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The Crystal Structure of Synthetic Copper Sodium Silicate: $\text{Cu}_3\text{Na}_2(\text{Si}_4\text{O}_{12})$

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The crystal structure of synthetic copper sodium silicate, $\text{Cu}_3\text{Na}_2(\text{Si}_4\text{O}_{12})$, *Pnma*, $a=7.519(4)$, $b=10.203(5)$, $c=13.567(8)$ Å, $Z=4$, has been determined with three-dimensional counter-measured intensities. The structure was deduced from Patterson syntheses and refined by both diagonal and full-matrix least-squares methods to $R=0.053$ for 1141 observed reflexions. The structure consists of bent Si–O chains, like those of haradaite [$\text{Sr}_2\text{V}_2\text{O}_7(\text{Si}_4\text{O}_{12})$] and batisite [$\text{Na}_2\text{BaTi}_2\text{O}_7(\text{Si}_4\text{O}_{12})$], linked by three kinds of Cu and two kinds of Na atoms. The Cu atoms have four nearest neighbours of O atoms. The coordination polyhedra of Na atoms are irregular in shape, with six nearest neighbours of O atoms. The bond lengths and angles about Si and Cu agree reasonably well with those of other structures.

Introduction

It is important from the viewpoint of coordination of divalent copper ions to investigate the crystal structure of copper silicates. But since the natural specimens are polycrystalline and very small in size, it is difficult to study them by the X-ray single-crystal method. Accordingly, synthesis of these minerals became important. As for the synthesis of copper silicates, Tarte (1964) attempted to synthesize the hydrated copper silicate minerals such as shattuckite [$\text{Cu}_5\text{Si}_4\text{O}_{12}(\text{OH})_2$], plancheite [$\text{Cu}_7\text{Si}_8\text{O}_{22}(\text{OH}) \cdot 2-3\text{H}_2\text{O}$], diopside ($\text{Cu}_6\text{Si}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$) and chrysocolla [$\text{Cu}_8\text{Si}_8\text{O}_{20}(\text{OH})_{12} \cdot n\text{H}_2\text{O}$]. He reported that these minerals could not be synthesized and that only chrysocolla was obtained. Recently, Kawamura, Kawahara &

Henmi (1976) succeeded in synthesizing both plancheite and shattuckite, and also obtained two new phases, both of which are anhydrous copper sodium silicates. These new phases have been found neither as natural minerals nor as synthetic products. The present paper reports the crystal structure of one of the new phases obtained.

Throughout the investigation, calculations were carried out at the Computer Center of Okayama University and also at the Computer Center of the University of Tokyo.

Experimental

Hydrothermal syntheses were carried out with the apparatus made by Kitahama Manufacturing Company, Osaka. This apparatus is of the test-tube type,

Table 1. *The conditions in the hydrothermal runs*

Starting materials	Temperature (°C)	Pressure (kg cm ⁻²)	Period (d)	By-products
CuSO ₄ + SiO ₂ + 2Na ₂ CO ₃	500	1000	8	CuO
	600	1100	7	Phase 2,* CuO, Cu ₂ O
CuO + SiO ₂ + 2Na ₂ CO ₃	600	1100	7	CuO, Cu ₂ O
	500	1000	7	

* Phase 2: $\text{CuO} \cdot \text{Na}_2\text{O} \cdot 4\text{SiO}_2$.

and the starting materials were shielded in a silver tube. Plancheite and shattuckite are hydrous silicate minerals containing only divalent Cu atoms. No reactions forming such minerals could be recognized under the conditions of pure oxide starting materials and temperature, pressure and duration of 500°C, 1000 kg cm⁻² and 7d respectively. Therefore, hydrothermal runs for the system CuSO₄-SiO₂-Na₂CO₃-H₂O were carried out, adding mineralizers to pure oxide compositions. At 350 and 400°C (both 1000 kg cm⁻², about 7d), plancheite and shattuckite were synthesized. At higher temperatures (500 and 600°C, 1000 kg cm⁻², 7d), no natural copper silicates could be synthesized; instead, two new phases were obtained in the same experiments. One of these new phases is tentatively called phase 1, and its chemical composition has been determined as 3CuO·Na₂O·4SiO₂ from EPMA analyses. This composition is consistent with the results of the crystal structure analysis as will be shown in the following paragraphs. Crystals thus obtained have a bluish colour and a rounded or columnar shape about 0.1–0.6 mm in size. The conditions in the hydrothermal runs to obtain this material, phase 1, are shown in Table 1.

The lattice constants and extinction rules were estimated by the precession method. The intensities of the reflexions were measured on an automated four-circle diffractometer using the 2θ-ω scan technique and Mo Kα radiation (λ=0.71069 Å) with a graphite monochromator. A crystal with approximate dimensions of 0.1×0.07×0.05 mm was mounted with the *a* axis approximately parallel to the φ axis of the diffractometer. Of a total of 1491 intensities measured up to 2θ=56°, 1141 were classified as observed with *I*>3σ above background. The integrated intensities were converted to structure factors by applying the Lorentz-polarization correction. No absorption corrections were made, because of the minute crystal size. The chemical formula and other crystal data, such as unit cell dimensions and their standard deviations measured by the same diffractometer, are shown in Table 2.

Table 2. Crystal data of synthetic copper sodium silicate

Chemical formula	Cu ₃ Na ₂ (Si ₄ O ₁₂) with Z=4
Space group	<i>Pnma</i>
Lattice dimensions	<i>a</i> = 7.519 (4) Å <i>b</i> = 10.203 (5) <i>c</i> = 13.567 (8)
Density	<i>D_m</i> = 3.50, <i>D_x</i> = 3.45 g cm ⁻³
Linear absorption coefficient	μ = 69.11 cm ⁻¹ (for Mo Kα)

The powder diffraction data were collected (λ=1.5418 Å) on a Rigaku powder diffractometer. The specimen was mixed with a small amount of metal silicon powder as internal standard. The peaks of the specimen were corrected by these silicon peaks. These data are shown in Table 3.

Table 3. The powder diffraction data

<i>D_{obs}</i>	<i>I</i> / <i>I</i> ₁ × 100	<i>hkl</i>	<i>D_{calc}</i>
8.15	35	011	8.1543
5.10	37	002	5.1015
4.08	23	022	4.0772
3.90	16	112	4.0309
3.77	86	200	3.7590
3.422	22	211	3.4142
3.306	100	013	3.2929
		220	3.2884
3.093	41	103	3.0988
		132	3.0859
3.023	14	202	3.0265
		113	3.0210
2.871	25	230	2.8911
2.770	19	231	2.7815
		222	2.7639
2.732	16	033	2.7181
2.648	37	142	2.6441
2.555	29	133	2.5562
		004	2.5508
2.525	16	203	2.5219
2.4694	37	151	2.4796
		241	2.4405
2.3235	13	223	2.3640
		321	2.2910
2.2629	25	060	2.2612
2.1371	17	322	1.2352
2.1241	14	053	2.1210
2.0425	25	153	2.0414
1.9701	17	341	1.9775
		144	1.9676
1.8849	23	125	1.8913
		400	1.8796

Structure determination and refinement

Diffraction symmetry and systematic absences show that the space group of this substance, phase 1, is either *Pnma* or *Pn2₁a*. The structure determination was attempted in *Pnma* because the morphological symmetry of the crystals appeared centrosymmetric. Three-dimensional Patterson syntheses were made and the positions of three kinds of Cu atoms were

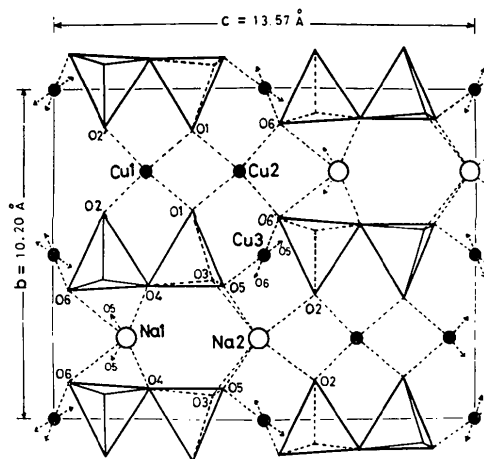


Fig. 1. Projection of the structure parallel to *a* showing that the silicate chains are connected to each other via the coordination polyhedra of Cu and Na atoms.

found in the map. The positions of the Si atoms were found from $(F_o - F_c)$ Fourier maps with the phases given by these Cu atoms. The parameters of all the atoms determined by both Patterson and difference Fourier methods were refined to $R=0.066$ with a diagonal least-squares program. In order to refine the atomic coordinates and the isotropic temperature factors more thoroughly, five cycles of full-matrix least-squares calculation were carried out; the value

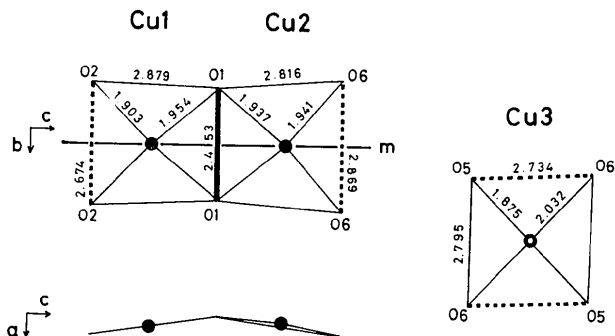


Fig. 2. Coordination squares of Cu(1), Cu(2) and Cu(3) in the structure. For the edges of the squares, a bold line represents the edges shared with only the coordination polyhedra of Cu atoms, and dashed bold lines represent the edges shared with those of both Cu and Na atoms.

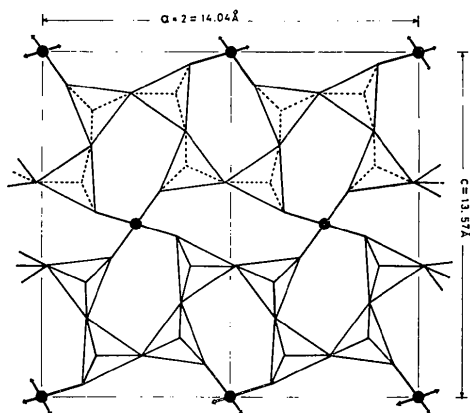


Fig. 3. View of the silicate chains in the crystal projected parallel to b .

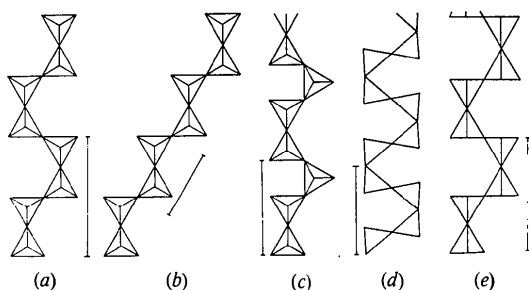


Fig. 4. Schematically shown silicate chains of (a) $\text{Cu}_3\text{Na}_2(\text{Si}_4\text{O}_{12})$, (b) pyroxenes, (c) wollastonite, (d) haradaite and (e) batisite. The repeat units of each structure are represented by the straight lines.

Table 4. Final positional parameters ($\times 10^4$) and temperature factors (\AA^2) with standard deviations in parentheses

	x	y	z	B
Cu(1)	2629 (2)	2500 (0)	2186 (1)	0.41 (4)
Cu(2)	2500 (0)	2500 (0)	4397 (1)	0.36 (4)
Cu(3)	0 (0)	0 (0)	0 (0)	0.37 (4)
Si(1)	2218 (3)	5281 (2)	3378 (2)	0.33 (5)
Si(2)	3200 (3)	5350 (2)	1233 (2)	0.31 (5)
Na(1)	319 (7)	7500 (0)	1737 (4)	1.38 (29)
Na(2)	1872 (6)	7500 (0)	4872 (4)	1.03 (25)
O(1)	2336 (7)	3702 (5)	3296 (4)	0.66 (16)
O(2)	2898 (7)	3811 (6)	1200 (4)	0.87 (18)
O(3)	291 (7)	5761 (5)	3804 (4)	0.79 (17)
O(4)	2391 (7)	5298 (5)	2277 (4)	0.59 (14)
O(5)	3715 (7)	5928 (5)	4043 (4)	0.52 (14)
O(6)	2171 (7)	6094 (5)	344 (4)	0.61 (15)

of R was reduced to 0.053. The final atomic parameters and isotropic temperature factors thus obtained are shown in Table 4.*

Description of the structure and discussion

The structure of phase 1, $\text{Cu}_3\text{Na}_2(\text{Si}_4\text{O}_{12})$, is shown in Fig. 1. As shown in the figure, there are three kinds of Cu atoms in special positions, Cu(1), Cu(2) and Cu(3) respectively. Cu(1) and Cu(2) are located on a mirror plane, with Cu(3) at an inversion centre, each having four near O atoms. Cu(3) has, however, two additional O atoms, O(2), at a longer distance of 2.98 Å. The four nearest O atoms about each Cu atom form a slightly distorted square, which is in accord with the dsp^2 hybrid orbital model (Fig. 2). The Cu-O distances range from 1.87 to 2.03 Å. As shown in Fig. 2, Cu(1) and Cu(3) are exactly on the planes of the squares through the O atoms, while Cu(2) lies at a slightly distorted position. Cu(1) and Cu(2) coordination squares share an edge, and the shared edge [O(1)-O(1): 2.453 Å] is much shorter than other unshared edges (mean 2.798 Å), suggesting that the structure has been stabilized in the way expected from the extended Pauling third rule (Kamb, 1968).

Each of Na(1) and Na(2) has six nearest neighbours of O atoms. The distances range from 2.25 to 2.75 Å. The coordination polyhedra of Na atoms are irregular in shape; they share edges with the nearest neighbour coordination squares, and also with silicon-oxygen tetrahedra.

Si(1) and Si(2) are situated among these Cu and Na coordination polyhedra and their coordination tetrahedra form the chain configuration shown in Figs. 1 and 3. Si-O distances are in the range 1.587-1.651 Å (Table 5). In the silicate chains the lengths of Si-O bridging bonds are significantly greater than

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31740 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

those of non-bridging bonds (Table 5), the mean values being 1.638 and 1.604 Å respectively. These results are, as for other silicates, consistent with the $d-\pi$ -bond model for silicates (Cruickshank, 1961). Fig. 1 is the projection parallel to a , in which the Si-O tetrahedra have been schematically drawn from paper models in order to show the configuration of the tetrahedra clearly.

Table 5. Bond lengths and angles

Si polyhedra			
Si(1)-O(1)	1.618 (6) Å	O(3)-O(6)	2.637 (8) Å
-O(3)	1.635 (6)	O(4)-O(6)	2.633 (8)
-O(4)	1.638 (5)	O(1)-Si(1)-O(3)	111.8 (3)°
-O(5)	1.587 (6)	-O(4)	109.5 (3)
Si(2)-O(2)	1.587 (6)	-O(5)	114.5 (3)
-O(3)	1.628 (6)	O(3)-	-O(4)
-O(4)	1.651 (5)	-O(5)	105.8 (3)
-O(6)	1.622 (6)	O(4)-	-O(5)
O(1)-O(3)	2.693 (8)	O(2)-Si(2)-O(3)	113.1 (3)
-O(4)	2.659 (8)	-O(4)	109.0 (3)
-O(5)	2.694 (8)	-O(6)	112.0 (3)
O(3)-O(4)	2.611 (7)	O(3)-	-O(4)
-O(5)	2.600 (8)	-O(6)	106.9 (3)
O(4)-O(5)	2.585 (8)	O(4)-	-O(6)
O(2)-O(3)	2.683 (8)	-O(6)	107.1 (3)
-O(4)	2.636 (8)	Si-O-Si bridging angles	
-O(6)	2.660 (8)	Si(1)-O(3)-Si(2)	140.1 (4)°
O(3)-O(4)	2.633 (8)	-O(4)-	131.9 (3)
Cu polyhedra			
Cu(1)-O(1)	1.954 (5) Å	O(6)-O(6)	2.869 (8) Å
-O(2)	1.903 (6)	O(5)-O(6)	1.795 (8)
Cu(2)-O(1)	1.937 (5)	O(5)-O(6)	2.734 (8)
-O(6)	1.941 (5)	O(1)-Cu(1)-O(1)	97.2 (2)°
Cu(3)-O(5)	1.875 (5)	O(1)-	-O(2)
-O(6)	2.032 (6)	O(2)-	-O(2)
-O(2)	2.978 (6)	O(1)-Cu(2)-O(1)	78.6 (2)
O(1)-O(1)	2.453 (8)	O(1)-	-O(6)
-O(2)	2.877 (8)	O(6)-	-O(6)
O(2)-O(2)	2.674 (8)	O(5)-Cu(3)-O(6)	91.3 (2)
O(1)-O(6)	2.811 (8)	O(5)-	-O(6)
Bond lengths about Na			
Na(1)-O(4)	2.353 (6) Å	Na(2)-O(2)	2.250 (7) Å
-O(5)	2.269 (6)	-O(3)	2.581 (6)
-O(6)	2.751 (7)	-O(6)	2.400 (6)

Four Si-O tetrahedra form one period of bent chains parallel to a . All pyroxene and pyroxenoid structures contain sheets of quasi-closest packed O atoms and sheets of approximately octahedrally coordinated cations (*e.g.* Ca, Mn, Mg) alternating with sheets of tetrahedrally coordinated silicon atoms between sheets of O atoms (Prewitt & Peacor, 1964).

In the structure of $\text{Cu}_3\text{Na}_2(\text{Si}_4\text{O}_{12})$, however, such quasi-closest packed arrays of O atoms are not observed; the difference may be ascribed to the presence of plane coordinations about Cu in the present structure. The structure of this substance is, therefore, similar to those of haradaite $[\text{Sr}_2\text{V}_2\text{O}_2(\text{SiO}_3)_4]$ (Takéuchi & Joswig, 1967) and batisite $[\text{Na}_2\text{BaTi}_2\text{O}_2(\text{SiO}_3)_4]$ (Nikitin & Belov, 1962) in the configuration of the chains of Si-O tetrahedra, while these substances differ from each other in the orientation of individual tetrahedra. These features of the arrangement of Si-O tetrahedra, together with those of pyroxenes and wollastonite, are compared schematically in Fig. 4. The structures of $\text{Cu}_3\text{Na}_2(\text{Si}_4\text{O}_{12})$, haradaite and batisite contain cations other than Si in the layers of silicate chains. In this respect also, these substances differ remarkably from pyroxenes and pyroxenoids such as wollastonite, rhodonite and pyroxmangite.

The valence of the electrostatic charges calculated with the method of Brown & Shannon (1973) is satisfactory. The sum of electrostatic charges reaching each O atom ranges from 1.96 to 2.14 v.u.

The bond distances and angles calculated are shown in Table 5.

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