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The Crystal Structure of Synthetic Copper Sodium Silicate: $\text{CuNa}_2\text{Si}_4\text{O}_{10}$

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The crystal structure of synthetic copper sodium silicate, $\text{CuNa}_2\text{Si}_4\text{O}_{10}$, $P\bar{1}$, $a = 10.613(5)$, $b = 7.850(4)$, $c = 6.944(3)$ Å, $\alpha = 118.20(3)$, $\beta = 116.53(3)$, $\gamma = 93.65(3)^\circ$, $Z = 2$, has been determined from three-dimensional counter-measured intensities by the symbolic addition method, and refined by full-matrix least-squares methods to $R = 0.042$ for 1741 observed reflexions with anisotropic temperature factors. It is isostructural with litidionite ($\text{CuNaKSi}_4\text{O}_{10}$) and fenaksite ($\text{FeNaKSi}_4\text{O}_{10}$), and consists of Si–O pipe-like channels, $(\text{Si}_8\text{O}_{20})^{8-}$, which are linked by the Cu and one of the two independent Na atoms. The pipe itself contains the other Na atom. The Cu atoms have four nearest O neighbours in the form of a square and one additional O atom. The Na atoms, both inside and outside the pipes, have seven nearest O neighbours which form irregular polyhedra. Because of the difference in ionic sizes of Na and K, the average Cu–O and Na–O distances in $\text{CuNa}_2\text{Si}_4\text{O}_{10}$ are shorter than those in litidionite, and the difference between the average bridging and non-bridging Si–O distances is greater. This material shows characteristic twinning, which is not observed in synthetic litidionite. The frequent occurrence of twins, in comparison with litidionite, is considered to be due to the increased flexibility of the Si–O pipes caused by the replacement of K by Na in the pipes.

Introduction

Studies on the crystal structure of copper silicates are important from the viewpoint of the coordination behaviour of divalent copper ions intercalated in Si–O tetrahedra. Since, however, the natural specimens are polycrystalline and very small, the synthesis of single crystals is of substantial importance. When Kawamura, Kawahara & Henmi (1976) first succeeded in synthesizing plancheite and shattuckite, they obtained two new phases of anhydrous copper sodium silicate. These new phases have been found neither as natural minerals nor as synthetic products. The structure of the one of the phases, phase 1 ($\text{Cu}_3\text{Na}_2\text{Si}_4\text{O}_{12}$), was reported as a chain silicate (Kawamura & Kawahara, 1976).

The present paper reports the crystal structure of the second of the two new phases, phase 2 ($\text{CuNa}_2\text{Si}_4\text{O}_{10}$), which has been obtained by hydrothermal syntheses.

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

Experimental

The conditions in the hydrothermal runs and the results are shown in Table 1. The composition of phase 2 is determined as $\text{CuNa}_2\text{Si}_4\text{O}_{10}$ from chemical analyses (Kawamura *et al.*, 1976). Crystals thus obtained have a greenish pale-blue colour and are elongated or platy, about 0.01–1 mm in size. In addition, plancheite and shattuckite were synthesized at 350–400°C and litidionite ($\text{CuNaKSi}_4\text{O}_{10}$) was synthesized under approximately the same conditions as for phase 2, KNaCO_3 being used instead of Na_2CO_3 .

The lattice dimensions and systematic absences were estimated from precession photographs. Three-dimensional intensity data were obtained from a fragment of the specimen, 0.01 × 0.02 × 0.04 mm, on an automated four-circle diffractometer with the 2θ – ω scan technique, Mo $K\alpha$ radiation ($\lambda = 0.70926$ Å) and a graphite monochromator. 2218 intensities were collected up to $2\theta = 56^\circ$; of these, 1741 with $I > 3\sigma$ above background were classified as observed. The measured intensities were converted to structure factors

Table 1. *The conditions in the hydrothermal syntheses*

Starting materials	Temperature (°C)	Pressure (kg cm ⁻²)	Period (d)	By-product
CuSO ₄ + 4SiO ₂ + 4Na ₂ CO ₃	500	1000	3	—
CuSO ₄ + SiO ₂ + 2NaCO ₃	600	1100	7	Phase 1, CuO Cu ₂ O

Phase 1: Cu₃Na₂(Si₄O₁₂).Table 2. *Crystal data for synthetic copper sodium silicate*Chemical formula: CuNa₂Si₄O₁₀Space group: *P* $\bar{1}$ *a* = 10.613 (5) Å*b* = 7.850 (4)*c* = 6.944 (3)*D_m* = 2.90, *D_x* = 2.97 g cm⁻³Linear absorption coefficient: $\mu = 33.5 \text{ cm}^{-1}$ (for Mo K α) $\alpha = 118.20 (3)^\circ$ $\beta = 116.53 (3)$ $\gamma = 93.65 (3)$

The powder diffraction data were collected ($\lambda = 1.5418 \text{ \AA}$) on a Rigaku powder diffractometer. The specimen was mixed with a small amount of metal Si powder as internal standard. The specimen peaks were corrected with reference to the Si peaks. These data are shown in Table 3 with those of litidionite (Pozas, Rossi & Tazzoli, 1975). These two data sets resemble one another in the indices of the strong lines, while for the weak lines observed indices and intensities differ.

Table 3. *X-ray powder data for phase 2 (CuNa₂Si₄O₁₀) and litidionite*

Phase 2: CuNa ₂ Si ₄ O ₁₀ *				Litidionite†			
<i>d</i> _{obs}	<i>I</i>	<i>hkl</i>	<i>d</i> _{calc}	<i>d</i> _{obs}	<i>I</i>	<i>hkl</i>	<i>d</i> _{calc}
6.48	65	110	6.48	6.75	35	110	6.76
6.40	7	010	6.41				
4.546	7	210	4.542	4.485	12	200	4.483
4.467	18	110	4.466	4.046	15	111	4.048
3.902	17	111	3.903	3.652	18	211	3.664
3.459	42	120	3.459				
3.341	13	112	3.378				
3.244	100	{220}	3.242	3.372	100	220	3.379
		{221}	3.240	3.223	75	210	3.226
3.210	33	020	3.205	3.046	10	{111}	3.033
3.152	41	{102}	3.144			{002}	3.020
		{210}	3.144			{311}	2.977
2.976	7	300	2.967	2.976	13	{212}	2.976
2.756	6	320	2.754			{202}	2.973
2.714	11	{311}	2.715	2.835	18	120	2.840
		{120}	2.709	2.675	37	311	2.673
2.644	6	321	2.639	2.567	13	302	2.563
2.574	6	221	2.574	2.460	7	032	2.457
2.406	6	410	2.400	2.409	85	230	2.413
2.293	61	{113}	2.293	1.980	10	122	1.982
		{230}	2.292	1.924	10	042	1.920
2.140	6	{421}	2.146	1.916	10	510	1.916
		{030}	2.137				
1.785	6	403	1.784	1.817	5	342	1.810
1.671	5	{214}	1.683	1.789	15	500	1.793
		{034}	1.667				
1.605	5	040	1.603				

* The unit-cell parameters have been converted so that the indices correspond to those of litidionite.

† Pozas *et al.* (1975).

by applying the Lorentz-polarization corrections. No absorption corrections were made because of the small crystal size. The crystal data are shown in Table 2.

Structure analysis

The symbolic addition method was used for the determination of the positional parameters. The 199 reflexions with $E \geq 1.50$ were selected from the 1741 non-zero reflexions with the program *SIGMA II* (Ashida, 1973). Next, 46 E values were given symbols with four variables, and 16 possible sets of signs were refined by the tangent formula program (Ashida, 1973). One of the 16 sets gave $R(\text{Karle}) = 0.336$. The E map based on this set revealed the positions of all the Cu, Si and Na atoms and nine of the O atoms. The position of the remaining O atom was obtained from Fourier maps calculated with the previously determined parameters. These parameters were refined by three cycles of full-matrix least squares with isotropic temperature factors;

Table 4. *Atomic coordinates with their standard deviations in parentheses*

	<i>x</i>	<i>y</i>	<i>z</i>
Cu	0.4259 (1)	0.2870 (1)	0.4702 (1)
Si(1)	0.8079 (1)	0.0601 (2)	0.1054 (2)
Si(2)	0.1461 (1)	0.2939 (2)	0.5152 (2)
Si(3)	0.7367 (1)	0.3452 (2)	0.4918 (2)
Si(4)	0.7494 (1)	0.3777 (2)	0.9433 (2)
Na(1)	0.0209 (3)	0.2413 (3)	0.9209 (4)
Na(2)	0.4205 (2)	0.2731 (3)	0.9564 (4)
O(1)	0.9875 (3)	0.1047 (5)	0.2856 (6)
O(2)	0.7399 (4)	0.1297 (5)	0.2883 (6)
O(3)	0.2678 (4)	0.1789 (5)	0.1096 (6)
O(4)	0.2826 (4)	0.2183 (5)	0.5466 (6)
O(5)	0.5731 (4)	0.3539 (5)	0.3931 (6)
O(6)	0.5790 (4)	0.3528 (5)	0.8167 (6)
O(7)	0.1442 (4)	0.3959 (5)	0.7819 (6)
O(8)	0.8189 (4)	0.3707 (5)	0.7729 (6)
O(9)	0.1444 (4)	0.4668 (5)	0.4481 (6)
O(10)	0.7951 (4)	0.2040 (5)	0.9961 (7)

Table 5. Anisotropic temperature factors ($\times 10^4$) with their standard deviations in parentheses

$$T = \exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2klB_{23} + 2hlB_{13})]$$

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	46 (1)	101 (1)	135 (2)	22 (1)	44 (1)	61 (1)
Si(1)	50 (1)	78 (3)	135 (4)	22 (2)	44 (2)	53 (3)
Si(2)	47 (1)	88 (3)	138 (4)	20 (2)	42 (2)	59 (3)
Si(3)	52 (1)	86 (3)	134 (4)	23 (2)	48 (2)	59 (3)
Si(4)	54 (2)	90 (3)	132 (4)	24 (2)	49 (2)	62 (3)
Na(1)	88 (3)	134 (5)	326 (9)	56 (3)	106 (4)	129 (6)
Na(2)	72 (3)	163 (5)	207 (7)	34 (3)	62 (4)	117 (5)
O(1)	41 (4)	89 (7)	180 (12)	111 (4)	32 (5)	52 (8)
O(2)	81 (5)	109 (8)	184 (12)	33 (5)	82 (6)	66 (8)
O(3)	59 (4)	83 (7)	150 (11)	18 (4)	44 (5)	50 (7)
O(4)	55 (4)	133 (8)	205 (12)	40 (5)	67 (6)	101 (9)
O(5)	63 (4)	127 (8)	180 (11)	37 (5)	64 (6)	95 (8)
O(6)	55 (4)	164 (9)	170 (12)	33 (5)	52 (6)	99 (9)
O(7)	61 (4)	98 (7)	153 (11)	25 (4)	59 (6)	58 (8)
O(8)	50 (4)	127 (7)	160 (11)	32 (4)	51 (5)	84 (8)
O(9)	62 (4)	110 (8)	191 (12)	36 (5)	64 (6)	86 (8)
O(10)	90 (5)	112 (8)	196 (12)	43 (5)	77 (7)	91 (8)

the R value was reduced to 0.050. Three successive cycles of anisotropic refinement converged to give an R of 0.042 for all observed reflexions (Sakurai, 1971).

Final atomic coordinates are given in Table 4, and anisotropic temperature factors in Table 5. Scattering factors corresponding to neutral atoms were used throughout (*International Tables for X-ray Crystallography*, 1962).*

Description of the structure

Phase 2 is isostructural with litidionite ($\text{CuNaKS}_4\text{O}_{10}$) and fenaksite ($\text{FeNaKS}_4\text{O}_{10}$). The structure is built up of silicate pipes, which have $(\text{Si}_8\text{O}_{20})^{8-}$ radicals as the repeat unit, linked by the Cu and one of the two non-equivalent Na atoms. Another Na atom is contained in

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32177 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

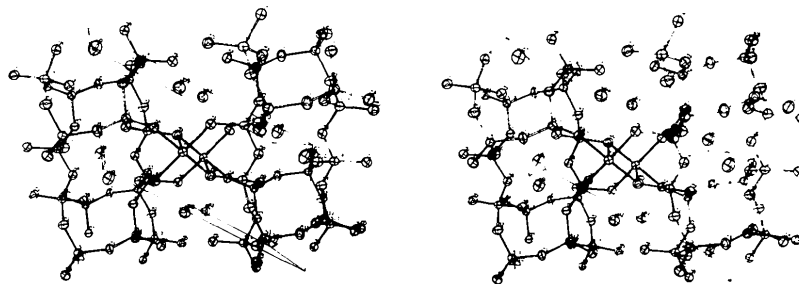


Fig. 1. Stereographic pair of the structure of $\text{CuNa}_2\text{Si}_4\text{O}_{10}$.

the silicate pipe. The Cu atoms have four nearest O neighbours in the form of a square and one additional O atom. Both Na atoms, which form irregular polyhedra, have seven O neighbours. Fig. 1 is a stereo

Table 6. Interatomic distances and principal bond angles

Cu—O(3)	1.965 (3) Å	O(3)—Cu—O(4)	92.8 (2)°
O(4)	1.943 (5)	O(5)	87.5 (2)
O(5)	1.977 (5)	O(5)'	90.5 (1)
O(5)'	2.511 (4)	O(4)	96.9 (2)
O(6)	1.981 (4)	O(5)	84.5 (2)
		O(5)	83.9 (2)
Si(1)—O(1)	1.640 (3)	O(6)	95.0 (2)
O(2)	1.626 (5)	O(6)	97.8 (1)
O(3)	1.576 (3)		
O(10)	1.615 (5)	O(1)—Si(1)—O(2)	108.7 (2)
Si(2)—O(1)	1.621 (3)	O(3)	106.5 (2)
O(4)	1.565 (4)	O(10)	106.8 (2)
O(7)	1.644 (5)	O(2)	110.9 (2)
O(9)	1.629 (5)	O(10)	108.7 (2)
		O(3)	115.0 (2)
Si(3)—O(2)	1.628 (4)	O(1)—Si(2)—O(4)	111.5 (2)
O(5)	1.576 (4)	O(7)	106.2 (2)
O(8)	1.643 (5)	O(9)	106.9 (2)
O(9)	1.629 (5)	O(4)	111.3 (2)
Si(4)—O(6)	1.567 (4)	O(7)	113.7 (3)
O(7)	1.640 (3)	O(9)	106.8 (2)
O(8)	1.634 (5)	O(2)—Si(3)—O(5)	112.5 (2)
O(10)	1.620 (5)	O(8)	106.5 (2)
		O(9)	107.6 (2)
Na(1)—O(1)	2.370 (4)	O(5)	113.6 (3)
O(3)	2.555 (5)	O(9)	114.0 (2)
O(7)	2.480 (6)	O(8)	101.9 (2)
O(8)	2.445 (5)		
O(8)'	2.584 (4)	O(6)—Si(4)—O(7)	111.7 (2)
O(9)	2.747 (5)	O(8)	114.9 (2)
O(10)	2.697 (6)	O(10)	116.4 (2)
		O(7)	102.7 (2)
Na(2)—O(2)	2.726 (5)	O(10)	107.8 (2)
O(3)	2.536 (6)	O(8)	102.1 (3)
O(4)	2.338 (5)		
O(5)	2.426 (5)	Si(1)—O(1)—Si(2)	141.0 (3)
O(6)	2.462 (6)	O(2)—Si(3)	136.4 (3)
O(6)'	2.593 (5)	O(10)—Si(4)	158.2 (4)
O(7)	3.047 (5)	Si(2)—O(9)—Si(3)	139.0 (2)
		O(7)—Si(4)	128.7 (3)
		Si(3)—O(8)—Si(4)	129.4 (2)

drawing of the structure. Bond lengths and angles are listed in Table 6.

The crystal structure of litidionite was precisely determined by Pozas *et al.* (1975) using three-dimensional intensity data collected with an automated single-crystal diffractometer, and that of fenaksite by Golovachev, Drozdov, Kuz'min & Belov (1971) using film methods. For a comparison of phase 2, litidionite and fenaksite, the cell parameters of phase 2 have been converted by the matrix (111/0 $\bar{1}\bar{1}$ /001), and the three sets of unit-cell data are shown in Table 7. The converted unit cell is used in the following discussion.

Table 7. Unit-cell data for phase 2, litidionite and fenaksite

	Phase 2* CuNa ₂ Si ₄ O ₁₀	Litidionite† CuNaKSi ₄ O ₁₀	Fenaksite‡ FeNaKSi ₄ O ₁₀
<i>a</i>	9.722 Å	9.80 Å	10.00 Å
<i>b</i>	7.637	8.01	8.18
<i>c</i>	6.944	6.97	6.98
α	115.06°	114.12°	114.7°
β	98.91	99.52	100.7
γ	105.71	105.59	105.0

* Cell parameters have been converted with the matrix (111/0 $\bar{1}\bar{1}$ /001).

† Pozas *et al.* (1975).

‡ Golovachev *et al.* (1971).

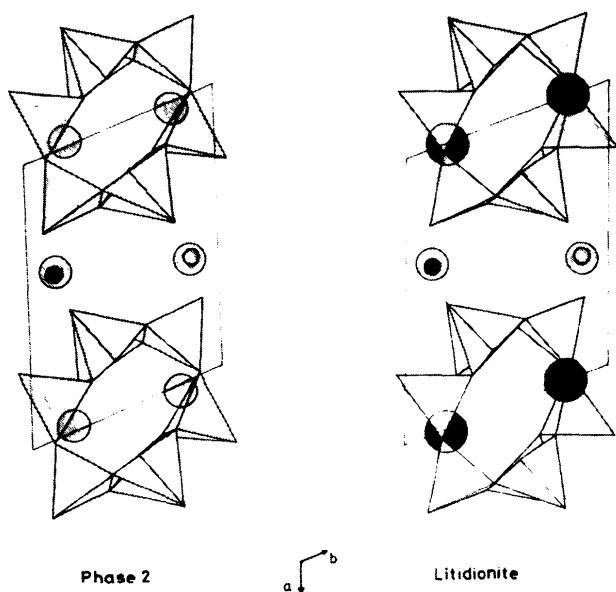


Fig. 2. Projection of the structure of CuNa₂Si₄O₁₀ and litidionite parallel to the *c* axis. The largest circles are K atoms, the smallest are Cu atoms, and the others are Na atoms.

The effect of substituting Na for K in litidionite to give phase 2 results in the following features. The unit-cell data of phase 2 and litidionite are very similar, but the *b* axis of phase 2 is shorter than that of litidionite. As shown in Fig. 2, the Na(1) position of phase 2 is located within the silicate pipe, unlike the K atom in litidionite, and thus gives rise to the difference in the *b* lengths.

Table 8 shows the coordination numbers, average values and ranges of interatomic distances in phase 2 and litidionite. The average distances of Cu—O and Na(2)—O in phase 2 are both shorter by about 0.01 Å than those in litidionite. The average Si—O distance is almost the same in the two materials, but the difference between bridging and non-bridging Si—O distances is 0.012 Å larger in phase 2 than that in litidionite. The average Si—O—Si angle in phase 2 is 3.7° smaller than that in litidionite.

Most of the crystals of phase 2 are twinned with (100) as the twin plane, while those of synthetic litidionite are not twinned, although the conditions in the hydrothermal syntheses of these two substances were almost the same. These are considered to be growth twins, because the crystal sizes are larger than those of litidionite. The postulated twinned structure of phase 2 is shown in Fig. 3. The twin lattice of phase 2 (Table 9) is, as shown, body-centred pseudomonoclinic with the twin index 1; this twinning is then characterized as pseudomerohedral, after Friedel (1926). Accordingly, the difference in the occurrence of twinning in these two materials cannot be explained along the

Table 8. Comparison of interatomic parameters for phase 2 and litidionite

	Phase 2	Litidionite*
Cu—O		
CN	5	5
Base (av.)	1.967 Å	1.978 Å
(range)	1.943–1.981	1.961–1.990
Apex	2.511	2.549
Si—O		
Average	1.607 Å	1.607 Å
Non-bridging (av.)	1.571	1.578
(range)	1.565–1.576	1.572–1.582
Bridging (av.)	1.631	1.626
(range)	1.615–1.644	1.614–1.635
Bridging angle (av.)	138.76°	142.44°
(range)	128.66–158.15	131.75–160.05
Na(1) or K—O		
CN	7 [Na (1)]	8 (K)
Average	2.554 Å	2.915 Å
Range	2.370–2.747	2.667–3.168
Na(2) or Na—O		
CN	7 [Na (1)]	7 (Na)
Average	2.590 Å	2.603 Å
Range	2.338–3.047	2.386–2.932

* Pozas *et al.* (1975)

lines of twin obliquity (Friedel, 1926). In this case it may be necessary to consider an increase in the flexibility of the silicate pipe by substitution of Na for K in the structure of phase 2.

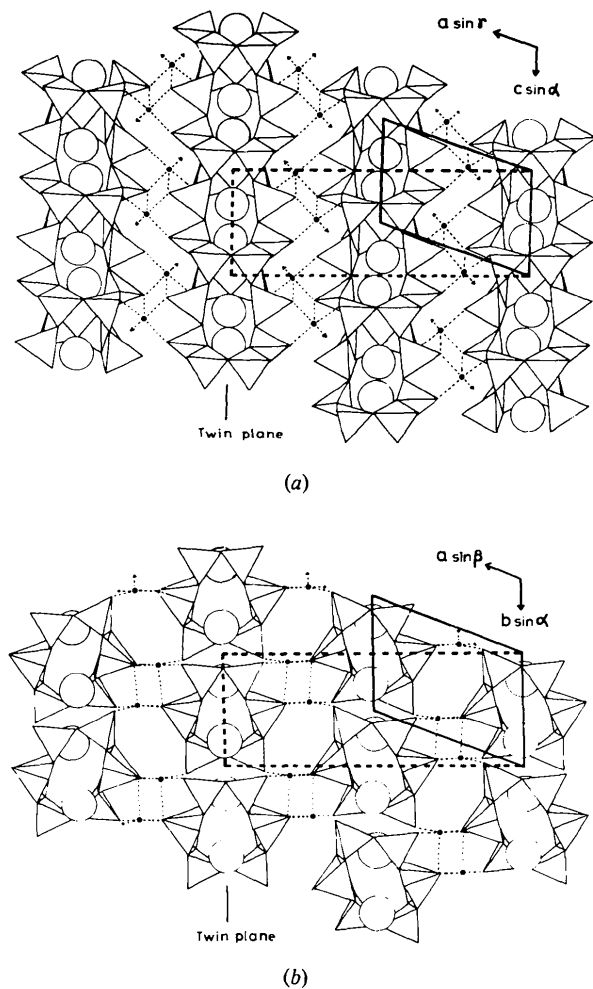


Fig. 3. The postulated twin structure. (a) Projection parallel to the *b* axis. (b) Projection parallel to the *c* axis. The solid bold line indicates the original unit cell, and the broken bold line the twin lattice.

Table 9. Twin lattice of phase 2 and litidionite

	Phase 2	Litidionite
<i>a</i>	7.64 Å	8.01 Å
<i>b</i>	17.82	17.94
<i>c</i>	6.94	6.97
α	87.76°	88.55°
β	115.06	114.12
γ	91.83	90.34
Space group	$I\bar{1}$	$I\bar{1}$
Twin index	1	1
Twin obliquity	3.7°	1.6°

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