Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). The scan range was $(0.8 + 0.35 \tan\theta)^\circ$ with a rate of 0.8–5.5° min^{-1}. Background counts were recorded for 25% of the range below and above each peak with a background/scan time ratio of 1/2. Cell refinement: *CAD*-4 *Software*. Data reduction, structure solution, structure refinement, molecular graphics and software used to prepare material for publication: *MolEN* (Fair, 1990).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1068). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Monoclinic $Y_2Al_3Si_2$ with a New Structure Type

T. I. Yanson, M. B. Manyako and O. I. Bodak

Department of Inorganic Chemistry, L'viv University, 6 Lomonosova Street, 290005 L'viv 5, Ukraine

R. E. Gladyshevskii, R. Cerny† and K. Yvon

Laboratoire de Cristallographie, Université de Genève, 24 quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

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Abstract

The structure of the title compound, trialuminium diyttrium disilicide, can be derived from the Au_2Mn_5 structure. The coordination polyhedron of Y has composition $[Si_5Al_7Y_5]$, those of the two Al sites have compositions $[Si_2Al_5Y_5]$ and $[Si_2Al_6Y_4]$, and that of Si has composition $[SiAl_3Y_5]$.

Comment

The ternary system Y–Al–Si at 773 K contains six compounds, four with known structures and compositions, *i.e.* YAl_2Si_2 [La_2O_2S *anti*-type structure (Murav'eva, Zarechnyuk & Gladyshevskii, 1971)], $YAl_{2.8}Si_{0.2}$ [Mg_3Cd *anti*-type structure (Murav'eva, Zarechnyuk & Gladyshevskii, 1971)], $YAl_{1.4}Si_{0.6}$ [own structure type (Yanson, 1975)] and Y_6Al_3Si [Tb_6Al_3Si type structure (Dubenko, Evdokimov & Titov, 1985)], and two with unknown structures and approximate compositions, *i.e.* YAl_2Si (Yanson, 1975) and $YAl_{1.1}Si_{0.9}$ (Murav'eva, Zarechnyuk & Gladyshevskii, 1971). Here we report the structure of 'YAl_2Si', which has the refined composition $Y_2Al_3Si_2$.

The structure can be considered to be a strongly distorted substitution variant of the Au_2Mn_5 type structure (Humble, 1964), which itself is an order substitution variant of cubic close packing, but should be considered as a new type. It contains the following coordination polyhedra (see Fig. 1): one Y-centred 17-fold polyhedron of composition $[Si_5Al_7Y_5]$, two Al-centred 12-fold polyhedra of compositions $[Si_2Al_5Y_5]$ for Al(1) and $[Si_2Al_6Y_4]$ for Al(2), and one Si-centred 9-fold polyhedron of composition $[SiAl_3Y_5]$. The polyhedron around Y can be described as a pentagonal prism formed by two Y, four Al and four Si atoms, with two Y atoms

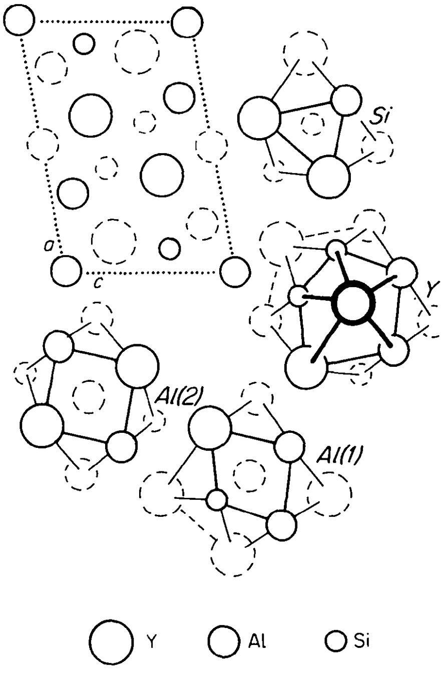

Fig. 1. Structural projection of monoclinic $Y_2Al_3Si_2$ along [010], showing coordination polyhedra. Full lines and circles are at height $\frac{1}{2}$, dashed lines and circles are at height 0.

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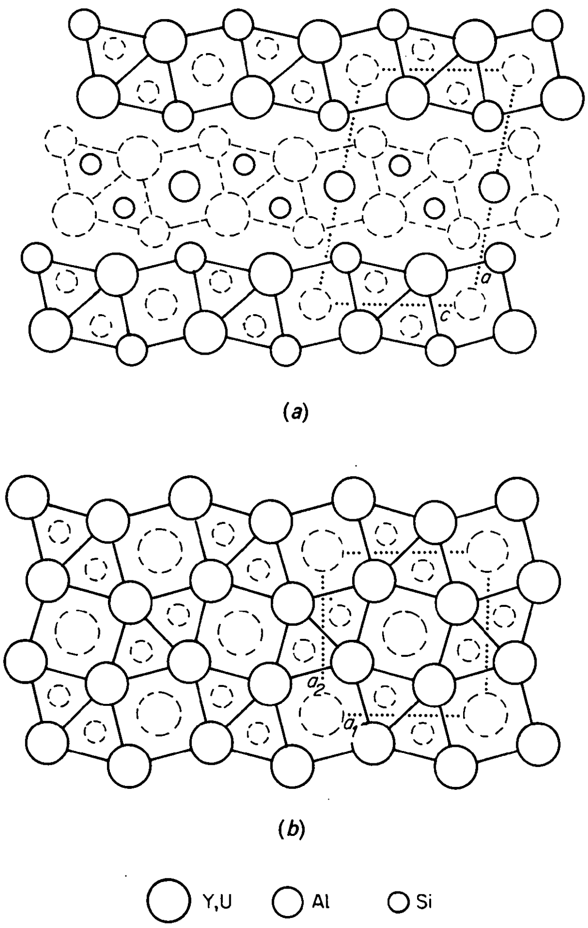
† On leave from Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic.

capping the pentagonal faces and one Y, three Al and one Si capping the rectangular faces. The two polyhedra around Al are distorted cuboctahedra, whereas the polyhedron around Si is a distorted trigonal prism formed by four Y and two Al atoms which is capped by one Y, one Al and one Si. Similar polyhedra are found in ternary aluminides containing rare earth and transition elements. In these compounds the transition element often plays the role of a non-metal such as B or Si. For example, in Pr_2Ni_2Al (W_2CoB_2 *anti*-type structure) Ni-centred trigonal $[Pr_4Al_2]$ prisms are interconnected *via* common Pr faces and Al edges (Rykhal', Zarechnyuk & Kuten', 1978). In the structures of Al-rich compounds, *e.g.* $YNiAl_3$ (Gladyshevskii & Parthé, 1992) and $YNiAl_4$ (Rykhal', Zarechnyuk & Yarmolyuk, 1972), Ni-centred trigonal prisms have the composition $[Y_2Al_4]$ and are isolated. In the present structure the Si-centred trigonal prisms are linked in pairs *via* common Y faces, giving rise to relatively short Si—Si distances.

The bond distances in $Y_2Al_3Si_2$ are in the usual range for metal-rich aluminides and silicides. Noteworthy are the short contacts within the Si pairs (Si—Si = 2.38 Å) and within the Al chains [Al(1)—Al(1) = 2.78 Å] running along [010]. An alternative way to describe the structure of $Y_2Al_3Si_2$ is as slabs (as shown in Fig. 2*a*) mutually shifted by *b*/2. The structural analogy with U_3Si_2 (Zachariasen, 1948) becomes apparent (Fig. 2*b*) from the way in which these slabs are intergrown.



(*a*)

(*b*)

Fig. 2. (*a*) Structural projection of monoclinic $Y_2Al_3Si_2$ along [010] and (*b*) comparison with the projection of tetragonal U_3Si_2 along [001]. Full lines and circles are at height $\frac{1}{2}$, dashed lines and circles are at height 0.

Experimental

Crystals were obtained *via* arc melting and annealing at 773 K for three weeks.

Crystal data

$Y_2Al_3Si_2$
$M_r = 314.93$
Monoclinic
$C2/m$
$a = 10.220$ (3) Å
$b = 4.0354$ (9) Å
$c = 6.617$ (2) Å
$\beta = 101.36$ (3)°
$V = 267.54$ (7) Å^3
$Z = 2$
$D_x = 3.909$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–17°
$\mu = 22.357$ mm^{-1}
$T = 293$ K
Needle
0.080 × 0.020 × 0.012 mm
Silverish

Data collection

Stoe Stadi 4 diffractometer
ω–2θ scans
Absorption correction: none
962 measured reflections
447 independent reflections
341 observed reflections $[|F| > 3\sigma(|F|)]$
$R_{\rm int} = 0.081$

$\theta_{\rm max} = 29.84°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 5$
$l = -9 \rightarrow 9$
2 standard reflections frequency: 60 min intensity variation: 2.2–2.7%

Refinement

Refinement on F
$R = 0.055$
$wR = 0.043$
$S = 1.75$
341 reflections
24 parameters
$w = 1/\sigma^2(|F|)$
$(\Delta/\sigma)_{\rm max} = 0.0001$
$\Delta\rho_{\rm max} = 3.8$ e Å^{-3}
$\Delta\rho_{\rm min} = -3.9$ e Å^{-3}

Extinction correction: Zachariasen (1968)
Extinction coefficient: $g = 0.021$ (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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}
Y	4 (*i*)	0.6202 (1)	0	0.3230 (2)	0.0082 (4)
Al(1)	4 (*i*)	0.3058 (4)	0	0.1342 (7)	0.014 (1)
Al(2)	2 (*a*)	0	0	0	0.016 (2)
Si	4 (*i*)	0.0931 (3)	0	0.6403 (6)	0.011 (1)

Table 2. *Selected interatomic distances* (Å)

Y—Si		2.892 (4)	Al(1)—Y		3.209 (4)
Y—Si	× 2	2.964 (3)	Al(1)—Y		3.260 (5)
Y—Si	× 2	3.015 (3)	Al(1)—Y		3.521 (5)
Y—Al(2)	× 2	3.019 (1)	Al(1)—Si		3.551 (5)
Y—Al(1)	× 2	3.188 (4)	Al(2)—Si	× 2	2.732 (4)
Y—Al(1)		3.209 (4)	Al(2)—Y	× 4	3.019 (1)
Y—Al(1)		3.260 (5)	Al(2)—Al(1)	× 2	3.076 (4)
Y—Al(1)		3.521 (5)	Al(2)—Al(1)	× 4	3.081 (4)
Y—Y		3.713 (2)	Si—Si		2.382 (5)
Y—Y	× 2	3.761 (2)	Si—Al(1)	× 2	2.599 (3)
[Y—Y	× 2	4.035 (1)]	Si—Al(2)		2.732 (4)
Al(1)—Si	× 2	2.599 (3)	Si—Y		2.892 (4)
Al(1)—Al(1)	× 2	2.780 (4)	Si—Y	× 2	2.964 (3)
Al(1)—Al(2)		3.076 (4)	Si—Y	× 2	3.015 (3)
Al(1)—Al(2)	× 2	3.081 (4)	Si—Al(1)		3.551 (5)
Al(1)—Y	× 2	3.188 (4)			

Structure solution was performed using *MULTAN*87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987). Least-squares refinement included varying a scale factor, isotropic extinction, atomic positional and anisotropic displacement parameters. Programs used for data reduction and structure refinement were from the *Xtal*3.2 system (Hall, Flack & Stewart, 1992).

Lists of structure factors, anisotropic displacement parameters and bond distances have been deposited with the IUCr (Reference: DU1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Synthetic Spheniscidite

M. Cavellec, D. Riou and G. Ferey

Laboratoire des Fluorures – URA 449 Faculté des Sciences, Université du Maine, 72017 Le Mans CEDEX, France

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Abstract

Spheniscidite, ammonium hydroxide iron phosphate dihydrate, $[Fe_2(NH_4)(OH)(PO_4)_2].2H_2O$, is known as a mineral isotypic with leucophosphite. Crystals were obtained by hydrothermal synthesis at medium temperature. The crystal structure determination confirms the leucophosphite structure type and provides detailed localization of the water molecules and ammonium cations inside the cavities of the framework.

Comment

With a view to synthesizing some oxyfluorinated phosphates of iron which have microporous frameworks, we investigated the system $FeO(OH)–H_3PO_4–HF$–1,3-diaminopropane (hereafter 1,3-DAP)–H_2O through the synthetic route described by Tapp, Milestone & Bibby (1988), which uses an organic amine as a template. Under our reaction conditions, 1,3-DAP decomposed and $[Fe_2(NH_4)(OH)(PO_4)_2].2H_2O$, which corresponds to the formula of spheniscidite (Wilson & Bain, 1986), was formed. The structure of mineral spheniscidite has not yet been described, but is claimed to be isotypic with leucophosphite $[KFe_2(PO_4)_2(OH)].2H_2O$ (Moore, 1972). Related substances with this well known structure type, but different chemical compositions, can be found in the literature: $GaPO_4.2H_2O$ (Mooney-Slater, 1966), also labelled $GaPO_4–C_7$ by Wang, Yang, Feng, Shang & Xu (1989), and $RbMo_2P_2O_{10}.1-xH_2O$ (Leclaire, Borel, Grandin & Raveau, 1994). The detailed structure determination of spheniscidite is presented here.

The three-dimensional network of spheniscidite is built up from octahedrally coordinated Fe^{III} and PO_4 tetrahedra. It can also be described as the corner sharing of octameric building units (Fig. 1*a*). This octamer consists of an edge-sharing bioctahedron of Fe^{III}, whose common edge is delimited by two OH groups which are also shared with the satellite octahedra. One vertex of each satellite octahedron is occupied by a terminal water molecule. The octamer is completed by four PO_4 tetrahedra, each sharing either two or three corners with the Fe octahedra of the octamer. After their linkage, these octamers adopt a quasi-cc lattice within the unit

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