composition was introduced in *REMOS*92 (Yamamoto, 1992*b*) in order to obtain a reasonable chemical composition. The partial occupancy of each site was also restrained to within a physically reasonable range by the penalty function. The point density and composition obtained from the refinement were 0.0674 $Å^{-3}$ and $Al_{77}Cr_{18}Ni_5$ ($Al_{14.6}Cr_{3.6}Ni_{0.9}$), respectively.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1993). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *ABSORP* (Yamamoto, 1992*a*). Program(s) used to solve structure: direct methods (*SIR*92; Altomare *et al.*, 1994). Program(s) used to refine structure: modified version of *REMOS*92. Molecular graphics: *PRJAP* (Yamamoto, 1992*c*).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1150). Services for accessing these data are described at the back of the journal.

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$Ca_3Y_2(Si_3O_9)_2$

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(*Received 17 January 1997; accepted 13 May 1997*)

Abstract

This new cyclosilicate, calcium yttrium cyclosilicate, crystallizes in space group *C*2/*c*. Ca and Y atoms are in eight-, seven- and sixfold coordination sites between the layers of ternary SiO_4 rings (Si_3O_9). The structural formula can be expressed as $(Ca_{0.89}Y_{0.11})_2(Ca_{0.54}Y_{0.46})_2(Ca_{0.14}Y_{0.86})(Si_3O_9)_2$.

Comment

Rings of three SiO_4 tetrahedra joined by sharing corners occur in a few rare silicates, such as $BaTiSi_3O_9$, benitoite and $K_2ZrSi_3O_9$. Wadeite, α-$CaSiO_3$ (pseudowollastonite, a high-temperature polymorph of $CaSiO_3$, stable above 1393 K), is another example of the three-membered ring silicates. The low-temperature polymorph of $CaSiO_3$ (wollastonite) consists of infinite SiO_3 chains. As noted by Hilmer (1963), it is difficult to prepare single crystals of pseudowollastonite large enough for X-ray diffraction analysis. Hilmer studied the crystal structure of $SrGeO_3$ instead, which allowed him to infer the structure of α-$CaSiO_3$. O'Keeffe & Hyde (1981) explained the rarity of SiO_4 'three-rings' (Si_3O_9) in silicate structures and the anomalously long strained Si—O bonds observed in the three-rings by using the ratio of a non-bonded radius, 2*R*(Si), and a standard Si—O bond length, *l*(Si—O). Three-rings are more common in germanates, as expected from a smaller *R*(Ge)/*l*(Ge—O) value. The crystal structure and polytypes of α-$CaSiO_3$ were later studied by Yamanaka & Mori (1981), who succeeded in preparing single crystals of pseudowollastonite using a $CaCl_2$ flux.

In the CaO–SiO_2–Y_2O_3 system, we found a new compound, $Ca_3Y_2(Si_3O_9)_2$, which contains Si_3O_9 rings. The compounds previously known in this system are $Ca_2Y_8(SiO_4)_6O_2$ (Ito, 1968; Wanmaker, Vrugt & Verlijsdonk, 1971), $Ca_3Y_6(SiO_4)_6$, $Ca_4Y_6(SiO_4)_6O$ (Wanmaker, Vrugt & Verlijsdonk, 1971) and $Ca_2Y_2Si_2O_9$ (Warshaw & Roy, 1962). $Ca_2Y_8Si_6O_{26}$, $Ca_3Y_6Si_6O_{24}$ and $Ca_4Y_6(SiO_4)_6O$ have apatite-type structures. Recently, we found $Ca_3Y_2(SiO_4)_3$ with a silicocarnotite-type structure (Yamane, Nagasawa, Shimada & Endo, 1997). In these four structures, SiO_4 tetrahedra are isolated and linked by Ca and Y atoms. $Ca_2Y_2Si_2O_9$ probably has a cuspidine-type structure in which two SiO_4 tetrahedra share one corner and make an Si_2O_7 complex. The present paper reports the crystal structure of the new calcium yttrium cyclosilicate $Ca_3Y_2(Si_3O_9)_2$.

Fig. 1 shows the crystal structure of the title compound. Two O atoms of every SiO_4 tetrahedron being shared with other SiO_4 tetrahedra results in a ternary Si_3O_9 ring (Fig. 2). Ca and Y atoms connect the Si_3O_9 rings. The structure of $Ca_3Y_2(Si_3O_9)_2$ can be described as Ca/Y atom layers and Si_3O_9 ring layers stacking along the $[10\bar{1}]$ direction (Fig. 3). Fig. 4 shows the O-atom polyhedra of a Ca/Y atom layer and the locations of the Si_3O_9 rings on the layer. There are three atom sites and one vacant site in the Ca/Y layer (Ca1/Y1:Ca2/Y2:Ca3/Y3:vacant = 2:2:1:1). The crystal structure of $Ca_3Y_2(Si_3O_9)_2$, represented as $(Ca^{2+}_{3}Y^{3+}_{2})_{5/6}(\text{vacant})_{1/6}SiO_3$, can be related to the structure of α-$CaSiO_3$, which is characterized by Ca atom layers with no vacancies and Si_3O_9 ring layers. Yamanaka & Mori (1981) found four-layer, six-layer and disordered-stacking-layer polytypes of α-$CaSiO_3$. The

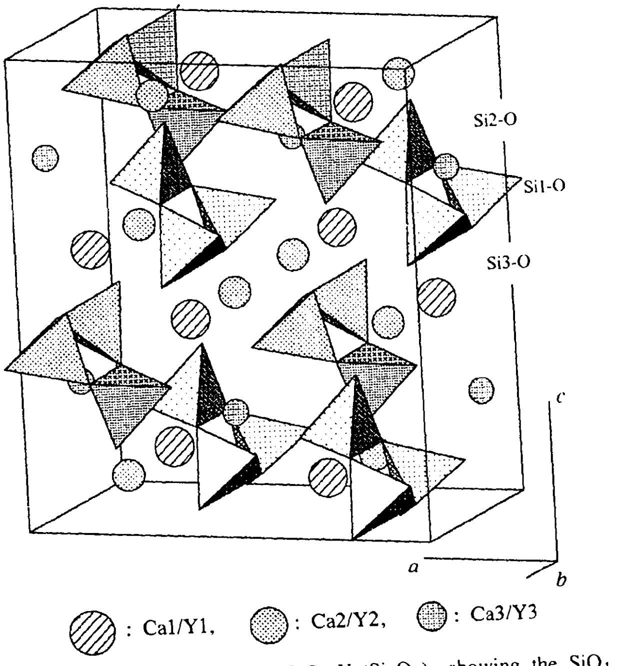


Fig. 1. The crystal structure of $Ca_3Y_2(Si_3O_9)_2$ showing the SiO_4 tetrahedra.

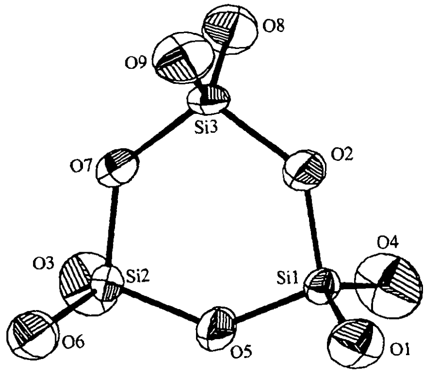


Fig. 2. The Si_3O_9 ring in $Ca_3Y_2(Si_3O_9)_2$. Displacement ellipsoids are drawn at the 99% probability level.

four-layer polytype is dominant among these polytypes. The position of the Si_3O_9 rings shifts in the sequence *ABCD*. $Ca_3Y_2(Si_3O_9)_2$ has a different four-layer stacking sequence. Two Si_3O_9 rings face each other across a vacant site of the Ca/Y atom layer and the position of the Si_3O_9 rings shifts in the sequence *AA'BB'*, as shown in Fig. 3.

The interatomic distances between Si atoms and Si—O—Si bridging O atoms are in the range 1.644–1.657 Å (average 1.650 Å). These values are larger than the standard Si—O bond length of 1.60 Å, but comparable with the values reported for $BaTiSi_3O_9$ (1.630–1.648 Å, average 1.639 Å; Fischer, 1969) and for α-$CaSiO_3$ (1.658–1.671 Å, average 1.664 Å; Yamanaka & Mori, 1981). The Si···Si distances [2*R*(Si)]

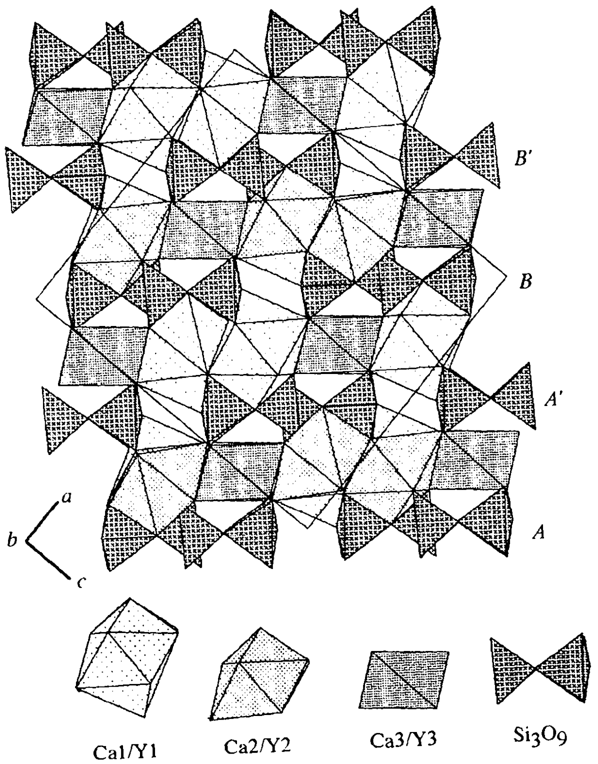


Fig. 3. A perspective view of $Ca_3Y_2(Si_3O_9)_2$ along the *b* axis.

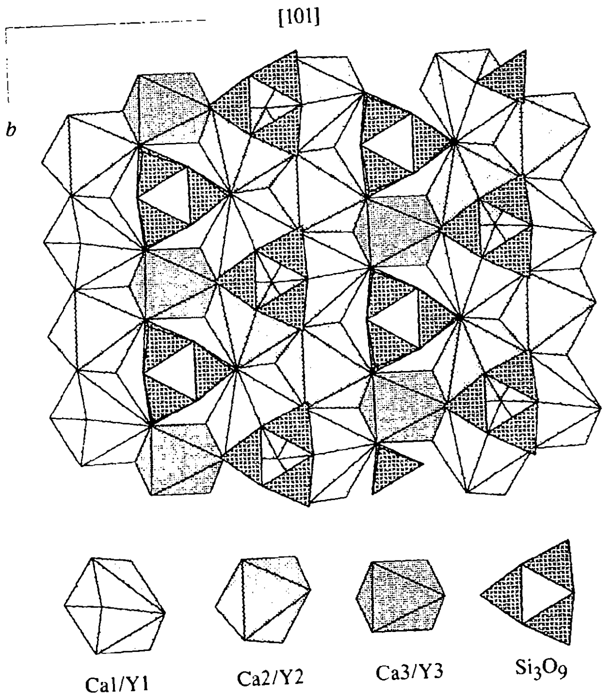
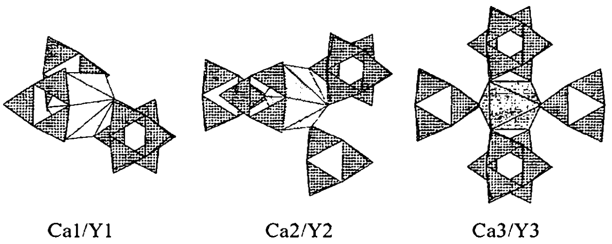


Fig. 4. The Ca/Y-centred O-atom polyhedron layer and the arrangement of the Si_3O_9 rings.

of the Si_3O_9 ring in $Ca_3Y_2(Si_3O_9)_2$ are 3.0311 (13) (Si1···Si2), 3.0345 (13) (Si2···Si3) and 3.0392 (13) (Si3···Si1) Å (average 3.035 Å), which are consistent with the non-bonding distance $2R$ = 3.06 Å for regular SiO_4 tetrahedra. All unshared O atoms of the Si_3O_9 ring in α-$CaSiO_3$ are coordinated by one Si and three Ca atoms (fourfold coordination). The average of the Si—O lengths is 1.587 Å. In the structure of $Ca_3Y_2(Si_3O_9)_2$, O3, O4 and O8 atoms on one side of the Si_3O_9 ring are surrounded by one Si and three Ca/Y atoms (total fourfold coordination). The average of the Si—O distances (1.607 Å) is almost equal to a standard bond length, l(Si—O) = 1.60 Å. The O atoms on the other side, O1, O6 and O9, are coordinated by one Si and two Ca/Y atoms (total threefold coordination) and the average Si—O distance is 1.583 Å. This side faces the vacant site of the Ca/Y layer.

Ca and Y atoms are coordinated by eight O atoms at the Ca1/Y1 site. The Ca/Y—O interatomic distances are in the range 2.301–2.619 Å (average 2.520 Å). These values are close to the Ca—O interatomic distances observed in α-$CaSiO_3$ (average 2.536 Å) where all Ca atoms have eightfold coordination. As shown in Fig. 5, six O atoms are edges of two Si_3O_9 rings and the remaining two are apices of the other two Si_3O_9 rings. The Ca2/Y2 site has sevenfold coordination with a Ca/Y—O distances in the range 2.275–2.588 Å (average 2.419 Å). Three O atoms comprise two edges of an Si_3O_9 ring. The remaining four O atoms are apices of Si_3O_9 rings. Ca and Y atoms in the Ca3/Y3 site are octahedrally coordinated by apex O atoms from six Si_3O_9 rings. The Ca/Y—O distances range from 2.228 to 2.352 Å (average 2.288 Å).



Ca1/Y1 Ca2/Y2 Ca3/Y3

Fig. 5. The arrangement of the Ca/Y-centred O-atom polyhedra and Si_3O_9 rings.

Bond-valence sums for Ca1/Y1, Ca2/Y2 and Ca3/Y3 sites, calculated using the bond-valence parameter for Y—O R_{YO} = 2.014 Å (Brese & O'Keeffe, 1991), are 2.160, 2.494 and 2.885, respectively. These values agree well with the average valences obtained from the occupancies of Ca and Y atoms in these sites (2.11, 2.46 and 2.86, respectively).

Experimental

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 and mixed in an appropriate amount of ethanol with an agate mortar. The mixture was pressed into a pellet and placed on a platinum plate. Polycrystalline $Ca_3Y_2(Si_3O_9)_2$ was prepared at 1673 K for 8 d from pellets with stoichiometric composition (Ca:Y:Si = 3:2:6 molar ratio). The refined lattice parameters obtained by X-ray powder diffraction at 293 K using Cu $K\alpha$ radiation are: monoclinic, a = 13.335 (7), b = 7.7261 (4), c = 14.7844 (8) Å, β = 90.285 (3)°. The single crystals were grown in the melt of a starting mixture with a composition of Ca:Y:Si = 1:1:3 by slow cooling from 1773 to 1673 K, with a cooling rate of 6.0 K h^{-1}. A colourless transparent single crystal was selected from the fragments of the crushed product and ground into a sphere for data collection.

Crystal data

$Ca_3Y_2(Si_3O_9)_2$
M_r = 754.60
Monoclinic
$C2/c$
a = 13.320 (3) Å
b = 7.729 (2) Å
c = 14.785 (2) Å
β = 90.256 (14)°
V = 1522.0 (5) Å^3
Z = 4
D_x = 3.293 Mg m^{-3}
D_m = 3.28 (1) Mg m^{-3}
D_m measured by pycnometry

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 28.98–29.92°
μ = 9.176 mm^{-1}
T = 298 (2) K
Sphere
0.076 mm (radius)
Transparent

Data collection

Rigaku AFC-7R diffractometer
$\omega/2\theta$ scans
Absorption correction: spherical
$T_{\min}$ = 0.365, $T_{\max}$ = 0.376
1781 measured reflections
1340 independent reflections
1068 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.018
$\theta_{\max}$ = 25.01°
$h = -15 \rightarrow 1$
$k = -9 \rightarrow 1$
$l = -17 \rightarrow 17$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.063
S = 1.063
1340 reflections
138 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 2.2321P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.328 e Å^{-3}
$\Delta\rho_{\min}$ = −0.735 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

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

	x	y	z	$U_{\rm eq}$
Ca1†	0.16155 (4)	0.11853 (7)	0.41270 (3)	0.0093 (2)
Y1‡	0.16155 (4)	0.11853 (7)	0.41270 (3)	0.0093 (2)
Ca2§	0.33485 (3)	0.12649 (5)	0.08416 (2)	0.0075 (2)

Y2¶	0.33485 (3)	0.12649 (5)	0.08416 (2)	0.0075 (2)
Ca3††	0	0.37890 (6)	1/4	0.0065 (2)
Y3‡‡	0	0.37890 (6)	1/4	0.0065 (2)
Si1	0.09475 (6)	0.07335 (11)	0.09901 (5)	0.0056 (2)
Si2	0.27403 (6)	0.37315 (11)	0.26967 (5)	0.0054 (2)
Si3	0.40206 (6)	0.18031 (11)	0.40679 (5)	0.0061 (2)
O1	0.0014 (2)	0.1754 (3)	0.13787 (14)	0.0114 (5)
O2	0.0630 (2)	0.1227 (3)	0.56374 (13)	0.0109 (4)
O3	0.1584 (2)	0.3787 (3)	0.29922 (14)	0.0132 (5)
O4	0.1588 (2)	0.1532 (3)	0.01777 (15)	0.0162 (5)
O5	0.1794 (2)	0.0447 (3)	0.17946 (14)	0.0114 (5)
O6	0.3048 (2)	0.3694 (3)	0.16674 (13)	0.0120 (5)
O7	0.3202 (2)	0.2041 (3)	0.32360 (13)	0.0105 (5)
O8	0.3352 (2)	0.1108 (3)	0.49013 (14)	0.0116 (5)
O9	0.5035 (2)	0.0737 (3)	0.12785 (14)	0.0133 (5)

† Site occupancy = 0.888 (3). ‡ Site occupancy = 0.111 (2). § Site occupancy = 0.538 (3). ¶ Site occupancy = 0.461 (2). †† Site occupancy = 0.145 (4). ‡‡ Site occupancy = 0.855 (4).

Table 2. *Selected geometric parameters (Å)*

Ca1/Y1—$O6^{i}$	2.301 (2)	Ca3/Y3—O3	2.228 (2)
Ca1/Y1—$O1^{ii}$	2.335 (2)	Ca3/Y3—O1	2.285 (2)
Ca1/Y1—$O8^{iii}$	2.538 (2)	Ca3/Y3—$O1^{ii}$	2.285 (2)
Ca1/Y1—O8	2.577 (2)	Ca3/Y3—$O9^{vii}$	2.352 (2)
Ca1/Y1—O7	2.582 (2)	Ca3/Y3—$O9^{viii}$	2.352 (2)
Ca1/Y1—O2	2.595 (2)	Si1—O1	1.582 (2)
Ca1/Y1—$O4^{iv}$	2.613 (2)	Si1—O4	1.600 (2)
Ca1/Y1—O3	2.619 (2)	Si1—O5	1.650 (2)
Ca2/Y2—$O4^{v}$	2.275 (2)	Si1—$O2^{vi}$	1.657 (2)
Ca2/Y2—O6	2.276 (2)	Si2—O6	1.578 (2)
Ca2/Y2—$O8^{vi}$	2.301 (2)	Si2—O3	1.604 (2)
Ca2/Y2—O9	2.370 (2)	Si2—$O5^{vii}$	1.644 (2)
Ca2/Y2—O4	2.547 (2)	Si2—O7	1.648 (2)
Ca2/Y2—$O3^{i}$	2.578 (2)	Si3—$O9^{ix}$	1.590 (2)
Ca2/Y2—O5	2.588 (2)	Si3—O8	1.616 (2)
Ca3/Y3—$O3^{ii}$	2.228 (2)		

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

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.

This work was partly supported by NEDO under the Synergy Ceramics Project of the Industrial Science and Technology Frontier Program promoted by AIST, MITI, Japan. MS is a member of the Joint Research Consortium of Synergy Ceramics. We would like to thank Kyota Ueda for help with X-ray diffraction data collection.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1157). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1536–1538

Zirconium–Nickel, Zr_7Ni_{10}: Space Group Revision for the Stoichiometric Phase

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(Received 21 February 1997; accepted 13 May 1997)

Abstract

The intermetallic compound Zr_7Ni_{10} is a structure-type representative which was previously reported to crystallize in the non-centrosymmetric space group *Aba*2. In the present work we show that the correct space group is centrosymmetric *Cmca*.

Comment

On the basis of metallographic data, Kirkpatrick & Larsen (1961) assigned the intermetallic phase Zr_7Ni_{10} a homogeneity range extending from 56.3 to 58.9 at.% Ni. In a separate investigation, Kirkpatrick, Smith & Larsen (1962) investigated its crystal structure as a function of composition and found that the nickel-

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