Les listes des facteurs de structure et des facteurs d'agitation thermique anisotrope ont été déposées au dépôt d'archives de l'UICr (Référence: DU1053). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

Références

Becker, P. & Coppens, P. (1974). *Acta Cryst.* **A31**, 417–425.
Busing, W. R. (1971). *Acta Cryst.* **A27**, 683–684.
Carpentier, J. D. & Hwu, S. J. (1992). *J. Solid State Chem.* **97**, 332–339.
Lemoine, P., Carré, D. & Guittard, M. (1984). *Acta Cryst.* **C40**, 910–912.
Lemoine, P., Tomas, A. & Guittard, M. (1992). *Acta Cryst.* **C48**, 774–776.
Mazurier, A., Jaulmes, S. & Guittard, M. (1987). *Acta Cryst.* **C43**, 1859–1861.
Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.
Patrie, M., Flahaut, J. & Domange, L. (1965). *Rev. Hautes Temp. Refract.* **2**, 187–198.
Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
Tomas, A., Vovan, T., Guittard, M., Flahaut, J. & Guymont, M. (1985). *Mater. Res. Bull.* **20**, 1027–1030.

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$BaCoS_2$

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Abstract

The structure of $BaCoS_2$ is a slightly distorted monoclinic version of the $BaNiS_2$ structure [Grey & Steinfink (1970). *J. Am. Chem. Soc.* **92**, 5093–5095.] The small change in the monoclinic angle from 90 to 90.43 (4)° brings the atoms closer together along the former $[1\bar{1}0]$ tetragonal direction and further apart along the former [110] direction.

Comment

As the existence of a phase $BaCoS_2$ had been reported previously (Grey & Steinfink, 1970), we attempted a survey of the Ba(Ni,Co)S_2 system using powder diffraction methods. The cell dimensions of the tetragonal phase $BaNiS_2$ vary with composition up to roughly 80 at.% Co, at which point several of the powder diffraction lines broadened, indicating either a change in symmetry or the existence of a new phase. The determination of the single-crystal structure of pure $BaCoS_2$ described here confirms the indication from the powder diffraction studies that a new phase is present at the cobalt-rich end

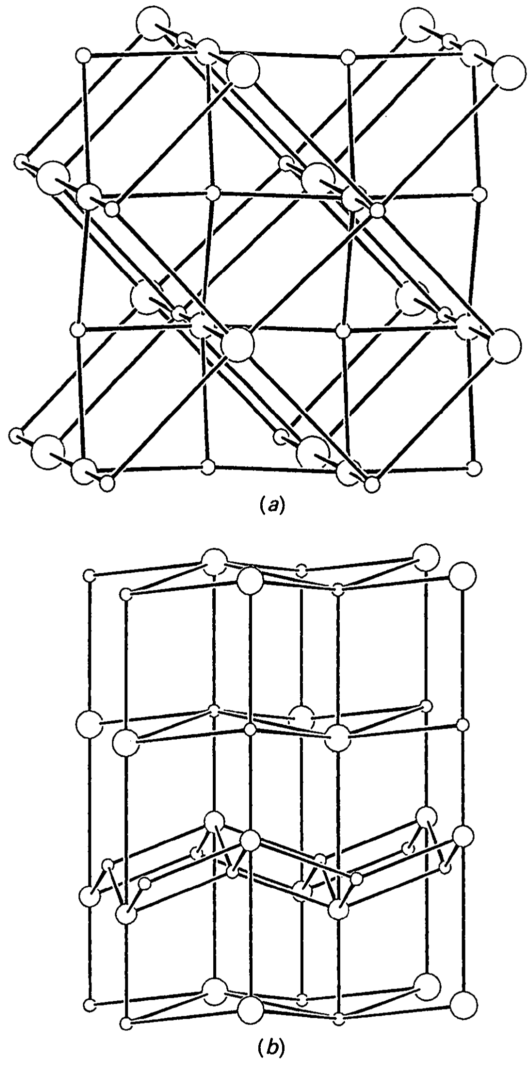

Fig. 1. The structure of $BaCoS_2$. Four unit cells are shown. Large circles represent Ba, small circles S. (*a*) Near plan view along the related $BaNiS_2$ tetragonal *c* axis (monoclinic *b* axis) showing edge-sharing CoS_4 groups (effectively Co_2S_2) sandwiched between the double BaS layers with the NaCl structure. (*b*) Near elevation view perpendicular to the $BaNiS_2$ tetragonal *c* axis showing the Co_2S_2 layer sandwiched between BaS layers.

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of the $BaCoS_2$–$BaNiS_2$ system. This phase differs only slightly from $BaNiS_2$. Although $BaNiS_2$ is a metallic conductor, $BaCoS_2$ is an antiferromagnetic semiconductor.

Note added in proof. During the review stage of this paper the authors received an advanced copy of a paper (Snyder, Gelabert & DiSalvo, 1994) which confirms the crystallographic work reported here.

Experimental

$BaCoS_2$ was prepared by mixing 0.8487 g of BaS and 0.8631 g of $CoS_{0.86}$ and pressing the mixture into pellets, which were then placed in a graphite crucible and sealed in a quartz tube under a vacuum. The mixture was heated at a rate of 10 K min^{-1} to 1223 K, held at this temperature for 16 h, and then cooled at a rate of 0.5 K min^{-1} to room temperature. Small thin square black crystals were then picked from the sample.

Crystal data

$BaCoS_2$
$M_r = 260.40$
Monoclinic
$P2/n$
$a = 4.573$ (3) Å
$b = 8.937$ (2) Å
$c = 4.570$ (2) Å
$\beta = 90.43$ (4)°
$V = 186.8$ (2) Å^3
$Z = 2$
$D_x = 4.632$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 20$–23.3°
$\mu = 15.79$ mm^{-1}
$T = 295$ K
Square platelet
0.12 × 0.12 × 0.026 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from θ–2θ scans
Absorption correction: analytical method of Templeton & Templeton (1973)
$T_{\min} = 0.247$, $T_{\max} = 0.665$
1316 measured reflections
358 independent reflections

292 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.022$
$\theta_{\max} = 25°$
$h = -5 \rightarrow 5$
$k = -10 \rightarrow 10$
$l = -5 \rightarrow 5$
3 standard reflections
frequency: 60 min
intensity variation: <0.4%

Refinement

Refinement on F
$R = 0.021$
$wR = 0.025$
$S = 1.062$
285 reflections
35 parameters
Calculated weights $w = 1/[\sigma^2(F) + (0.01F)^2 + 1.0]$
$(\Delta/\sigma)_{\max} = 0.11$

$\Delta\rho_{\max} = 1.3$ e Å^{-3}
$\Delta\rho_{\min} = -1.2$ e Å^{-3}
Extinction correction: $F_c^* = F_c/(1 + gI_c)$
Extinction coefficient: 5.0 (1) × 10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

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

	x	y	z	$U_{\rm eq}$
Ba	3/4	0.1976 (1)	3/4	0.0133 (11)
Co	3/4	0.5938 (2)	3/4	0.0157 (3)
S(1)	3/4	0.8490 (3)	3/4	0.0146 (5)
S(2)	3/4	1/2	1/4	0.0305 (6)

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

Ba—Co	3.541 (1)	Co—S(1)	2.281 (3)
Ba—S($1^{\rm i}$)	3.115 (2)	Co—S(2)	2.434 (1)
Ba—S($1^{\rm ii}$)	3.247 (3)	Co—S($2^{\rm vi}$)	2.434 (1)
Ba—S($1^{\rm iii}$)	3.271 (3)	Co—S($2^{\rm iii}$)	2.435 (1)
Ba—S($1^{\rm iv}$)	3.271 (3)	Co—S($2^{\rm v}$)	2.435 (1)
Ba—S($1^{\rm v}$)	3.247 (3)		
Co—Ba—S($1^{\rm i}$)	180.00	S($2^{\rm vi}$)—Co—S($2^{\rm iii}$)	82.81 (2)
Co$^{\rm ii}$—Ba—S($1^{\rm i}$)	120.07 (7)	S($2^{\rm vi}$)—Co—S($2^{\rm v}$)	83.57 (2)
Co$^{\rm iii}$—Ba—S($1^{\rm i}$)	119.88 (7)	S($2^{\rm iii}$)—Co—S($2^{\rm v}$)	139.73 (6)
Co$^{\rm iv}$—Ba—S($1^{\rm i}$)	119.08 (7)	Ba$^{\rm vii}$—S(1)—Co$^{\rm vii}$	180.0
Co$^{\rm v}$—Ba—S($1^{\rm i}$)	120.06 (7)	Ba$^{\rm vii}$—S(1)—Ba$^{\rm ii}$	97.37 (4)
S($1^{\rm i}$)—Ba—S($1^{\rm ii}$)	82.63 (4)	Ba$^{\rm vii}$—S(1)—Ba$^{\rm iii}$	97.31 (4)
S($1^{\rm i}$)—Ba—S($1^{\rm iii}$)	82.68 (4)	Ba$^{\rm vii}$—S(1)—Ba$^{\rm iv}$	97.31 (4)
S($1^{\rm i}$)—Ba—S($1^{\rm iv}$)	82.68 (4)	Ba$^{\rm vii}$—S(1)—Ba$^{\rm v}$	97.37 (4)
S($1^{\rm i}$)—Ba—S($1^{\rm v}$)	82.63 (4)	Co—S(1)—Ba$^{\rm ii}$	82.63 (4)
S($1^{\rm ii}$)—Ba—S($1^{\rm iii}$)	89.03 (9)	Co—S(1)—Ba$^{\rm iii}$	82.68 (4)
S($1^{\rm ii}$)—Ba—S($1^{\rm iv}$)	89.10 (9)	Co—S(1)—Ba$^{\rm iv}$	82.68 (4)
S($1^{\rm ii}$)—Ba—S($1^{\rm v}$)	165.26 (4)	Co—S(1)—Ba$^{\rm v}$	82.63 (4)
S($1^{\rm iii}$)—Ba—S($1^{\rm iv}$)	165.37 (6)	Ba$^{\rm ii}$—S(1)—Ba$^{\rm iii}$	89.03 (1)
S($1^{\rm iii}$)—Ba—S($1^{\rm v}$)	89.10 (9)	Ba$^{\rm ii}$—S(1)—Ba$^{\rm iv}$	89.10 (1)
S($1^{\rm iv}$)—Ba—S($1^{\rm v}$)	89.03 (9)	Ba$^{\rm ii}$—S(1)—Ba$^{\rm v}$	165.26 (8)
Ba—Co—S(2)	69.85 (9)	Ba$^{\rm iii}$—S(1)—Ba$^{\rm iv}$	165.27 (8)
Ba—Co—S($2^{\rm vi}$)	69.85 (9)	Ba$^{\rm iii}$—S(1)—Ba$^{\rm v}$	89.10 (1)
Ba—Co—S($2^{\rm iii}$)	69.87 (8)	Ba$^{\rm iv}$—S(1)—Ba$^{\rm v}$	89.03 (1)
Ba—Co—S($2^{\rm v}$)	69.87 (8)	Co$^{\rm viii}$—S(2)—Co	139.71 (4)
S(1)—Co—S($2^{\rm iii}$)	110.13 (3)	Co$^{\rm viii}$—S(2)—Co$^{\rm ii}$	97.19 (1)
S(1)—Co—S($2^{\rm v}$)	110.13 (3)	Co$^{\rm viii}$—S(2)—Co$^{\rm iv}$	96.43 (1)
S(2)—Co—S($2^{\rm vi}$)	139.71 (6)	Co—S(2)—Co$^{\rm ii}$	96.43 (1)
S(2)—Co—S($2^{\rm iii}$)	83.57 (2)	Co—S(2)—Co$^{\rm iv}$	97.19 (1)
S(2)—Co—S($2^{\rm v}$)	82.81 (2)	Co$^{\rm ii}$—S(2)—Co$^{\rm iv}$	139.73 (4)

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

The structure was determined by analogy with the structure of $BaNiS_2$. Intensity data were averaged based on the monoclinic cell, averaging the Friedel equivalents. Anisotropic refinements were carried out in space groups Pn and $P2/n$. For Pn, 285 observations/36 parameters, $R = 0.0219$, $wR = 0.0270$, $S = 1.160$; for $P2/n$, 285 observations/21 parameters, $R = 0.0211$, $wR = 0.0255$, $S = 1.097$. Because neutral-atom scattering factors were used for all elements, the site occupancies were refined, arbitrarily setting the occupancy of the Ba site to unity. In $P2/n$ the refined site occupancies were Co 0.996 (3), S(1) 1.007 (6) and S(2) 1.006 (6); 285 observations/24 parameters, $R = 0.0211$, $wR = 0.0254$, $S = 1.062$. In Pn the refined site occupancies were Co 0.987 (3), S(1) 1.035 (6) and S(2) 1.003 (6); 285 observations/39 parameters, $R = 0.0212$, $wR = 0.0251$, $S = 1.084$, extinction parameter = 1.71 (6) × 10^{-6}. The atom positions and bond distances and angles quoted in this work are based on the refinement carried out in $P2/n$ which included refinement of the site occupancies, although there are no significant differences among the values for any of the refinements listed here. The atomic displacement parameters are about twice as large in the monoclinic ac plane (the tetragonal ab plane) as in the direction perpendicular to this plane. These parameters did not vary significantly among the different refinements either.

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.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Grey, I. E. & Steinfink, H. (1970). *J. Am. Chem. Soc.* **92**, 5093–5095.

Snyder, G. J., Gelabert, M. C. & DiSalvo, F. J. (1994). *J. Solid State Chem.* Submitted.

Templeton, L. & Templeton, D. (1973). *Proc. Am. Crystallogr. Assoc.* Storrs, CT, p. 143, Abstract E10.

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Monoclinic $Y_2Al_3Si_2$ with a New Structure Type

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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

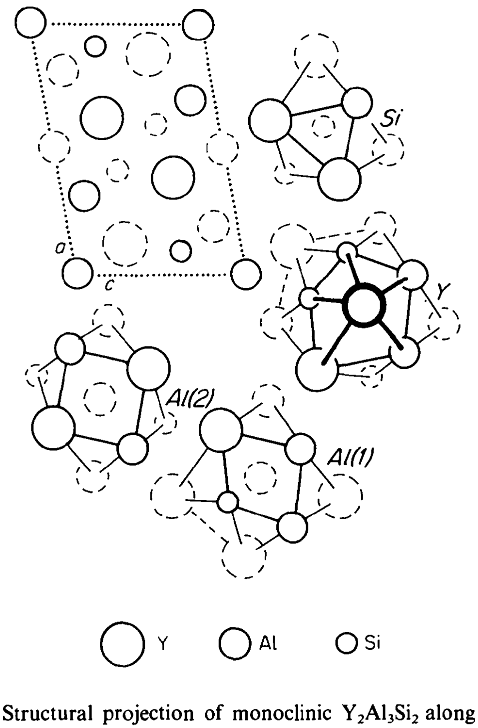

Fig. 1. Structural projection of monoclinic $Y_2Al_3Si_2$ along [010], showing coordination polyhedra. Full lines and circles are at height $\frac{1}{2}$, dashed lines and circles are at height 0.

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