

Ag_{3.5}Bi_{7.5}S₁₃, a new member (*N* = 8) of the homologous series [Bi₂S₃]₂·[AgBiS₂]_{(*N*-1)/2}

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The silver bismuth tridecasulfide Ag_{3.5}Bi_{7.5}S₁₃ crystallizes in the monoclinic space group *C2/m*. Its structure is built up of two alternating kinds of layered modules parallel to (001). In the module denoted *A*, octahedra around the metal positions (*M* = Ag/Bi, *M2* and an S atom on *2/m*, other atoms on *m*) alternate with paired monocapped trigonal prisms around Bi. The NaCl-type module *B* is composed of parallel eight-membered chains of edge-sharing octahedra running diagonally across it. Ag_{3.5}Bi_{7.5}S₁₃ is the member with *N* = 8 of the pavonite homologous series ^{*N*}*P* of ternary compounds with the general formula [Bi₂S₃]₂·[AgBiS₂]_{(*N*-1)/2}.

Comment

Current knowledge of ternary sulfides with silver and bismuth is somewhat incomplete. Only the existence of AgBiS₂ (Geller & Wernick, 1959), 'AgBi₆S₉' (*N* = 4; Mumme, 1990), Ag₂Bi₆S₁₀ (*N* = 5; Makovicky *et al.*, 1977) and Ag₃Bi₇S₁₂ (*N* = 7; Herbert & Mumme, 1981) have been reported to date. All these phases lie on the Ag₂S–Bi₂S₃ pseudo-binary section in the ternary Ag–Bi–S system. The three latter compounds crystallize in the monoclinic space group *C2/m* and adopt structures that are closely related to each other. Their structures are built up of two alternating kinds of layered modules, denoted *A* and *B*. Module *A* is composed of double chains of monocapped trigonal prisms around Bi atoms, which alternate in the [100] direction with octahedrally coordinated metal atoms (*M* = Ag or Bi). Module *B* represents NaCl-like fragments of varying thickness defined by the parameter *N*, which corresponds to the number of octahedra within the chain of edge-sharing octahedra that runs diagonally across the module (Fig. 1). The structures of the above-mentioned phases with *N* = 4, 5 and 7 belong to the homologous series [Bi₂S₃]₂·[AgBiS₂]_{(*N*-1)/2} (pavonite series), denoted by ^{*N*}*P* (Makovicky *et al.*, 1977). Known and hypothetical members of the series can be derived from the first member, Ag_{0.5}Bi_{4.5}S₇ (*N* = 2), by successive additions of (AgBiS₂)_{0.5} equivalents to the NaCl-like module *B*, AgBiS₂ being the end member with *N* = ∞.

The title compound, Ag_{3.5}Bi_{7.5}S₁₃, represents the member with *N* = 8 of the homologous series [Bi₂S₃]₂·[AgBiS₂]_{(*N*-1)/2}. It crystallizes in the monoclinic space group *C2/m* and is isotypic with Cu_{1.34}Ag_{2.38}Pb_{1.44}Bi_{6.28}S₁₃ (Mumme, 1990). Its structure is built up according to the principle described above. The NaCl-type module *B* is, in this case, eight octahedra thick (Fig. 2). Therefore, Ag_{3.5}Bi_{7.5}S₁₃ can be denoted by the symbol ⁸*P*, according to the nomenclature of pavonite homologues.

Atom Bi1 displays a slightly distorted monocapped trigonal prismatic coordination of S atoms (Table 1). The cations *M2* to *M6* exhibit octahedral environments with varying degrees of distortion. The 'octahedron' around *M2* is the most distorted, with two short bonds [2.564 (3) Å] in *trans* positions and four elongated bonds [2.870 (8) Å] in the equatorial plane. This type of distortion towards a linear coordination ([2+4] geometry) is commonly observed for Ag atoms in the struc-

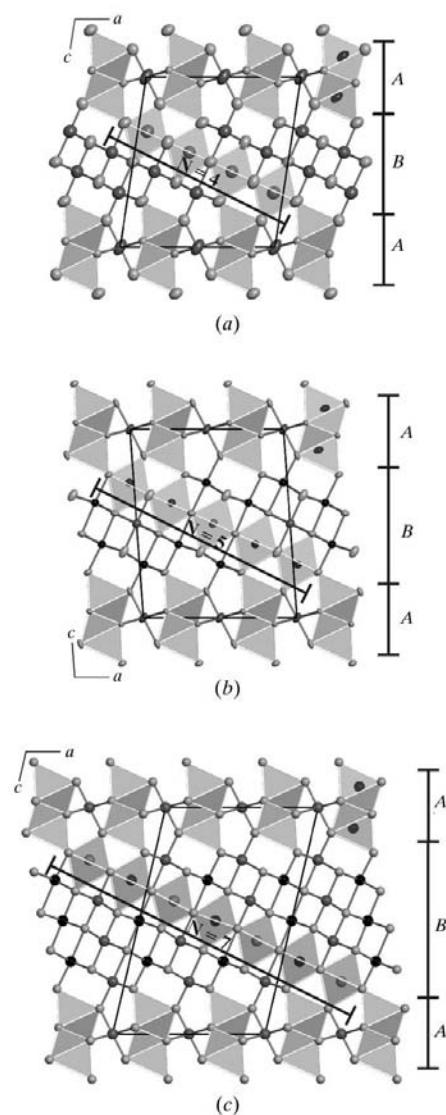


Figure 1
Comparison of the structures of three [Bi₂S₃]₂·[AgBiS₂]_{(*N*-1)/2} homologues, viz. (a) 'AgBi₆S₉' (*N* = 4), (b) Ag₂Bi₆S₁₀ (*N* = 5, pavonite) and (c) Ag₃Bi₇S₁₂ (*N* = 7). Bi atoms are represented by black spheres, Ag/Bi by medium-grey spheres and S atoms by light-grey spheres.

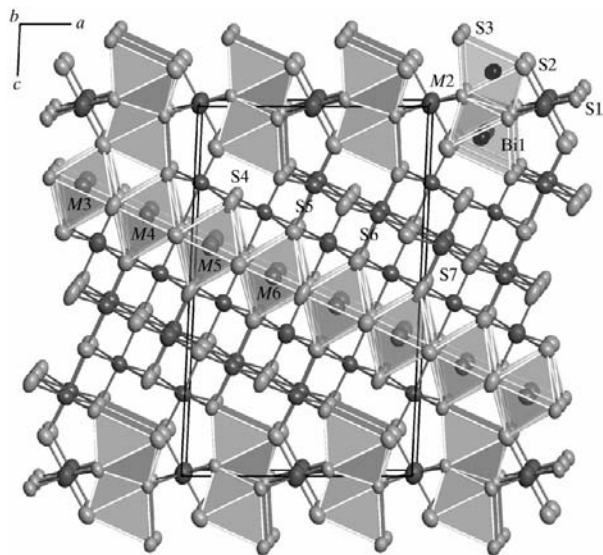


Figure 2
The crystal structure of $\text{Ag}_{3.5}\text{Bi}_{7.5}\text{S}_{13}$. Displacement ellipsoids are drawn at the 95% probability level for all atoms. *M* denotes Ag/Bi.

tures of multinary silver-containing bismuth chalcogenides. Typical examples are various members of the pavonite homologous series. The octahedra around the *M3* and *M4* positions are distorted towards [1+2+2+1] geometry, with short bonds *trans* to long bonds. Similar coordination environments are usually observed for Bi atoms in many multinary bismuth sulfosalts. The *M5* and *M6* positions display more regular octahedral environments, with bond distances ranging between 2.754 (2) and 2.899 (2) Å.

All octahedral metal positions show Ag/Bi mixed occupancy. The composition of each position obtained from the refinement is consistent with the above analysis of the distortion of their coordination polyhedra. The *M2* position shows a preference for Ag atoms (79%), while the *M3* and *M4* positions are predominantly occupied by Bi atoms (78% for *M3* and 84% for *M4*). In the *M5* position, Ag dominates, while in *M6* more Bi is found. The Ag/Bi disorder generally observed in octahedrally coordinated metal positions in the structures of pavonite homologues can be related to their general formula. For odd members ($N = 5$ and 7), an ordered distribution of Ag and Bi between the metal positions may be envisaged, while for even members ($N = 4$ and 8), some octahedral positions will necessarily be of mixed occupancy or a superstructure must be established.

Experimental

Single crystals of $\text{Ag}_{3.5}\text{Bi}_{7.5}\text{S}_{13}$ were obtained as a by-product of a solid-state reaction involving AgI and Bi_2S_3 in the molar ratio 1:1. The mixture of the starting materials was thoroughly ground and loaded into a silica tube, which was flame-sealed under a pressure of 10^{-2} Torr (1 Torr = 133.322 Pa). The tube was placed in a tubular oven, heated at 850 K for 7 d and then rapidly cooled to room temperature. The product consisted of a mixture of black plate-shaped crystals of AgBiS_2 (Geller & Wernick, 1959), $\text{Ag}_2\text{Bi}_6\text{S}_{10}$ (Makovicky *et al.*, 1977) and $\text{Ag}_{3.5}\text{Bi}_{7.5}\text{S}_{13}$ (about 30% of the product),

together with grey needle-shaped crystals of $(\text{Bi}_2\text{S}_3)_9\text{BiI}_3$ (Miehe & Kuřcik, 1971). Qualitative energy-dispersive X-ray analysis performed on the single crystal of $\text{Ag}_{3.5}\text{Bi}_{7.5}\text{S}_{13}$ used for this study revealed an average composition $\text{Ag}_{3.43(2)}\text{Bi}_{7.48(2)}\text{S}_{13}$. No indication of iodine was detected in the crystal.

Crystal data

$\text{Ag}_{3.5}\text{Bi}_{7.5}\text{S}_{13}$
 $M_r = 2361.80$
Monoclinic, $C2/m$
 $a = 13.3237$ (2) Å
 $b = 4.0455$ (4) Å
 $c = 21.484$ (3) Å
 $\beta = 92.90$ (1)°
 $V = 1156.5$ (2) Å³
 $Z = 2$

$D_x = 6.782$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 1295 reflections
 $\theta = 2.9$ – 26.0 °
 $\mu = 60.9$ mm⁻¹
 $T = 297$ (2) K
Plate, black
 $0.14 \times 0.04 \times 0.02$ mm

Data collection

Stoe IPDS-1 diffractometer
 φ oscillation scans
Absorption correction: numerical [*X-RED32* (Stoe & Cie, 2001); crystal description using *FACEIT* (Stoe & Cie, 1999), optimization using equivalent reflections (*X-SHAPE*; Stoe & Cie, 1999)]
 $T_{\min} = 0.067$, $T_{\max} = 0.343$

3944 measured reflections
1295 independent reflections
980 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\text{max}} = 26.0$ °
 $h = -16 \rightarrow 16$
 $k = -4 \rightarrow 4$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.104$
 $S = 1.07$
1295 reflections
81 parameters
 $w = 1/[\sigma^2(F_o^2) + (0.041P)^2 + 88.7342P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.009$
 $\Delta\rho_{\text{max}} = 1.90$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.47$ e Å⁻³
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.00038 (6)

Table 1

Selected interatomic distances (Å) (*M* = Ag/Bi).

Bi1–S1 ⁱ	2.607 (3)	M4–S5	2.885 (2)
Bi1–S2	2.791 (7)	M4–S6	3.004 (2)
Bi1–S1	2.901 (2)	M5–S4	2.754 (2)
Bi1–S3	3.466 (3)	M5–S6	2.851 (2)
M2–S2 ⁱ	2.564 (3)	M5–S5 ⁱⁱ	2.860 (1)
M2–S1	2.870 (8)	M5–S7 ⁱⁱⁱ	2.899 (2)
M3–S2	2.610 (2)	M6–S6 ^{iv}	2.787 (2)
M3–S3 ⁱⁱⁱ	2.781 (8)	M6–S5	2.797 (2)
M3–S4	2.929 (2)	M6–S7	2.854 (10)
M3–S5 ⁱⁱⁱ	2.980 (2)	M6–S6	2.856 (10)
M4–S3	2.630 (2)		
M4–S4	2.813 (9)		

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

In the first stage of the refinement, the Bi positions *M3*, *M4* and *M6* showed displacement parameters larger than that of *M1* = Bi1. This suggested that, in addition to Bi, these positions are partially occupied by the lighter element Ag. On the other hand, the displacement parameters of the Ag positions *M2* and *M5* were smaller than that of Bi1 and mixed occupancy with the heavier element Bi was also considered for these positions. The SUMP restraint was used to ensure the electroneutrality of the compound. The final occupancies of these positions obtained from the refinement were: *M2* = 79% Ag + 21% Bi, *M3* = 22% Ag + 78% Bi, *M4* = 16% Ag + 84% Bi, *M5* = 64% Ag + 36% Bi and *M6* = 33% Ag + 67% Bi.

Data collection: *EXPOSE* (Stoe & Cie, 2000); cell refinement: *CELL* (Stoe & Cie, 2000); data reduction: *INTEGRATE* (Stoe & Cie, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL97* and *DIAMOND*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1196). Services for accessing these data are described at the back of the journal.

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