INORGANIC COMPOUNDS

Ca$_3$Y$_2$(SiO$_4$)$_3$

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Fig. 1. A perspective view of the crystal structure of Ca$_3$Y$_2$(SiO$_4$)$_3$ along the *a* axis [AB_2C_2(SiO$_4$)$_3$: *A* Ca3 and Y3, *B* Ca1 and Y1, *C* Ca2 and Y2, tetrahedra around *X* (Si2—O2 × 2, O6, O7) and *Y* (Si1—O1, O3, O4, O5)].

Abstract

Crystals of a new nesosilicate, tricalcium diyttrium trisilicon oxide, were prepared from a silicate melt by slow cooling. The structure was refined in space group *Pnma* and has nine-, eight- and seven-coordinate sites for Ca^{2+} and Y^{3+} cations. The structural formula can be expressed as (Ca$_{0.84}$Y$_{0.16}$)(Ca$_{0.41}$Y$_{0.59}$)$_2$(Ca$_{0.67}$Y$_{0.33}$)$_2$(SiO$_4$)$_3$.

Comment

Previously reported calcium yttrium silicates are Ca$_2$Y$_8$Si$_6$O$_{26}$ (Ito, 1968; Wanmaker, Vrugt & Verlijsdonk, 1971), Ca$_3$Y$_6$(SiO$_4$)$_6$ (Wanmaker, Vrugt & Verlijsdonk, 1971) and Ca$_2$Y$_2$Si$_2$O$_9$ (Warshaw & Roy, 1962). Ca$_2$Y$_8$Si$_6$O$_{26}$ and Ca$_3$Y$_6$(SiO$_4$)$_6$ have apatite-type structures. Ca$_2$Y$_2$Si$_2$O$_9$ was prepared by Ca and Si substitution of Y and Al in Y$_4$Al$_2$O$_9$. Here we report the crystal structure of a new calcium yttrium silicate, Ca$_3$Y$_2$(SiO$_4$)$_3$.

Ca$_3$Y$_2$(SiO$_4$)$_3$ is isostructural with Ca$_5$(PO$_4$)$_2$SiO$_4$ ('silico-carnotite', space group *Pnma*, *a* = 6.737, *b* = 15.508, *c* = 10.132 Å; Dickens & Brown, 1971). Fig. 1 shows a perspective view of the crystal structure along the *a* axis. The formula Ca$_3$Y$_2$(SiO$_4$)$_3$ is similar to that of a garnet, a very common group of nesosilicates. In the A_3B_2(SiO$_4$)$_3$ garnet structure, atoms *A* and *B* are, respectively, in eightfold triangular dodecahedral sites and sixfold octahedral sites. The combination of Ca^{2+} and Y^{3+} radii for the *A* and *B* sites is slightly out of the stability field for silicate garnets predicted by Novak & Gibbs (1971) using the effective radii of Shannon & Prewitt (1969).

The structural formula of Ca$_3$Y$_2$(SiO$_4$)$_3$ can be represented as AB_2C_2(SiO$_4$)$_3$, where *A*, *B* and *C* refer, respectively, to nine-, eight- and seven-coordinate cation sites. As shown by the site-occupancy factors in Table 1, more than 80% of the *A* site is occupied by
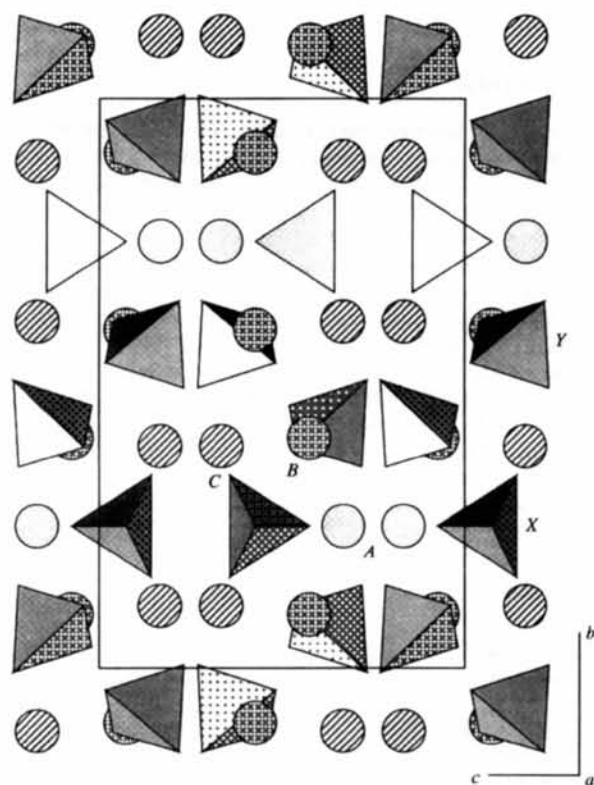
Ca atoms. The *B* and *C* sites contain Y and Ca in Ca:Y ratios of 4:6 and 7:3, respectively. The average interatomic distance between the *A*-site atom (Ca3/Y3) and the coordinated O atoms is 2.616 Å, which is comparable to the Ca—O bond distance (2.58 Å) expected from the effective ionic radius of Ca^{2+} in ninefold coordination (Shannon & Prewitt, 1969). The average distance between the *B*-site (Ca1/Y1) atom and the coordinated O atoms (2.454 Å) is close to that between the *C*-site (Ca2/Y2) atom and the coordinated O atoms (2.419 Å). Assuming that all the sites are occupied by Ca or Y alone, bond-valence sums at the *A*, *B* and *C* sites, calculated using the bond-valence parameters presented by Brese & O'Keeffe (1991), are, respectively, 1.831, 2.437 and 2.128 for Ca, and 2.079, 2.767 and 2.416 for Y. These values, implying the mixed occupation of Ca and Y atoms and their preference at each site, are relatively consistent with the refined occupancies. The mean Si1—O and Si2—O bond lengths (1.627 and 1.628 Å) of the SiO$_4$ tetrahedra are in agreement with that of the garnet almandine, (Fe,Mg,Ca,Mn)$_3$Al$_2$(SiO$_4$)$_3$ (1.628 Å; Novak

& Gibbs, 1971). The bond-valence sums at Si1 and Si2 are 3.970 and 3.957, respectively, and are nearly equal to 4.

Experimental

The starting materials were powders of Y_2O_3 (99.9% purity; Nippon Yttrium Company), $CaCO_3$ (99.99% purity; Rare Metallic Co., Ltd) and SiO_2 (extra pure grade; Wako Pure Chemical Ind., Ltd). These powders were weighed, mixed in an appropriate amount of ethanol in an agate mortar and pressed into pellets at 100 MPa. Polycrystalline $Ca_3Y_2(SiO_4)_3$ was prepared by heating pellets with a stoichiometric composition (3:2:3 Ca:Y:Si molar ratio) on a platinum plate at 1873 K for 48 h. The refined lattice parameters obtained by X-ray powder diffraction at 293 K using Cu $K\alpha$ radiation were: orthorhombic, $a = 6.5546$ (1), $b = 15.5999$ (3), $c = 10.0358$ (2) Å. Single crystals were produced from a starting mixture with composition Ca:Y:Si = 7:4:8 by slow cooling of a melted pellet from 1823 to 1673 K at a rate of 6.0 K h^{-1}. Colourless, transparent single crystals, of size 0.3–0.6 mm, were retrieved from the smashed pellet.

Crystal data

$Ca_3Y_2(SiO_4)_3$	Mo $K\alpha$ radiation
$M_r = 574.33$	$\lambda = 0.71069$ Å
Orthorhombic	Cell parameters from 23
$Pnma$	reflections
$a = 6.536$ (4) Å	$\theta = 14.39$–$14.80°$
$b = 15.626$ (3) Å	$\mu = 13.196$ mm^{-1}
$c = 10.029$ (2) Å	$T = 293$ (2) K
$V = 1024.2$ (6) Å^3	Ellipsoid
$Z = 4$	$0.22 \times 0.17 \times 0.17$ mm
$D_x = 3.725$ Mg m^{-3}	Colourless
$D_m = 3.72$ (4) Mg m^{-3}	
D_m measured by pycnometry	

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.0161$
$\omega/2\theta$ scans	$\theta_{max} = 27.47°$
Absorption correction:	$h = -8 \to 1$
spherical	$k = -1 \to 20$
$T_{min} = 0.190$, $T_{max} = 0.201$	$l = -1 \to 13$
1692 measured reflections	3 standard reflections
1224 independent reflections	every 150 reflections
1152 reflections with	intensity decay: none
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.828$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.035$	$\Delta\rho_{min} = -1.087$ e Å^{-3}
$wR(F^2) = 0.100$	Extinction correction:
$S = 1.038$	empirical (Sheldrick,
1224 reflections	1993)
104 parameters	Extinction coefficient:
$w = 1/[\sigma^2(F_o^2) + (0.0728P)^2$	0.0048 (8)
$+ 2.8100P]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	*International Tables for*
$(\Delta/\sigma)_{max} < 0.001$	*Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Y1†	0.37596 (7)	0.09501 (3)	0.07374 (5)	0.0114 (2)
Ca1‡	0.37596 (7)	0.09501 (3)	0.07374 (5)	0.0114 (2)
Y2§	0.17542 (10)	0.60961 (4)	0.16640 (6)	0.0122 (3)
Ca2¶	0.17542 (10)	0.60961 (4)	0.16640 (6)	0.0122 (3)
Y3††	0.0238 (2)	1/4	0.16761 (12)	0.0227 (4)
Ca3‡‡	0.0238 (2)	1/4	0.16761 (12)	0.0227 (4)
Si1	0.3534 (2)	0.06897 (7)	0.37215 (10)	0.0104 (3)
Si2	0.0260 (3)	1/4	0.57266 (15)	0.0123 (3)
O1	0.0365 (5)	0.1114 (2)	0.0395 (3)	0.0155 (6)
O2	0.0425 (5)	0.6608 (2)	0.3579 (3)	0.0170 (6)
O3	0.1879 (4)	0.0374 (2)	0.4822 (3)	0.0130 (6)
O4	0.2566 (5)	0.1462 (2)	0.2820 (3)	0.0160 (6)
O5	0.4173 (5)	0.5062 (2)	0.2690 (3)	0.0150 (6)
O6	0.2746 (7)	1/4	0.5746 (5)	0.0195 (9)
O7	0.4129 (7)	1/4	0.0739 (4)	0.0150 (8)

† Occupancy = 0.590 (4).   ‡ Occupancy = 0.409 (4).   § Occupancy = 0.331 (3).   ¶ Occupancy = 0.668 (4).   †† Occupancy = 0.156 (6). ‡‡ Occupancy = 0.844 (6).

Table 2. *Selected geometric parameters* (Å, °)

Ca1/Y1—O1	2.259 (3)	Ca3/Y3—O4^{ix}	2.437 (3)
Ca1/Y1—O3^i	2.298 (3)	Ca3/Y3—O4^{ix}	2.503 (3)
Ca1/Y1—O3^{ii}	2.302 (3)	Ca3/Y3—O4	2.503 (3)
Ca1/Y1—O4	2.369 (3)	Ca3/Y3—O1	2.520 (3)
Ca1/Y1—O7	2.4338 (8)	Ca3/Y3—O1^{ix}	2.520 (3)
Ca1/Y1—O2^{iii}	2.455 (3)	Ca3/Y3—O7^{viii}	2.692 (4)
Ca1/Y1—O5^{iv}	2.531 (3)	Ca3/Y3—O7	2.711 (5)
Ca1/Y1—O4^i	2.987 (3)	Ca3/Y3—O6^{viii}	2.925 (5)
Ca2/Y2—O2	2.254 (3)	Si1—O5^{ix}	1.620 (3)
Ca2/Y2—O3^v	2.342 (3)	Si1—O3	1.623 (3)
Ca2/Y2—O6^{vi}	2.402 (2)	Si1—O1^i	1.630 (3)
Ca2/Y2—O5^{vii}	2.424 (3)	Si1—O4	1.635 (3)
Ca2/Y2—O5	2.484 (3)	Si2—O2^x	1.621 (3)
Ca2/Y2—O1^{viii}	2.487 (3)	Si2—O2^{xi}	1.621 (3)
Ca2/Y2—O2^i	2.540 (4)	Si2—O6	1.625 (5)
Ca3/Y3—O4^{viii}	2.437 (3)	Si2—O7^{iii}	1.645 (4)
O5^{ix}—Si1—O3	112.7 (2)	O2^x—Si2—O2^{xi}	118.6 (2)
O5^{ix}—Si1—O1^i	116.9 (2)	O2^x—Si2—O6	105.71 (15)
O3—Si1—O1^i	104.1 (2)	O2^{xi}—Si2—O6	105.71 (15)
O5^{ix}—Si1—O4	106.4 (2)	O2^x—Si2—O7^{iii}	105.06 (14)
O3—Si1—O4	110.0 (2)	O2^{xi}—Si2—O7^{iii}	105.06 (14)
O1^i—Si1—O4	106.6 (2)	O6—Si2—O7^{iii}	117.4 (2)

Symmetry codes: (i) $\frac{1}{4} + x, y, \frac{1}{4} - z$; (ii) $\frac{1}{4} - x, -y, z - \frac{1}{4}$; (iii) $\frac{1}{4} - x, y - \frac{1}{4}, z - \frac{1}{4}$; (iv) $x, \frac{1}{4} - y, z$; (v) $\frac{1}{4} - x, \frac{1}{4} + y, z - \frac{1}{4}$; (vi) $\frac{1}{4} - x, 1 - y, z - \frac{1}{4}$; (vii) $x - \frac{1}{4}, y, \frac{1}{4} - z$; (viii) $-x, \frac{1}{4} + y, -z$; (ix) $x - \frac{1}{4}, \frac{1}{4} - y, \frac{1}{4} - z$; (x) $-x, 1 - y, 1 - z$; (xi) $-x, y - \frac{1}{4}, 1 - z$.

Precession photographs indicated orthorhombic symmetry and showed systematic extinction conditions ($0kl$: $k + l = 2n$; $hk0$: $h = 2n$; $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$; space group $Pnma$). The single crystal for data collection was ground to an ellipsoidal shape. Spherical absorption corrections were applied by approximating the ellipsoid as a sphere and using the average value of the ellipsoid axes for the radius ($r = 0.09$ mm). The largest peak in the difference map was located at (0.1361, 0.25, 0.5862), 0.73 Å from Si2, and the largest hole at (0.2986, 0.0943, 0.1464), 0.89 Å from Y1.

Data collection: *CONTROL* (Rigaku Corporation, 1992). Cell refinement: *CONTROL*. Data reduction: *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ATOMS*2.0 (Dowty, 1991). Software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1145). Services for accessing these data are described at the back of the journal.

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Brochantite

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Abstract

A new refinement of a single monoclinic crystal of brochantite, $Cu_4SO_4(OH)_6$, from Socorro, New Mexico, USA, yielded new, accurate positions for Cu, S and O. Five of the six H atoms were located from F_o-F_c syntheses.

Comment

As part of the research program of the Geo/Soil/Enviro Sector of the Consortium of the Advanced Photon Source, Argonne National Laboratory, we are selecting various minerals for testing the advances in crystallographic techniques. One of these is brochantite, the crystal structure of which was determined from a twinned crystal by Cocco & Mazzi (1959), using Cu *K*α radiation from a sealed-tube source. Particularly interesting are the positions of the H atoms, which were not located by Cocco & Mazzi. By carrying out a new structure determination on a single crystal, using X-rays from an Mo *K*α rotating-anode source, it was possible to improve on the old determination as well as to locate five of the six H atoms. A reference aliquot of the sample, from the University of Chicago Mineral Collection (No. 51 of unlabelled micromount collection) has been deposited in the American Museum of Natural History in New York.

Sabelli & Trosti-Ferroni (1985) classified brochantite in division 14 of the sheet type of sulfate minerals: 'In brochantite, there are two kinds of Cu-polyhedral chains, corner-linked and edge-linked, which are connected together to form sheets. The SO_4 tetrahedra bond these undulating sheets directly to one another, through weak apical Cu—O bonds'.

The cell dimensions of the monoclinic unit cell match within experimental uncertainty those of Cocco & Mazzi (1959). The atomic coordinates of the Cocco & Mazzi determination were obtained for a twinned crystal in a pseudo-orthorhombic cell. The present coordinates for a single crystal are inherently more accurate and were refined directly in the true monoclinic cell.
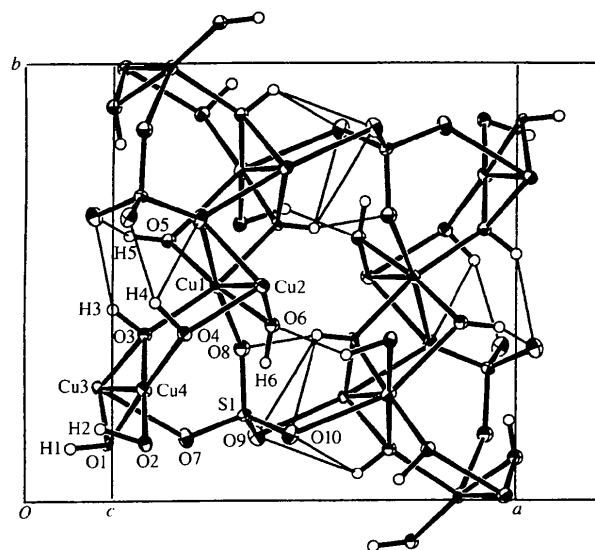

Fig. 1. An *ORTEP*II (Johnson, 1976) plot of the title compound showing the layers linked by Cu—O bonding and hydrogen bonding; displacement ellipsoids are drawn at the 50% probability level.