Structure of Aluminium Indium Trisulphide

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Abstract. AlInS$_3$, hexagonal, $P6_1$, $a = 6\cdot6712$ (7), $c = 17\cdot835$ (8) Å, $V = 687\cdot4$ Å^3, $Z = 6$, $D_c = 3\cdot45$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6\cdot48$ mm^{-1}, F(000) = 660; final $R = 0\cdot026$. The structure is closely related to that of In$_2$Se$_3$. In is fivefold coordinated by S whereas Al is tetrahedrally coordinated.

Introduction. During our studies of the Al$_2$S$_3$–In$_2$S$_3$ system we found the new compound AlInS$_3$. Its crystal growth was performed by chemical vapour transport with iodine in sealed, evacuated quartz ampoules and a temperature gradient of 1073–1023 K. Crystals form light-yellow transparent hexagonal pyramids. A single crystal (75 × 75 × 325 μm) was taken for Laue, Weissenberg and precession photographs showing hexagonal symmetry and systematically absent reflections for 000l, $l \neq 6n$. Since a positive SHG effect was detected there remain four possible noncentrosymmetric space groups: $P6_1$, $P6_5$, $P6_122$, and $P6_522$. To suppress extinction effects, the crystal was quenched several times in liquid nitrogen. Intensities were collected on an automatic four-circle diffractometer (Enraf–Nonius CAD-4) with graphite-monochromatized Mo $K\alpha$ radiation and an ω–2θ scan mode.

All calculations were performed with a Geneva version of the XRAY system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). 2929 reflections were measured in the range $\theta < 35°$, which reduced to 939 independent reflections with $I > 3\sigma(I)$. Intensities were corrected for absorption and Lorentz–polarization effects. From a Patterson map the position of the In atom was found. Subsequent Fourier maps yielded the Al and three S atom positions.

Refinement of the atomic positions and isotropic thermal parameters resulted in $R = 0\cdot075$ with the correct space group $P6_1$. Additional refinement with anisotropic thermal parameters and isotropic extinction yielded the final $R = 0\cdot026$* and an average shift/error of 10^{-4}. Scattering factors for Al, In and S (Cromer & Mann, 1968) were used and corrected for anomalous

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Table 1. *Fractional atomic coordinates* (×10^4)

	x	y	z
In	6687 (1)	−50 (1)	1250 (0)
Al	3199 (4)	3309 (3)	1529 (1)
S(1)	2945 (3)	−56 (3)	1152 (1)
S(2)	285 (4)	3677 (4)	1078 (1)
S(3)	6779 (3)	6356 (3)	1418 (1)

Table 2. *Interatomic distances* (Å) *and angles* (°)

In–S(1)	2·500 (3)	Al–S(1)	2·267 (4)
–S(2)	2·463 (2)	–S(2)	2·228 (4)
–S(3)	2·447 (3)	–S(3)	2·240 (3)
–S(2')	2·678 (2)	–S(1')	2·310 (3)
–S(3')	2·683 (3)		

S(1)–In–S(2)	117·4 (1)	S(1)–Al–S(2)	111·4 (1)
S(1)–In–S(3)	121·4 (1)	S(1)–Al–S(3)	113·0 (1)
S(1)–In–S(3')	84·0 (1)	S(1)–Al–S(1')	102·6 (1)
S(1)–In–S(2')	90·5 (1)	S(2)–Al–S(3)	117·5 (1)
S(2)–In–S(3)	121·0 (1)	S(2)–Al–S(1')	111·3 (1)
S(2)–In–S(3')	87·9 (1)	S(3)–Al–S(1')	99·3 (1)
S(2)–In–S(2')	95·1 (1)		
S(3)–In–S(3')	94·2 (1)		
S(3)–In–S(2')	88·3 (1)		
S(3')–In–S(2')	174·4 (1)		

dispersion. The atomic coordinates are listed in Table 1, interatomic distances and angles in Table 2.

Discussion. Fig. 1 shows a section parallel to (0001) at height $z \sim 0\cdot13$. The structure is built up by six of these layers. Fig. 2 shows the (01$\bar{1}$0) plane.

In and S form a slightly distorted trigonal bipyramid. Three S are located in the equatorial plane [S(1), S(2), and S(3)] with In–S distances of 2·500, 2·463, and 2·447 Å; the two others lie above [S(2')] and below [S(3')] the In atom at 2·678 and 2·683 Å, building the axis of the bipyramid parallel to z. The Al atom is coordinated by a S tetrahedron. Three S are located in a plane parallel to (0001), the fourth lying above Al, the Al–S distances being 2·267, 2·228, 2·240 and 2·310 Å.

The structure of AlInS$_3$ is closely related to that of In$_2$Se$_3$ (Likforman, Carré & Hillel, 1978). The relation-
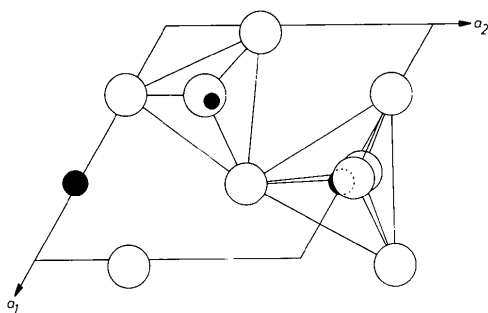
Fig. 1. View of the structure at $z \sim 0 \cdot 13$. The small dot is Al, the medium In; open circles are S.
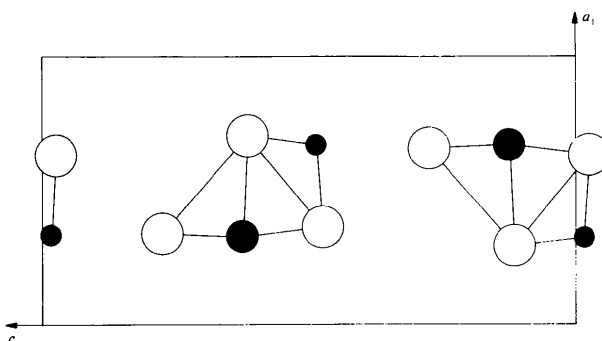

Fig. 2. Atomic positions on the $(01\bar{1}0)$ plane.

ships to the wurtzite structure type are: from ZnS to Al_2S_3 the hexagonal close packing of S is maintained but only $\frac{2}{3}$ of the corresponding tetrahedral voids are occupied by the metal; from Al_2S_3 to In_2Se_3 a strong distortion of some of the anion positions parallel to c is found, setting up a new fivefold coordination of one half of the voids. These are now occupied by In(1) in In_2Se_3 and by In in $AlInS_3$. The other half of the voids remain tetrahedrally coordinated and are occupied by In(2) in In_2Se_3 and Al in $AlInS_3$.

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Structure of Threadgoldite

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Abstract. $Al[(PO_4)_2(UO_2)_2].OH.8H_2O$ (a mineral from Kobokobo, Kivu, Zaïre), monoclinic, *Cc*, $a = 20 \cdot 168\,(8)$, $b = 9 \cdot 847\,(2)$, $c = 19 \cdot 719\,(4)$ Å, $\beta = 110 \cdot 71\,(2)°$, $Z = 8$, $V = 3663$ Å³, $D_m = 3 \cdot 4$, $D_c = 3 \cdot 33$ Mg m⁻³; structure type: torbernite. The $[(PO_4)(UO_2)]_n^{n-}$ layers are connected principally by Al_2O_{10} groups which are composed of two octahedra.

Introduction. Threadgoldite is a mineral recently described by Deliens & Piret (1979). The results are here completed with the structure determination. The space group *Cc* or *C2/c* was determined from

Weissenberg and precession photographs (systematic absences: hkl: $h + k = 2n + 1$; $h0l$: $l = 2n + 1$). However, if a few weak reflexions are neglected, the following unit cell is found: $a' = 9 \cdot 530$, $b' = 9 \cdot 847$, $c' = 9 \cdot 860$ Å, $\beta' = 98 \cdot 2°$, $V' = V/4$ with $a' = a/2 + c/4$, $b' = -b$, $c' = -c/2$, space group $A2$, Am or $A2/m$.

Refinement of the structure with this unit cell or with the true unit cell (see *Abstract*) in space group $C2/c$ displays apparent disorder, especially for the Al_2O_{10} group. Consequently, the true space group is *Cc*, for which no disorder appears. Cell dimensions and intensities were measured on a Syntex $P2_1$ four-circle