Acta Cryst. (1993). **C49**, 1555–1559

Structure of α-Dicalcium Silicate Hydrate

By T. Yano

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, *Japan*

K. Urabe

Faculty of Science and Engineering, Ryukoku University, Ohtsu, Shiga 520-21, *Japan*

H. Ikawa

Faculty of Engineering, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-02, *Japan*

T. Teraushi

Ceramics and Refractories Division, Asahi Glass Co. Ltd, Takasago, Hyougo 670, *Japan*

N. Ishizawa

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Yokohama 227, *Japan*

and S. Udagawa

Faculty of Engineering, Chiba Institute of Technology, Narashino, Chiba 275, *Japan*

(*Received* 6 *June* 1991; *accepted* 12 *May* 1993)

Abstract. $Ca_2(SiO_3OH)(OH)$, $M_r = 190.26$, orthorhombic, $P2_12_12_1$, $a = 9.487\,(4)$, $b = 9.179\,(4)$, $c = 10.666\,(7)$ Å, $V = 928.8\,(8)$ Å, $Z = 8$, $D_x = 2.72$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 25.07$ cm^{-1}, $F(000) = 768$, $T = 293$ K, final $R = 0.054$ for 1677 unique non-zero reflections having $I > 3\sigma(I)$. The crystal was hydrothermally synthesized from a mixture of CaO and quartz at 403 K. The structure was redetermined by means of Patterson synthesis and refined by least-squares calculations. Hydrogen bonds were assigned by the balance of electrostatic valences of O atoms. The structure consists of Ca^{2+}, $(SiO_3OH)^{3-}$ and OH^- ions. Calcium ions are coordinated by six or seven O atoms. Calcium polyhedra are linked together with shared edges to form a waved polyhedral sheet parallel to {001}. These sheets are bridged along the [001] direction by isolated SiO_3OH tetrahedra and hydrogen bonds.

Introduction. In the CaO–SiO_2–H_2O system, over 20 hydrated crystalline phases are known (Taylor, 1964). Several phases such as tobermorite and xonotlite are very important as dominant calcium silicate phases synthesized in an autoclave. α-Dicalcium silicate hydrate is produced primarily in the process used to form 11 Å-tobermolite when a suspension of calcium hydroxide and fairly large size quartz is hydrothermally treated at about 433 K (Nobugai, Tokonami, Takahashi & Mitsuda, 1980).

The thermal and spectroscopic properties of this phase have been reported (Heller, 1954; Ryskin & Stavitskaya, 1961). Whereas the reassignment of powder diffraction peaks has been reported (Ingram & Taylor, 1977), the crystal structure has not been refined since Heller's original study (1952). Therefore a refinement of the crystal structure is highly desirable.

Experimental. CaO, which was obtained from $CaCO_3$ through calcination, and Brazil quartz (< 10 μm) were mixed and hydrothermally treated at 403 K for 70 d in a Morey-type pressure tube. The Ca/Si ratio of the starting mixture was 0.8 and the water/solid ratio was 10. After hydrothermal treatment, α-dicalcium silicate hydrate, $Ca(OH)_2$ and unreacted quartz were detected using a powder X-ray diffractometer (Rigaku, Type 2038). The crystals of α-dicalcium silicate hydrate were prismatic in shape with a maximum length of 0.1–0.15 mm.

The lattice parameters of α-dicalcium silicate hydrate were measured by powder X-ray diffractometry using Si ($a = 5.43088$ Å) as an internal standard [$\lambda(\text{Cu } K\alpha) = 1.54178$ Å, 14 reflections, $21 < 2\theta < 55°$, $T = 293$ K], and then refined by

Acta Crystallographica Section C
ISSN 0108-2701 © 1993

a least-squares program in the *UNICS* system (Sakurai, 1967).

A colorless clear twinless crystal of dimensions 0.05 × 0.02 × 0.15 mm was selected for the structure determination under a polarizing microscope. Rotation and Weissenberg photographs of the crystal were obtained to determine diffraction symmetry and extinction rules. $0kl$ reflections if $k = 2n$, $hk0$ reflections if $h = 2n$, and $h0l$ reflections if $l = 2n$ were observed, but some very weak reflections violating the latter two rules were also detected. The extinction rules were consistent with those of the space group $P2_12_12_1$, as reported by Heller (1952).

Three-dimensional intensity data were collected using a Rigaku-AFC automated four-circle X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). The intensities of 2250 reflections in one quadrant of a hemisphere of reciprocal space up to 120° of 2θ, with $h_{\max} = 18$, $k_{\max} = 18$, $l_{\max} = 21$ ($\sin\theta/\lambda < 1.22$ Å^{-1}), were measured employing the ω–2θ scan technique. The intensities of three standard reflections (202, 211, 122) were monitored every 60 reflections and no variation of the intensities was observed. 1677 reflections with $I > 3\sigma(I)$ were selected for analysis. The observed intensities were corrected for Lp factors but not for absorption because the crystal was small and μR (=0.13) was negligible. Throughout the calculations, *UNICS* (Sakurai, 1967) and *LINUS* (Coppens & Hamilton, 1970) programs were used on the HITAC M200 computer at the computer center of the Tokyo Institute of Technology. The atomic scattering factors for Ca^{2+}, $Si^{0\pm}$ and O^- given by Cromer & Mann (1968), and the anomalous-dispersion coefficients of Cromer (1965) were used. An extinction correction was not applied.

Since least-squares refinement with the positional parameters reported by Heller (1952) did not give a reasonable residual factor, the structure analysis was based on the space group *Pbca*, because the space group $P2_12_12_1$ was one of the subgroups of *Pbca* and most of the reflections matched the extinction rules consistent with *Pbca*. Firstly, a three-dimensional Patterson function was evaluated. Several distinct peaks found in the Patterson sections revealed a set of atomic positional parameters: Ca(1) (0.45, 0.16, 0.07), Ca(2) (0.35, 0.0, 0.39) and Si (0.23, 0.21, 0.16). The positions of five O atoms were distinguished on subsequent difference Fourier synthesis. Least-squares calculations with the atomic positional parameters of the eight atoms mentioned above and with isotropic temperature factors reduced the residual factor ($R = \sum||F_o| - |F_c||/\sum|F_o|$) to 0.073.

Broad positive peaks near given atomic positions were observed in the difference Fourier maps calculated after least-squares refinement. This phenomenon indicated that the crystal showed lower symmetry than *Pbca*, thus the space group was altered to $P2_12_12_1$ derived from extinction-rule analysis. Further least-squares calculations based on the space group $P2_12_12_1$ were carried out. Anisotropic temperature factors for Ca and Si atoms and isotropic temperature factors for O atoms were calculated. Final $R = 0.054$; 95 variables. The ratio of maximum least-squares shift to e.s.d. in the final refinement cycle was less than 0.30. Maximum positive and negative electron densities in the final difference Fourier synthesis were 1.1 and −1.7 e Å^{-3}, respectively. The final positional and isotropic or equivalent thermal parameters are listed in Table 1.* Selected interatomic bond distances and angles are listed in Table 2.

Table 1. *Final atomic coordinates and isotropic or equivalent thermal factors* (Å^2) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{iso}/U_{eq}^*
Ca(1)	0.4808 (4)	0.1703 (5)	0.0660 (4)	0.0055 (12)*
Ca(2)	0.5120 (4)	0.8312 (5)	0.9286 (4)	0.0086 (14)*
Ca(3)	0.3471 (4)	0.0066 (3)	0.3886 (3)	0.0020 (9)*
Ca(4)	0.6563 (5)	0.9953 (5)	0.6107 (5)	0.0131 (17)*
Si(1)	0.1687 (7)	0.2095 (7)	0.1639 (6)	0.0050 (19)*
Si(2)	0.8306 (7)	0.7838 (7)	0.8440 (6)	0.0051 (17)*
O(1)	0.0619 (11)	0.1324 (11)	0.0656 (13)	0.0096 (30)
O(2)	0.9498 (9)	0.8563 (10)	0.9343 (11)	0.0039 (22)
O(3)	0.2432 (13)	0.3487 (16)	0.0735 (15)	0.0135 (40)
O(4)	0.7458 (12)	0.6572 (14)	0.9264 (13)	0.0077 (29)
O(5)	0.2981 (15)	0.1044 (16)	0.1950 (15)	0.0145 (42)
O(6)	0.7065 (12)	0.9041 (13)	0.8132 (12)	0.0067 (26)
O(7)	0.1099 (10)	0.2900 (12)	0.2812 (11)	0.0070 (25)
O(8)	0.9069 (10)	0.7060 (12)	0.7218 (12)	0.0078 (27)
O(9)	0.3946 (16)	0.4492 (17)	0.3912 (16)	0.0118 (38)
O(10)	0.6067 (14)	0.5458 (14)	0.6009 (13)	0.0062 (28)

As a result of the chemical analysis (Heller, 1954), 16 H atoms (four independent atoms) are included in the unit cell, although no clear evidence was obtained from the difference Fourier maps at the last stage of refinement. The positions of the H atoms were estimated by consideration of the electrostatic valences of the O atoms using the method proposed by Donnay & Allmann (1970). The sum of the electrostatic valences for each anion and cation was calculated based on the bond distances (Table 3).

The valences of bonds emanating from cations summed over the bonded anions were 2.002–2.050 for Ca^{2+} and 3.996–4.001 for Si^{4+}. These values agree very well with the ideal valences of the cations. Among the ten O atoms, the valence sums of O(1) and O(2) are close to 2.0, and those of O(9) and

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71140 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: OH0018]

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Silicon coordination

$Si(1)O_4$ tetrahedron		$Si(2)O_4$ tetrahedron	
Si(1)—O(1)	1.62 (1)	Si(2)—O(2)	1.63 (1)
—O(3)	1.75 (2)	—O(4)	1.67 (1)
—O(5)	1.60 (2)	—O(6)	1.65 (1)
—O(7)	1.56 (2)	—O(8)	1.65 (1)
Mean	1.63	Mean	1.65
O(1)—O(3)	2.63 (2)	O(2)—O(4)	2.66 (2)
—O(5)	2.65 (2)	—O(6)	2.68 (2)
—O(7)	2.76 (2)	—O(8)	2.69 (2)
O(3)—O(5)	2.64 (2)	O(4)—O(6)	2.60 (2)
—O(7)	2.61 (2)	—O(8)	2.70 (2)
O(5)—O(7)	2.63 (2)	O(6)—O(8)	2.81 (2)
Mean	2.65	Mean	2.69
O(1)—Si(1)—O(3)	102.3 (7)	O(2)—Si(2)—O(4)	108.0 (6)
—O(5)	110.6 (8)	—O(6)	109.9 (7)
—O(7)	120.2 (7)	—O(8)	109.9 (7)
O(3)—Si(1)—O(5)	104.2 (8)	O(4)—Si(2)—O(6)	103.1 (7)
—O(7)	103.9 (8)	—O(8)	109.0 (7)
O(5)—Si(1)—O(7)	113.3 (8)	O(6)—Si(2)—O(8)	116.4 (7)

Calcium coordination

$Ca(1)O_7$ polyhedron		$Ca(2)O_7$ polyhedron	
Ca(1)—O(1^{i})	2.42 (1)	Ca(2)—O(2^{iv})	2.34 (1)
—O(3)	2.79 (2)	—O(4)	2.73 (1)
—O(3^{i})	2.91 (2)	—O(4^{iv})	2.96 (1)
—O(5)	2.30 (2)	—O(6)	2.32 (1)
—O(8^{ii})	2.28 (1)	—O(7^{v})	2.25 (1)
—O(9^{iii})	2.39 (2)	—O(9^{vi})	2.38 (2)
—O(10^{iii})	2.27 (1)	—O(10^{vi})	2.29 (2)
Mean	2.48	Mean	2.47
O(1^{i})—O(3)	3.37 (2)†	O(2^{iv})—O(4)	3.18 (2)†
—O(3^{i})	2.63 (2)*	—O(4^{iv})	2.66 (2)*
—O(5)	4.45 (2)	—O(6)	4.35 (2)
—O(8^{ii})	3.15 (2)†	—O(7^{v})	3.15 (2)†
—O(9^{iii})	4.29 (2)	—O(9^{vi})	3.20 (2)
—O(10^{iii})	3.38 (2)	—O(10^{vi})	4.13 (2)
O(3)—O(3^{i})	5.31 (3)	O(4)—O(4^{iv})	5.28 (3)
—O(5)	2.64 (2)*	—O(6)	2.60 (2)*
—O(8^{ii})	3.71 (2)	—O(7^{v})	3.75 (2)
—O(9^{iii})	5.04 (2)	—O(9^{vi})	3.57 (2)
—O(10^{iii})	3.64 (2)	—O(10^{vi})	4.90 (2)
O(3^{i})—O(5)	5.12 (2)	O(4^{iv})—O(6)	5.21 (2)
—O(8^{ii})	3.70 (2)	—O(7^{v})	3.62 (2)
—O(9^{iii})	2.99 (2)†	—O(9^{vi})	3.57 (2)
—O(10^{iii})	3.47 (2)	—O(10^{vi})	2.98 (2)†
O(5)—O(8^{ii})	3.31 (2)	O(6)—O(7^{v})	3.51 (2)
—O(9^{iii})	3.37 (2)	—O(9^{vi})	3.32 (2)
—O(10^{iii})	3.33 (2)	—O(10^{vi})	3.37 (2)
O(8^{ii})—O(9^{iii})	3.39 (2)	O(7^{v})—O(9^{vi})	4.61 (2)
—O(10^{iii})	4.54 (2)	—O(10^{vi})	3.33 (2)
O(9^{iii})—O(10^{iii})	3.14 (2)*	O(9^{vi})—O(10^{vi})	3.14 (2)*

$Ca(3)O_6$ polyhedron		$Ca(4)O_6$ polyhedron	
Ca(3)—O(1^{vii})	2.44 (1)	Ca(4)—O(1^{v})	2.43 (1)
—O(2^{ii})	2.35 (1)	—O(2^{x})	2.53 (1)
—O(4^{viii})	2.57 (1)	—O(3^{xi})	2.57 (2)
—O(5)	2.30 (2)	—O(6)	2.37 (1)
—O(8^{ix})	2.35 (1)	—O(7^{xii})	2.33 (1)
—O(10^{ix})	2.33 (2)	—O(9^{xii})	2.32 (2)
Mean	2.39	Mean	2.43
O(1^{vii})—O(2^{ii})	3.08 (2)†	O(1^{v})—O(2^{x})	3.08 (2)†
—O(4^{viii})	3.18 (2)	—O(3^{xi})	3.37 (2)†
—O(5)	4.70 (2)	—O(6)	3.68 (2)
—O(8^{ix})	3.15 (2)†	—O(7^{xii})	3.90 (2)
—O(10^{ix})	3.70 (2)	—O(9^{xii})	4.67 (2)
O(2^{ii})—O(4^{viii})	3.18 (2)†	O(2^{x})—O(3^{xi})	3.34 (2)
—O(5)	3.52 (2)	—O(6)	4.83 (2)
—O(8^{ix})	3.86 (2)	—O(7^{xii})	3.15 (2)†
—O(10^{ix})	4.57 (2)	—O(9^{xii})	3.86 (2)
O(4^{viii})—O(5)	4.09 (2)	O(3^{xi})—O(6)	4.18 (2)
—O(8^{ix}	4.81 (2)	—O(7^{xii})	4.76 (2)
—O(10^{ix})	2.98 (2)†	—O(9^{xii})	2.99 (2)†
O(5)—O(8^{ix})	3.16 (2)	O(6)—O(7^{xii})	3.12 (2)
—O(10^{ix})	3.15 (2)	—O(9^{xii})	3.12 (2)
O$(8)^{\mathrm{ix}}$—O(10^{ix})	3.46 (2)	O(7^{xii})—O(9^{xii})	3.28 (2)

Table 2 (*cont.*)

Oxygen–oxygen distances less than 3.2 Å

O(3^{xii})—O(6)	2.59 (2)	O(7)—O(10^{xiv})	3.19 (2)
O(4)—O(5^{xiii})	2.77 (2)	O(8)—O(9^{xv})	2.97 (2)

Symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (ii) $\frac{3}{2}-x, 1-y, -\frac{1}{2}+z$; (iii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iv) $-\frac{1}{2}+x, \frac{3}{2}-y, 2-z$; (v) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (vi) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (vii) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (viii) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$; (ix) $-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (x) $\frac{3}{2}-x, 2-y, -\frac{1}{2}+z$; (xi) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (xiii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (xiv) $\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$; (xv) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$.

* Edge shared by tetrahedron and deca/octahedron.

† Edge shared by two deca/octahedra.

Table 3. *Bond lengths* (Å) *and estimated bond valences in valence units*

ΣA^{v} values are valences of bonds from cations summed over the bonded anions, ΣC^{v} are valences of bonds reaching to anions and $\Sigma C^{\mathrm{v}*}$ are corrected valences for hydrogen bonds.

	Ca(1)	Ca(2)	Ca(3)	Ca(4)	Si(1)	Si(2)	ΣC^{v}	$\Sigma C^{\mathrm{v}*}$	Anion type
O(1)	2.42		2.44	2.43	1.62				
	0.309		0.314	0.333	1.020		1.976		O^{2-}
O(2)		2.34	2.35	2.53		1.63			
		0.334	0.349	0.292		1.043	2.018		O^{2-}
O(3)	2.79			2.57	1.75				
	0.171			0.276	0.760		1.333	1.073	OH^-
O(3)′	2.91								
	0.126								
O(4)		2.73	2.57			1.67			
		0.191	0.263			0.958	1.518	1.343	OH^-
O(4)′		2.96							
		0.106							
O(5)	2.30		2.30		1.60				
	0.365		0.370		1.062		1.797	1.972	O^{2-}
O(6)		2.32		2.37		1.65			
		0.349		0.359		1.000	1.708	1.968	O^{2-}
O(7)		2.25		2.33	1.56				
		0.384		0.377	1.154		1.915	1.980	O^{2-}
O(8)	2.28		2.35			1.65			
	0.375		0.349			1.000	1.724	1.829	O^{2-}
O(9)	2.39	2.38		2.32					
	0.322	0.322		0.382			1.026	0.921	OH^-
O(10)	2.27	2.29	2.33						
	0.380	0.364	0.357				1.101	1.036	OH^-
ΣA^{v}	2.048	2.050	2.002	2.019	3.996	4.001			

O(10) are close to 1.0. These were considered to correspond to O^{2-} and OH^-, respectively. The latter O atoms are not coordinated to the Si atom. The sums of electrostatic valences for six O atoms [O(3) to O(8)] are intermediate between 1.0 and 2.0. Four irregularly short O—O distances less than 3.2 Å, O(3)—O(6), O(4)—O(5), O(7)—O(10) and O(8)—O(9), indicate that these are not at the edge of any cation polyhedron. If we suppose that hydrogen bonds exist between these atoms, the valence sums of each O atom become quite normal ($\Sigma C^{\mathrm{v}*}$ corrected for the hydrogen bonds in Table 3). O(3) and O(4) are OH^- anions and O(5), O(6), O(7) and O(8) are O^{2-}. O(3) and O(4) are tetrahedral O atoms in the Si(1) and Si(2) tetrahedra, respectively. Consequently, the structural formula of α-dicalcium silicate hydrate is expressed as $Ca_2(SiO_3OH)(OH)$.

Discussion. α-Dicalcium silicate hydrate is classified as an orthosilicate. The calculated structural parameters are different from those of Heller (1952), the structural basis of which is confirmed in this determination. The $Ca(1,2)O_6$, $Ca(3,4)O_7$ and SiO_3OH polyhedra connect through shared edges or corners and build up the three-dimensional framework of the structure. Fig. 1 shows a projection of the structure along [001]. There are a pair of O atoms, O(9) and O(10), which are not first neighbors of the Si atoms; these are described as 'free oxygen' by Heller (1952).

The structure is pseudo *Pbca* and the difference in shape of equivalent cation polyhedra (in *Pbca*) is generally small. Two crystallographically independent Si tetrahedra are observed in the structure. Each of the Si atoms has one OH^- and three O^{2-} anions as its first neighbors. The $Si(1)O_4$ tetrahedron is distorted, whereas the $Si(2)O_4$ tetrahedron is regular in shape. One of the reasons for this irregularity seems to be concerned with the hydrogen bond. The Si—O(—H) distances of 1.75 Å are longer than the other Si—O distances, 1.56–1.62 Å. Otherwise the distortion of the $Si(2)O_4$ tetrahedron is small. The reason for the difference in the degree of distortion within the two tetrahedra is not clear.

Two types of Ca polyhedra are observed. The Ca(1) atom is seven-coordinated, by four OH^- and three O^{2-}, and the Ca—O distances vary from 2.27 to 2.91 Å, with an average Ca—O distance of 2.48 Å. The Ca(3) atom is six-coordinated, by two OH^- and four O^{2-}, and the Ca—O distances vary from 2.30 to 2.57 Å, with an average Ca—O distance of 2.39 Å. The corresponding Ca—O distances observed in other calcium silicate hydrates are 2.31–2.75 Å in tobermorite (Hamid, 1981), 2.29–2.92 Å in rosenhahnite (Wan & Ghose, 1977), 2.32–2.87 Å in afwillite (Malik & Jeffery, 1976), for the CaO_7 decahedra, and 2.31–2.51 Å in rosenhahnite (Wan & Ghose, 1977), 2.24–2.51 Å in nekoite (Alberti & Galli, 1980), 2.30–2.44 Å in γ-Ca_2SiO_4 (Udagawa, Urabe, Natsume & Yano, 1980) and 2.27–2.47 Å in kilchoanite (Taylor, 1971) for the CaO_6 octahedra.

The Ca—O distances larger than 2.7 Å in the Ca(1) and Ca(2) decahedra involve the O atoms of OH^- groups coordinated to the tetrahedra and are longer than the other Ca—O distances (2.25–2.42 Å). The same phenomena are observed in the interlayer Ca polyhedra in tobermorite (3.31 Å) (Hamid, 1981), in rosenhahnite (2.92 Å) (Wan & Ghose, 1977) and in afwillite (2.87 Å) (Malik & Jeffery, 1976).

The $Ca(1)O_7$ polyhedron is linked to two $Si(1)O_3OH$ and one $Si(2)O_3OH$ tetrahedra by shared edges and corners, respectively. The same polyhedron is linked to four other CaO_x polyhedra by shared edges (Fig. 1). The $Ca(3)O_6$ polyhedron is linked to two $Si(1)O_3OH$ and three $Si(2)O_3OH$ tetrahedra by shared corners. The $Ca(3)O_6$ polyhedron is linked to another four CaO_x polyhedra by shared edges. The edges shared by two CaO_x polyhedra link continuously and run along the [100] direction. All

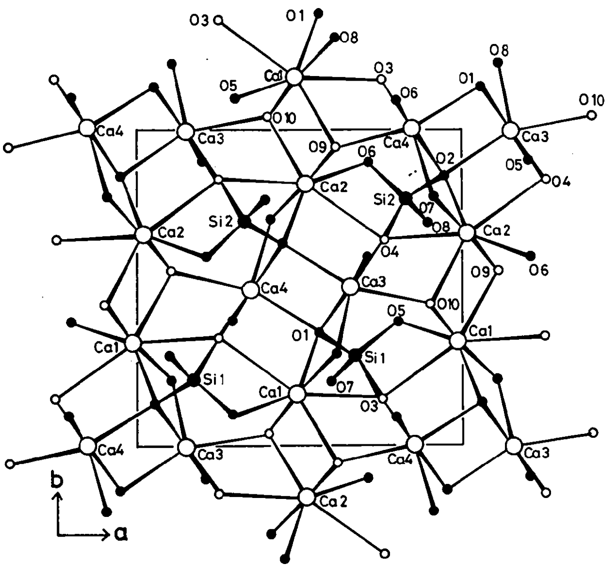

Fig. 1. Partial view of the structure along [001]. The two-dimensional network of calcium polyhedra is observed.

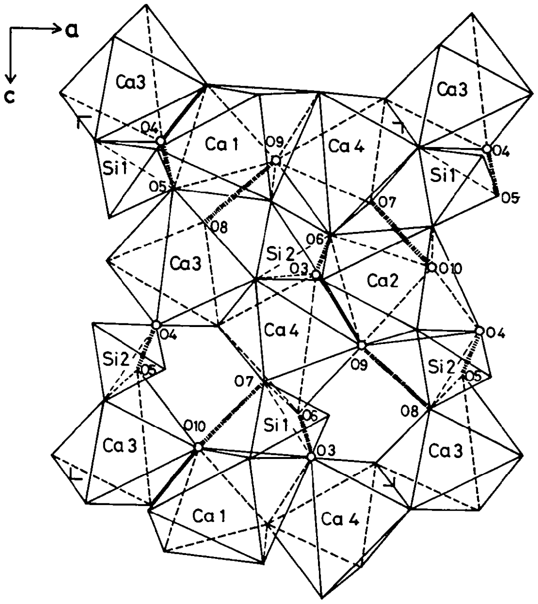

Fig. 2. Polyhedral illustration of the structure viewed along [010]. The estimated hydrogen bonds are also presented as dashed lines.

Ca polyhedra connect together along both the [100] and [010] directions, and build up a relatively dense Ca polyhedral sheet parallel to {001}. This polyhedral sheet is waved compared to the flat octahedral sheet observed in $Ca(OH)_2$. As shown in Fig. 2, SiO_3OH tetrahedra and hydrogen bonds bridge the Ca polyhedral sheets lying along the {001} plane. Between the polyhedral sheets, there are oval-shaped hollow spaces.

References

ALBERTI, A. & GALLI, E. (1980). *Am. Mineral.* **65**, 1270–1276.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

DONNAY, G. & ALLMANN, R. (1970). *Am. Mineral.* **55**, 1003–1015.

HAMID, S. G. (1981). *Z. Kristallogr.* **154**, 189–198.

HELLER, H. (1952). *Acta Cryst.* **5**, 724–728.

HELLER, H. (1954). *Proc. 3rd Int. Symp. Chem. Cem.* pp. 237–244, London.

INGRAM, L. & TAYLOR, H. F. W. (1977). Grant-in-Aid Report to JCPDS.

MALIK, K. M. A. & JEFFERY, J. W. (1976). *Acta Cryst.* B**32**, 475–480.

NOBUGAI, G., TOKONAMI, M., TAKAHASHI, K. & MITSUDA, T. (1980). *J. Mineral. Soc. Jpn*, **14** (special issue 2), 172–180.

RYSKIN, YA. I. & STAVITSKAYA, G. P. (1961). *Opt. Spectrosc.* **9**, 320–324.

SAKURAI, T. (1967). Editor. *Universal Crystallographic Computation Program System.* The Crystallographic Society of Japan, Tokyo, Japan.

TAYLOR, H. F. W. (1964). *The Chemistry of Cement.* London: Academic Press.

TAYLOR, H. F. W. (1971). *Mineral. Mag.* **38**, 26–31.

UDAGAWA, S., URABE, K., NATSUME, M. & YANO, T. (1980). *Cem. Concr. Res.* **10**, 139–144.

WAN, C. & GHOSE, S. (1977). *Am. Mineral.* **62**, 503–512.

Acta Cryst. (1993). C**49**, 1559–1561

Structure of $Ag_3Cu_{12}Y_5$, a New Ternary Compound

BY ZENG LINGMIN, LI DEXUAN AND ZHUANG YINGHONG

Department of Physics, Guangxi University, Nanning 530004, *People's Republic of China*

(*Received* 4 *January* 1993; *accepted* 13 *April* 1993)

Abstract. Dodecacopper trisilver pentayttrium, $Ag_3Cu_{12}Y_5$, $M_r = 1530.62$, cubic, $P4_132$ (O^7), $a = 7.127$ (4) Å, $V = 362.0$ (7) Å^3, $Z = 1$, $D_m = 7.09$, $D_x = 7.02$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $\mu = 76.31$ mm^{-1}, $F(000) = 684$, $T = 298$ K. The new cubic phase is of the β-Mn(A13) type. The three Ag atoms and five Y atoms occupy 8(c) positions with $x = 0$ and the 12 Cu atoms occupy 12(d) positions with $x = 0.135$.

Introduction. A new ternary compound has been found in our recent investigation of the 773 K isothermal section of the Ag–Cu–Y system (Li, Zeng & Zhuang, 1993). The new phase, which is $Ag_3Cu_{12}Y_5$, has a limited solid solubility. The compositional range is 23–27% Y, 9–19% Ag and 68–54% Cu. We have therefore determined its crystal structure.

Experimental. The alloy sample of 15 g was prepared in a high-frequency induction furnace. Stoichiometric quantities of high-purity component materials, 99.98% silver, 99.99% copper and 99.9% yttrium, were melted in a MgO crucible under a pure argon atmosphere. The weight loss during melting was 0.2%. The ingot was annealed at 1123 K for four weeks in a quartz tube under vacuum, then cooled at a rate of 10 K h^{-1} to room temperature. Samples for X-ray diffraction analysis were powdered and annealed at 773 K for five days under vacuum.

The X-ray powder diffraction data were collected at 298 K on a Rigaku (3015) X-ray diffractometer. Cu $K\alpha$ radiation was employed and 5N purity Si powder was used as an internal standard. The scanning rate was 0.5° min^{-1} and the data were taken over the 2θ Bragg angle range 15–140°. The pattern lines were assigned using a computer program and were indexed successfully according to cubic structure. The lattice constant was calculated by least-squares methods.

Each unit cell contains 20 atoms based on the lattice parameter ($a = 7.127$ Å) and density ($D_m = 7.09$ g cm^{-3}) measured by the specific gravity bottle method. In agreement with the formula $Ag_3Cu_{12}Y_5$, three atoms are silver, five atoms are yttrium and 12 atoms are copper. The employed atomic scattering factors and Lorentz–polarization factors are those listed in *International Tables for X-ray Crystallography* (1974, Vol. IV). The absorption factor and Debye–Waller temperature factor are neglected in the intensity calculation. The quantity $R = \sum|I_o - I_c|/\sum I_o \simeq 0.14$ shows that the reflections (Table 1) are