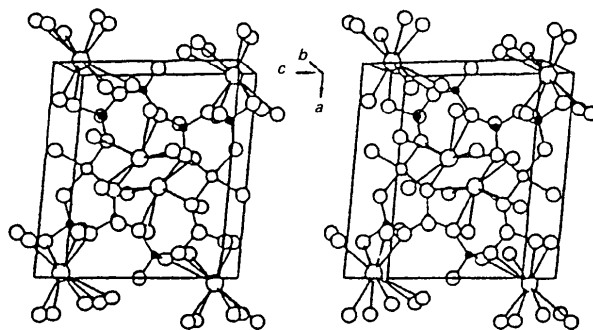


Fig. 1. Stereographic drawing of the structure of  $\text{Rb}_2\text{Cu}_2\text{Si}_8\text{O}_{19}$ . The figure represents the connection of one of the double sheets of  $\text{SiO}_4$  tetrahedra with Cu and Rb atoms. Here Si, Cu and Rb atoms correspond to small solid, small open and large open circles, respectively.

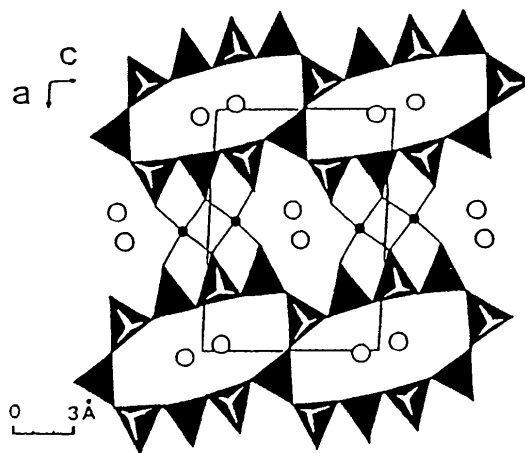


Fig. 2. Diagram showing the linkage of the ten-membered rings in double sheets. The large open circles and small solid ones correspond to Rb and Cu atoms, respectively.

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

Cu—O(2 <sup>i</sup> )	1.894 (6)	Si(3)—O(10 <sup>h</sup> )	1.593 (4)
Cu—O(3 <sup>v</sup> )	1.961 (6)	Si(4)—O(6 <sup>vi</sup> )	1.619 (7)
Cu—O(3 <sup>iii</sup> )	1.965 (5)	Si(4)—O(8 <sup>iii</sup> )	1.551 (7)
Cu—O(8 <sup>iii</sup> )	1.895 (7)	Si(4)—O(9 <sup>iii</sup> )	1.653 (6)
Si(1)—O(2 <sup>iii</sup> )	1.574 (6)	Si(4)—O(12)	1.608 (4)
Si(1)—O(4 <sup>iii</sup> )	1.637 (7)	Rb(1)—O(2) × 2 <sup>i</sup>	3.010 (7)
Si(1)—O(7 <sup>iii</sup> )	1.637 (7)	Rb(1)—O(2) × 2 <sup>iv,ix</sup>	3.164 (7)
Si(1)—O(11 <sup>v</sup> )	1.621 (4)	Rb(1)—O(4) × 2 <sup>v,iii</sup>	3.111 (7)
Si(2)—O(1)	1.613 (3)	Rb(1)—O(8) × 2 <sup>ix</sup>	3.180 (7)
Si(2)—O(3 <sup>iii</sup> )	1.597 (6)	Rb(2)—O(6) × 2 <sup>vi,vii</sup>	3.294 (7)
Si(2)—O(7 <sup>ix</sup> )	1.629 (6)	Rb(2)—O(7) × 2 <sup>iii</sup>	3.041 (7)
Si(2)—O(9 <sup>iv</sup> )	1.628 (6)	Rb(2)—O(9) × 2 <sup>x,xi</sup>	3.131 (7)
Si(3)—O(4)	1.592 (6)	Rb(2)—O(9) × 2 <sup>ii,viii</sup>	3.097 (7)
Si(3)—O(5 <sup>iv</sup> )	1.577 (3)	Rb(2)—O(10 <sup>iv</sup> )	3.092 (13)
Si(3)—O(6 <sup>vi</sup> )	1.610 (7)	Rb(2)—O(12 <sup>v</sup> )	3.246 (13)
O(2 <sup>i</sup> )—Cu—O(3 <sup>v</sup> )	95.9 (2)	O(3 <sup>iii</sup> )—Si(2)—O(9 <sup>iv</sup> )	111.5 (3)
O(2 <sup>i</sup> )—Cu—O(8 <sup>iii</sup> )	92.0 (3)	O(7 <sup>ix</sup> )—Si(2)—O(9 <sup>iv</sup> )	106.4 (4)
O(3 <sup>iii</sup> )—Cu—O(3 <sup>v</sup> )	79.1 (2)	O(4)—Si(3)—O(5 <sup>iv</sup> )	111.3 (3)
O(3 <sup>iii</sup> )—Cu—O(8 <sup>iii</sup> )	94.9 (3)	O(4)—Si(3)—O(6 <sup>vi</sup> )	112.1 (4)
O(2 <sup>iii</sup> )—Si(1)—O(4 <sup>iii</sup> )	108.4 (4)	O(4)—Si(3)—O(10 <sup>h</sup> )	109.0 (5)
O(2 <sup>iii</sup> )—Si(1)—O(7 <sup>iii</sup> )	112.3 (3)	O(5 <sup>iv</sup> )—Si(3)—O(6 <sup>vi</sup> )	108.7 (3)
O(2 <sup>iii</sup> )—Si(1)—O(11 <sup>v</sup> )	115.1 (5)	O(5 <sup>iv</sup> )—Si(3)—O(10 <sup>h</sup> )	109.7 (5)
O(4 <sup>iii</sup> )—Si(1)—O(7 <sup>iii</sup> )	107.8 (3)	O(6 <sup>vi</sup> )—Si(3)—O(10 <sup>h</sup> )	105.9 (6)
O(4 <sup>iii</sup> )—Si(1)—O(11 <sup>v</sup> )	106.3 (4)	O(6 <sup>iii</sup> )—Si(4)—O(8 <sup>iii</sup> )	114.0 (4)
O(7 <sup>iii</sup> )—Si(1)—O(11 <sup>v</sup> )	106.6 (4)	O(6 <sup>iii</sup> )—Si(4)—O(9 <sup>iii</sup> )	103.9 (3)
O(1)—Si(2)—O(3 <sup>iii</sup> )	113.2 (5)	O(6 <sup>iii</sup> )—Si(4)—O(12)	106.4 (6)
O(1)—Si(2)—O(7 <sup>ix</sup> )	107.5 (4)	O(8 <sup>iii</sup> )—Si(4)—O(9 <sup>iii</sup> )	112.1 (4)
O(1)—Si(2)—O(9 <sup>iv</sup> )	107.4 (5)	O(8 <sup>iii</sup> )—Si(4)—O(12)	116.5 (6)
O(3 <sup>iii</sup> )—Si(2)—O(7 <sup>ix</sup> )	110.6 (4)	O(9 <sup>iii</sup> )—Si(4)—O(12)	102.6 (5)

Symmetry code: (i)  $1-x, -\frac{1}{2}+y, 1-z$ ; (ii)  $x, \frac{1}{2}-y, 1+z$ ; (iii)  $1-x, 1-y, 1-z$ ; (iv)  $1-x, 2-y, 1-z$ ; (v)  $1-x, \frac{1}{2}+y, 1-z$ ; (vi)  $-1+x, -1+y, z$ ; (vii)  $-1+x, \frac{1}{2}-y, z$ ; (viii)  $-x, 1-y, 1-z$ ; (ix)  $x, \frac{1}{2}-y, z$ ; (x)  $x, y, 1+z$ ; (xi)  $-x, -\frac{1}{2}+y, 1-z$ ; (xii)  $1-x, -y, 1-z$ ; (xiii)  $x, \frac{1}{2}-y, z$ ; (xiv)  $1+x, y, z$ ; (xv)  $1-x, 1-y, -z$ ; (xvi)  $x, -1+y, z$ .

repeating unit along the shortest period of the cell. CuO<sub>4</sub> squares share corners with SiO<sub>4</sub> tetrahedra. Two kinds of Rb atom site have eight and ten nearest O-atom neighbours, respectively, and are located in the cavity of the six-membered rings.

The interatomic distances and bond angles are listed in Table 2. Si—O and Cu—O distances agree with previous data (Kawamura & Kawahara, 1976;

1977; Kawamura, Kawahara & Iiyama, 1978; Kawamura & Iiyama, 1981; Heinrich & Gramlich, 1982). In the SiO<sub>4</sub> double sheets, the bridging Si—O distance to other Si atoms (mean 1.626 Å) is significantly longer than those to Cu and Rb atoms (mean 1.578 Å). The average Si—O distances for the four SiO<sub>4</sub> tetrahedra are 1.617, 1.617, 1.593 and 1.608 Å, and the distortion indices,  $[d(M—O)_{\max} - d(M—O)_{\min}]/d(M—O)$ , of SiO<sub>4</sub> tetrahedra (Liebau, 1985) are  $3.92 \times 10^{-2}$ ,  $1.98 \times 10^{-2}$ ,  $2.02 \times 10^{-2}$  and  $6.34 \times 10^{-2}$ , respectively. The bonding of SiO<sub>4</sub> tetrahedra and CuO<sub>4</sub> squares is directional and rigid compared with Rb—O polyhedra, which are irregular in shape and have ionic character. Accordingly, the latter are considered to compensate for all the strains resulting from the framework constructed by these rigid and rather covalent *sp*<sup>3</sup> tetrahedra of SiO<sub>4</sub> and the *dsp*<sup>2</sup> planar CuO<sub>4</sub> squares. Here the alkali metals may play an important role in the stabilization of the structure. In fact, the number of phases containing  $A_x\text{Cu}_y\text{Si}_p\text{O}_q$  ( $A$  = alkali metal) is much larger than that containing only  $\text{Cu}_x\text{Si}_p\text{O}_q$ .

## References

- HEINRICH, A. & GRAMLICH, V. (1982). *Naturwissenschaften*, **69**, 142–143.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 KAWAMURA, K. & IYAMA, J. T. (1981). *Bull. Miner.* **104**, 387–395.  
 KAWAMURA, K. & KAWAHARA, A. (1976). *Acta Cryst.* **B32**, 2419–2422.  
 KAWAMURA, K. & KAWAHARA, A. (1977). *Acta Cryst.* **B33**, 1071–1075.  
 KAWAMURA, K., KAWAHARA, A. & IYAMA, J. T. (1978). *Acta Cryst.* **B34**, 3181–3185.  
 LIEBAU, F. (1985). *Structural Chemistry of Silicates*, pp. 69–75, 121–126, 232, 250, 267. Berlin: Springer.  
 SAKURAI, T. (1971). Editor. *The Universal Crystallographic Computation Program System*. Tokyo: The Crystallographic Society of Japan.

*Acta Cryst.* (1993). **C49**, 856–861

## Structure of Potassium Paradodecatungstate 7½-Hydrate

BY HOWARD T. EVANS JR

*US Geological Survey, Reston, Virginia 22092, USA*

AND ULI KORTZ AND GEOFFREY B. JAMESON

*Department of Chemistry, Georgetown University, Washington, DC 20057, USA*

(Received 26 September 1991; accepted 16 November 1992)

**Abstract.** K<sub>10</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>42</sub>].7½H<sub>2</sub>O,  $M_r = 3406.3$ , triclinic,  $P\bar{1}$ ,  $a = 13.126$  (2),  $b = 16.274$  (7),  $c = 11.756$  (4) Å,  $\alpha = 96.77$  (2),  $\beta = 90.04$  (2),  $\gamma =$

$77.77$  (2)°,  $V = 2436.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 4.645$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 280.5$  cm<sup>-1</sup>,  $F(000) = 2982$ ,  $T = 296$  K,  $R = 0.051$ ,  $wR = 0.067$  and  $S =$