Refinement

$R_p = 0.029$
$R_{wp} = 0.039$
$R_{\rm exp} = 0.021$
$R_B = 0.069$
$2\theta_{\rm min} = 10.0$, $2\theta_{\rm max} = 152.5°$
Increment in $2\theta = 0.05°$
Excluded region(s): none
Least-squares refinement against χ^2
Profile function: pseudo-Voigt
31 parameters
All H-atom parameters refined
Preferred orientation correction: none

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

	x	y	z	$U_{\rm iso}$
Cs(1)	0	0	0	0.020 (1)
Cs(2)	0.1976 (5)	0	0.6081 (6)	0.028 (1)
Se	0.4266 (3)	0	0.2342 (3)	0.0174 (5)
O(1)	0.4862 (3)	0.2123 (4)	0.6893 (4)	0.0254 (6)
O(2)	0.3921 (4)	0	0.0209 (5)	0.0294 (8)
O(3)	0.2883 (5)	0	0.2633 (5)	0.0323 (9)
H†	0.525 (1)	0	0.005 (2)	0.028 (3)

† Site occupancy = 0.5.

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

Cs-atom coordination			
Cs(1)—O(1$^{\rm i}$) ×4	3.159 (3)	Cs(2)—O(1$^{\rm iii}$) ×2	3.217 (6)
Cs(1)—O(2$^{\rm ii}$) ×4	3.431 (2)	Cs(2)—O(1) ×2	3.246 (5)
Cs(1)—O(3) ×2	3.077 (4)	Cs(2)—O(1$^{\rm iv}$) ×2	3.138 (4)
Average	3.251	Cs(2)—O(2$^{\rm v}$)	3.314 (5)
		Cs(2)—O(3)	3.412 (8)
		Cs(2)—O(3$^{\rm vi}$) ×2	3.358 (2)
		Average	3.264
SeO_4 ion			
Se—O(1$^{\rm vii}$) ×2	1.640 (3)	O(1)···O(1$^{\rm viii}$)	2.712 (3)
Se—O(2)	1.694 (5)	O(1)···O(2$^{\rm ix}$)	2.666 (4)
Se—O(3)	1.615 (6)	O(1)···O(3$^{\rm ix}$)	2.698 (5)
Average	1.647	O(2)···O(3)	2.689 (7)
		Average	2.691
O(1$^{\rm ix}$)—Se—O(1$^{\rm vii}$)	111.5 (2)	O(1$^{\rm ix}$)—Se—O(2) ×2	106.2 (2)
O(1$^{\rm ix}$)—Se—O(3) ×2	111.9 (2)	O(2)—Se—O(3)	108.7 (2)
		Average	109.4
Hydrogen bridge			
O(2)···H	1.51 (2)	O(2)—H$^{\rm x}$	1.01 (2)
O(2)···O(2$^{\rm x}$)	2.506 (7)	H···H$^{\rm x}$	0.52 (2)
O(2)···H—O(2$^{\rm x}$)	173 (2)	Se—O(2)···H	105.4 (7)
Se—O(2)—H$^{\rm x}$	112 (1)		

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

Neutron diffraction measurements were performed at the high-resolution powder diffractometer D2B of the ILL in Grenoble (Hewat, 1986) in the high intensity mode. The 64 counters, spaced at 2.5° intervals, were moved by steps of 0.05° to give a complete diffractogram up to 160° in 2θ.

The program *FULLPROF* (Rodriguez-Carvajal, 1992) was used to refine the structure.

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A New Hexagonal κ Phase of Al–Cr–Ni

A. Sato,[a] A. Yamamoto,[a] X. Z. Li,[b] K. Hiraga,[b]
T. Haibach[c] and W. Steurer[c]

[a]*National Institute for Research in Inorganic Materials, Namiki 1, Tsukuba 305, Japan,* [b]*Institute for Materials Research, Tohoku University, Sendai 980, Japan, and* [c]*Laboratorium für Kristallographie, Eidgenssiche Technische Hochschule-Zentrum, CH-8092 Zürich, Switzerland. E-mail: yamamoto@nirim.go.jp*

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Abstract

A new hexagonal aluminium–chromium–nickel phase, $Al_{14.4}Cr_{3.4}Ni_{1.1}$, is described. The structure includes 12 icosahedral clusters in the unit cell, each of which consists of a transition metal (TM) atom at the center and 11 aluminium and one TM atom on the fivefold vertices of the icosahedron. Pairs of the clusters are linked along the *c* axis by sharing a triangular face. Two pairs of the clusters are joined by two trigonal antiprisms, constructing a column along the *c* axis. Six such columns are included in the unit cell and form the crystal structure. The second neighboring atoms connecting the columns are on the threefold axes of the icosahedral cluster.

Comment

It is important to know approximate crystalline structures for the understanding of quasicrystals. One of the authors (XZL) has reported a new hexagonal phase coexisting with the decagonal quasicrystalline phase in the Al–Cr–Ni and Al–Mn–Ni alloys (Zhou, Li & Kuo, 1989). Another crystalline phase in the Al–Cr–Ni system related to icosahedral quasicrystals is analyzed in this paper. This is hereafter called the κ phase.

The κ phase, $Al_{14.4}Cr_{3.4}Ni_{1.1}$, includes 12 icosahedral clusters in the unit cell. Pairs of the clusters are linked along the c axis by sharing a triangular face (Fig. 1). Two pairs of the clusters are joined by two trigonal antiprisms, constructing a column along the c axis. Six such columns are included in the unit cell and form the crystal structure. The Cr—Cr interatomic distance is 2.62 (1) Å, while the Cr—Al and Al—Al distances are 2.177 (8)–2.82 (1) and 2.64 (1)–2.83 (1) Å, respectively.

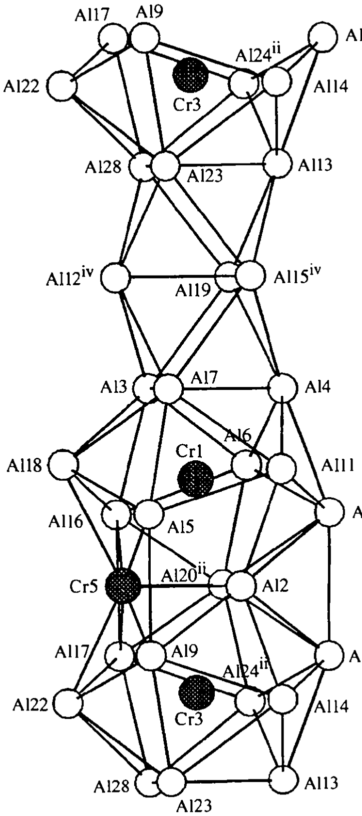

Fig. 1. Linkage of the icosahedral atom clusters in hexagonal κ-Al–Cr–Ni along the c axis. Shaded and open circles represent transition metal and Al atoms, respectively.

Experimental

An alloy with a nominal composition of $Al_{80}Cr_{10}Ni_{10}$ was prepared by melting high-purity metals in an arc furnace under an argon atmosphere. Single crystals of the κ phase were formed in slowly cooled ingots and extracted electrolytically from the aluminium-rich solid solution. They were gray and had a marked hexagonal prismatic appearance. The chemical composition of the κ phase is approximately $Al_{76}Cr_{18}Ni_6$ ($Al_{14.4}Cr_{3.4}Ni_{1.1}$), as obtained using a JEOL-2000FX electon microscope equipped with an energy-dispersive X-ray spectrometer.

Crystal data

$Al_{14.4}Cr_{3.4}Ni_{1.1}$
$M_r = 629.9$
Hexagonal
$P6_3$
$a = 17.674\ (3)$ Å
$c = 12.516\ (3)$ Å
$V = 3385.83$ Å^3
$Z = 12$
$D_x = 3.71$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 20.5$–$27.5°$
$\mu = 5.99$ mm^{-1}
$T = 298$ K
Tablet
$0.10 \times 0.05 \times 0.05$ mm
Gray

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: by integration
$T_{\min} = 0.248$, $T_{\max} = 0.985$
8649 measured reflections
3389 independent reflections
2452 reflections with $F > 3\sigma(F)$

$R_{\rm int} = 0.025$
$\theta_{\max} = 28.44°$
$h = -25 \rightarrow 0$
$k = -25 \rightarrow 25$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.052$
$wR = 0.057$
$S = 2.5$
2452 reflections
175 parameters
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 4.3$ e Å^{-3}
$\Delta\rho_{\min} = -1.3$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). Displacement parameters were isotropic. Since the κ phase is a ternary alloy, each atom site may be expected to be occupied by three atoms statistically. Two occupation probabilities for each site are needed provided that each site is fully occupied by three atoms. It is, however, difficult to determine such occupation probabilities using only X-ray diffraction because of the strong correlation between the occupation probabilities. Therefore, we assumed that each site is occupied by only two atoms and refined one occupation parameter for each site. In order to choose the pair of atoms, we assumed that the sites showing the 8 strongest peaks in the output list of *SIR*92 (Altomare *et al.*, 1994) were occupied by Cr and Ni and the sites with the next 13 strongest peaks were occupied by Al and Cr or Al and Ni so as to obtain reasonable displacement factors and a reasonable chemical composition. For a few sites, the displacement factors are zero within their standard uncertainties, implying that a third atom may also be present. However, there is no direct evidence that any site is occupied by the atoms shown in the supplementary data. It should be also noted that there is a correlation between the occupation probability and the displacement factor of a site, so that the standard uncertainties given have only limited significance. A penalty function constraining the total chemical 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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$Ca_3Y_2(Si_3O_9)_2$

Hisanori Yamane,[a] Toru Nagasawa,[a] Masahiko Shimada[a] and Tadashi Endo[b]

[a]*Institute for Advanced Materials Processing, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-77, Japan, and* [b]*Department of Materials Chemistry, Graduate School of Engineering, Tohoku University, Aramaki, Aoba-ku, Sendai 980-77, Japan. E-mail: yamane@ibis.iamp.tohoku.ac.jp*

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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 $(Ca_3^{2+}Y_2^{3+})_{5/6}(\text{vacant})_{1/6}SiO_3$, 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