

the bonding O atoms [O(L)] do not take part in such a network.

Fig. 1 depicts a projection of this structure along the c axis. The drawing has been produced using the program *STRUPLO* (Fischer, 1985).

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$\text{Ba}_3\text{CaCuSi}_6\text{O}_{17}$: A New $\{\text{B}, 1^1_\infty\}[\text{Si}_6\text{O}_{17}]$ Chain Silicate

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Abstract. Tribarium calcium copper hexasilicate, $\text{Ba}_3\text{CaCuSi}_6\text{O}_{17}$ (ideal stoichiometry), $M_r = 956.12$, orthorhombic, $B2mb$ [symmetry operators $(0,0,0), (\frac{1}{2}, 0, \frac{1}{2}) + x, y, z; x, -y, -z; x, \frac{1}{2} - y, z; x, \frac{1}{2} + y, -z]$, $a = 14.405$ (2), $b = 16.077$ (2), $c = 7.088$ (2) Å, $V = 1641.5$ (5) Å³, $Z = 4$, $D_x = 3.87$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu = 92.2$ cm⁻¹, room temperature, $F(000) = 1748$, $R = 0.052$, $wR = 0.050$ for 684 observed reflections. Crystals were formed as a by-product of the synthesis of Tl–Cu–Ca–Ba superconductors. The structure consists of SiO_4 tetrahedra which share corners to form distorted six-membered rings which in turn are linked by two corners to other rings to form chains of six-membered rings. The overall silicate anion topology is $\{\text{B}, 1^1_\infty\}[\text{Si}_6\text{O}_{17}]$ [in the notation of Liebau (1985). *Structural Chemistry of Silicates*. Berlin: Springer–Verlag]. Calcium and barium sites are eight coordinated, and the copper is in square-planar coordination.

Introduction. Hazen, Finger, Angel, Prewitt, Ross, Hadidiacos, Heaney, Veblen, Sheng, Ali & Hermann (1988) described the crystallography of a number of superconducting phases in the Tl–Ba–Ca–Cu–O system originally synthesized by Sheng & Hermann (1988*a,b*). These syntheses were carried out by annealing the experimental charge in a silica container, and in addition to the various superconducting phases found in the bulk of the sample,

reaction between the charge and the container produced a number of brilliantly coloured transparent phases. At least two of these were novel silicates of barium and copper. The structure of $\text{BaCuSi}_2\text{O}_6$, recently reported by Finger, Hazen & Hemley (1989), contains four-membered rings of silicate tetrahedra not connected into a framework by other tetrahedral sites. The structure of the second silicate, present as only a few minute multiple crystals, is described here.

Experimental. The largest clear, turquoise-coloured crystal from the experimental charge supplied by Sheng & Hermann (1988*a,b*) was selected for diffraction experiments. Approximately 20% of the volume of this crystal (approximate dimensions $0.04 \times 0.04 \times 0.015$ mm) was a second individual, misoriented by about 4° from the parent crystal. Preliminary experiments indicated that reflections with $h + l$ odd in hkl and k odd in $hk0$ were systematically absent. Data were collected with a Rigaku AFC-5 goniometer equipped with a rotating anode generator providing Mo $K\alpha$ radiation via a graphite monochromator out to $(\sin\theta)/\lambda = 0.7$ Å⁻¹, with $-20 < h < 20$, $0 < k < 22$, $0 < l < 9$, together with their Friedel pairs (four asymmetric units). The 240, $20\bar{2}$ and 042 reflections were monitored as intensity and orientation standards every 150 reflections; their intensities varied randomly by up to 5% from their means. No correction was made to the measured intensities for this variation, but the weights assigned in the least-squares procedures were modified appropriately (see below). A total of 4955 symmetry-allowed reflections were measured, of which 2724 were observed at $I >$

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Table 1. Atomic positions and equivalent isotropic temperature factors (\AA^2)

Temperature factor: $\exp(-\beta_{ij}h_ih_j)$.

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

	x	y	z	$B_{\text{eq}}/B_{\text{iso}}$
Ca*	0.0054 (8)	0.0000	0.0000	0.67
Ba1*	-0.0040 (3)	0.2500	0.0307 (4)	0.69
Ba2	0.2500†	0.1125 (1)	0.2587 (4)	0.84
Cu	0.5271 (4)	0.0000	0.0000	0.73
Si1	-0.0809 (9)	0.2500	0.5215 (19)	0.68
Si2	0.1234 (9)	0.2500	0.5404 (22)	0.96
Si3	0.1640 (6)	0.0942 (6)	0.7844 (14)	0.89
Si4	0.3753 (6)	0.0890 (6)	0.7674 (14)	0.81
O1	0.0206 (21)	0.2500	0.6265 (45)	1.3 (6)
O2	0.1729 (15)	0.1689 (13)	0.6220 (29)	1.2 (4)
O3	0.2711 (14)	0.0749 (13)	0.8486 (30)	1.5 (4)
O4	0.4179 (19)	0.1689 (17)	0.8831 (35)	2.8 (5)
O5	-0.1557 (23)	0.2500	0.6791 (49)	1.3 (6)
O6	0.1317 (22)	0.2500	0.3055 (47)	1.0 (6)
O7	0.1220 (13)	0.0094 (16)	0.6955 (36)	1.6 (4)
O8	0.1043 (13)	0.1214 (12)	0.9663 (33)	0.8 (4)
O9	0.3779 (14)	0.1074 (13)	0.5461 (31)	0.6 (3)
O10	0.4346 (14)	-0.0063 (16)	0.2004 (35)	1.5 (4)

* Refined occupancies of these two sites are: Ca = 0.966 (9) Ca + 0.034 Ba, Ba1 = 0.966 (9) Ba + 0.034 Ca.

† The x coordinate of Ba2 was fixed to define the origin.

$2\sigma_r$. Unit-cell parameters were determined from the positions of 24 centred reflections in the range $22 < 2\theta < 36^\circ$. Absorption corrections were made with the *AGNOST* program supplied as part of the diffractometer control software, which uses numerical integration to determine path lengths from measurements of the crystal size and shape. Calculated transmission coefficients ranged from 71 to 78%. Equivalent reflections were averaged in Laue class *mmm* with $R_{\text{int}} = 0.057$ for those with $I > 2\sigma_I$ to give 1265 unique reflections of which 684 with $I > 2\sigma_I$ were used for structure solution and refinement.

The systematic absences indicated that the diffraction symbol was *mmmB.b*, allowing three possible space groups: *Bmmb*, *Bm2₁b*, and *B2mb*. Intensity statistics indicated a non-centrosymmetric space group, so structure solutions were attempted by analysis of the Patterson function in both *Bm2₁b* and *B2mb*. All attempts to solve the structure in *Bm2₁b* were unsuccessful, with no solution achieving an *R* value of less than 0.25. By contrast, the heavy atoms were successfully located in *B2mb*. Remaining atom positions were located by several cycles of phasing and full least-squares refinement of the structure was then carried out. A weight of $w = [\sigma^2(F_o) + 0.005F_o^2]^{-1}$ was assigned to each reflection, where $\sigma(F_o)$ is the e.s.d. derived from counting statistics, and the factor of 0.005 was derived from the measured fluctuations in the intensities of the standard reflections. The scale factor, and all positional and thermal parameters (anisotropic for the cations, isotropic for the O) were refined by least squares [the function = $\sum w(|F_o| - |F_c|)^2$] was minimized using

Table 2. Selected interatomic distances (\AA) and angles ($^\circ$)

Ca—O7 ⁱⁱ	2.74 (2) × (2)	Cu—O7 ^{vi, vii}	1.95 (2) × (2)
Ca—O8 ⁱⁱ	2.43 (2) × (2)	Cu—O10 ^{v, vi}	1.95 (2) × (2)
Ca—O9 ^{iii, iv}	2.54 (2) × (2)	Ba2—O2	2.95 (2)
Ca—O10 ^{iii, iv}	2.36 (2) × (2)	Ba2—O3 ⁱ	2.98 (2)
Ba1—O1 ⁱ	2.89 (3)	Ba2—O3 ⁱⁱ	3.12 (2)
Ba1—O4 ^{iii, viii}	3.03 (3) × (2)	Ba2—O5 ^s	2.66 (2)
Ba1—O6	2.76 (3)	Ba2—O6	2.81 (2)
Ba1—O8 ^{ix}	2.63 (2) × (2)	Ba2—O7 ⁱⁱ	2.71 (2)
Ba1—O9 ^{iii, viii}	2.86 (2) × (2)	Ba2—O8 ⁱ	2.95 (2)
Si1—O1	1.64 (3)	Ba2—O9	2.75 (2)
Si1—O4 ^{iii, viii}	1.63 (3) × (2)	Si2—O1	1.60 (3)
Si1—O5	1.55 (4)	Si2—O2 ^{ax}	1.60 (2) × (2)
Si3—O2	1.67 (2)	Si2—O6	1.67 (4)
Si3—O3	1.64 (2)	Si4—O3	1.62 (2)
Si3—O7	1.62 (3)	Si4—O4	1.64 (3)
Si3—O8	1.61 (2)	Si4—O9	1.60 (2)
		Si4—O10 ⁱ	1.60 (3)
O1—Si1—O4 ⁱⁱⁱ	106. (1)	O1—Si2—O2	106. (1)
O1—Si1—O5	107. (2)	O1—Si2—O6	117. (2)
O4 ⁱⁱⁱ —Si1—O4 ⁱⁱⁱ	106. (2)	O2—Si2—O2 ⁱⁱ	110. (2)
O4 ⁱⁱⁱ —Si1—O5	115. (1)	O2—Si2—O6	109. (1)
O2—Si3—O3	105. (1)	O3—Si4—O4	106. (1)
O2—Si3—O7	111. (1)	O3—Si4—O9	110. (1)
O2—Si3—O8	113. (1)	O3—Si4—O10 ⁱⁱ	109. (1)
O3—Si3—O7	107. (1)	O4—Si4—O9	110. (1)
O3—Si3—O8	109. (1)	O4—Si4—O10 ⁱⁱ	112. (1)
O7—Si3—O8	110. (1)	O9—Si4—O10 ⁱⁱ	106. (1)
Si1—O1—Si2	131. (2)	Si2—O2—Si3	144. (1)
Si3—O3—Si4	138. (1)	Si4—O4—Si1 ⁱⁱ	158. (2)

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

RFINE88, a development version of *RFINE4* (Finger & Prince, 1974). Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The refinement was terminated when the maximum least-squares shift of any parameter was less than 0.005 e.s.d. Final agreement indices on the observed reflections were $R = 0.052$, $wR = 0.050$ and $S = 0.82$. Final atomic coordinates and isotropic temperature factors are reported in Table 1.* Selected interatomic distances and angles are given in Table 2. The final difference electron density has maxima and minima of $\pm 2 e \text{\AA}^{-3}$; part of this is due to interference in the diffraction pattern from the second individual noted above.

Discussion. The results of the structure refinement suggested that a small quantity of a heavier element is substituted on the Ca site (Table 1). Given the original chemistry of the experimental charge this heavier element is probably either Ba or Tl. There

* Lists of structure factors, anisotropic thermal parameters and a full list of bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53145 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

was insufficient quantity of this turquoise phase available for electron microprobe analysis, and attempts to synthesize pure $\text{Ba}_3\text{CaCuSi}_6\text{O}_{17}$ in the absence of Tl were unsuccessful. Two structure models were therefore refined in order to try to identify the nature of this heavy element. In the first, Tl was allocated to the Ca site; the refined composition was $\text{Ba}_3(\text{Ca}_{0.98}\text{Tl}_{0.02})\text{CuSi}_6\text{O}_{17}$. In the second model the distribution of Ba and Ca among the Ca, Ba1, and Ba2 sites was refined subject to the constraint of the ideal stoichiometry, $\text{Ba}_3\text{CaCuSi}_6\text{O}_{17}$. The occupancy of the Ba2 site remained at 1.00 (1) Ba, so further refinement of this second model proceeded with Ca and Ba distributed between the Ca and Ba1 sites alone. Although the two models cannot be distinguished on the basis of our data, the positions of the maxima in the difference electron density are suggestive of oxygen positions coordinating a smaller atom than Ba on the Ba1 site, and are thus supportive of the second model. Refined parameters from this model are therefore reported in Table 1. It is also conceivable that these results arise from the presence of stacking mistakes or other forms of structural disorder within the crystal.

All of the Si atoms within the structure are tetrahedrally coordinated by oxygens. These tetrahedra share corners to form distorted six-membered rings which in turn are linked by two corners to other rings to form chains of six-membered rings. The topology of the silicate anion (Fig. 1) may therefore be described as 'loop-branched' following the terminology of Liebau (1985). This same topology, $\{\text{1B}, \text{1}^1_\infty\}[\text{4Si}_6\text{O}_{17}]$ (Liebau, 1985), is found in the mineral structures deerite (Fleet, 1977) and howieite

(Wenk, 1974), but with a different conformation of the six-membered rings. The silicate anions within the structure of the mineral pellyite $[\text{Ba}_2\text{Ca}(\text{Fe}, \text{Mg})_2\text{Si}_6\text{O}_{17}]$; Meagher, 1976] have an almost identical conformation, but the chains not only display a doubled periodicity arising from the inversion of alternate rings but are arranged differently in relation to one another because of the coordination requirements of the different cation content. Both Ba sites in $\text{Ba}_3\text{CaCuSi}_6\text{O}_{17}$ display somewhat irregular eightfold coordination by oxygen, while the Ca site is smaller, and closer to a cube in shape. Cation-oxygen distances are Ba1—O 2.63 (2)–3.03 (3) Å (average 2.84 Å), Ba2—O 2.66 (2)–3.12 (2) Å (average 2.87 Å), Ca—O 2.36 (2)–2.74 (2) Å (average 2.51 Å). The coordination of the copper site is close to an ideal square plane [Cu—O 1.95 (2) Å]; in contrast to some copper sites in superconducting and related ceramics (e.g. Hazen, Finger, Angel, Prewitt, Ross, Mao, Hadidiacos, Hor, Meng & Chu, 1987) there is no capping oxygen to form a five-coordinated polyhedron. All of the coordination polyhedra including the silicate tetrahedra are therefore typical for the cations present, so the unusual configuration of the silicate anion must be due solely to the unusual mixed chemistry of the phase.

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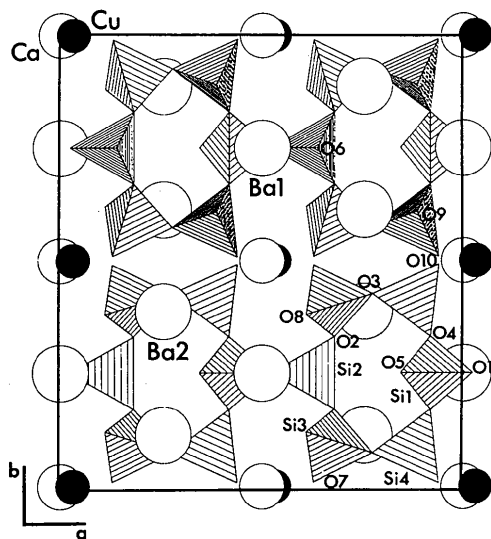


Fig. 1. Polyhedral representation (STRUPLO; Fischer, 1985) of the structure of $\text{Ba}_3\text{CaCuSi}_6\text{O}_{17}$ showing the arrangement of two adjacent chains of the silicate anion.

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