Poster

The Trigonal Crystal Structure of Matildite-Type $AgBiS_2$ Revisited

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If it appears as a mineral, the ternary sulfide $AgBiS_2$ can crystallize as schapbachite (cubic, space group: $Fm3m$, $a = 564.8$ pm, $Z = 2$) with a cation-disordered rock-salt structure (Ag^+/Bi^{3+} at 4*a*, S at 4*b*) [1] or as an ordered trigonal variety (matildite). The latter was first considered as adopting the delafossite structure of α-$NaFeO_2$ with layerwise ordering of the still octahedrally coordinated cations within a cubic close packing of the S^{2-} anions [1]. The space group, however, given as $P3m1$ instead of $R3m$, was conflicting with this structure model. We now were able to refine the crystal structure of maltildite-type $AgBiS_2$ in a similar trigonal unit cell ($a = 407.75(4)$, $c = 1898.3(2)$ pm) again, but with an ordered cinnabar-related set up, adopting the space group $P3_221$. The ordering of the involved ions on the Wyckoff positions 3*b* (Ag^+), 3*a* (Bi^{3+}) and 6*c* (S^{2-}) brings several advantages for the cations. Their different sizes is nicely reflected by the individual distances (d(Ag–S) = 253.0 pm (2×), 285.5 pm (2×) and 312.7 pm (2×) versus d(Bi–S) = 267.8 pm (2×), 286.3 pm (2×) and 304.8 pm (2×)) and their stereochemical demands are fulfilled by their local geometry (short linear S–Ag–S links for *C.N.* = 2 (Ag^+: [Kr]$4d^{10}$) versus four rather similar Bi–S contacts for *C.N.* = 4 with a sew-saw conformation allowing for the development of stereochemically active lone-pair of electrons at the Bi^{3+} cation ([Xe]$6sp5d^{10}$) pointing to the remote edge of the distorted $[BiS_6]^{9-}$ octahedron (Figure 1). This is illustrated in Figure 1 as compared to the cinnabar-type structure of HgS (a = 414.89(2), c = 949.47(5) pm [2]), where the diversification is hidden behind the Hg–S distances (d(Hg–S) = 237.7 pm (2×), 309.3 pm (2×) and 327.9 pm (2×)) for the unique Hg^{2+} cation ([Xe]$5d^{10}$).

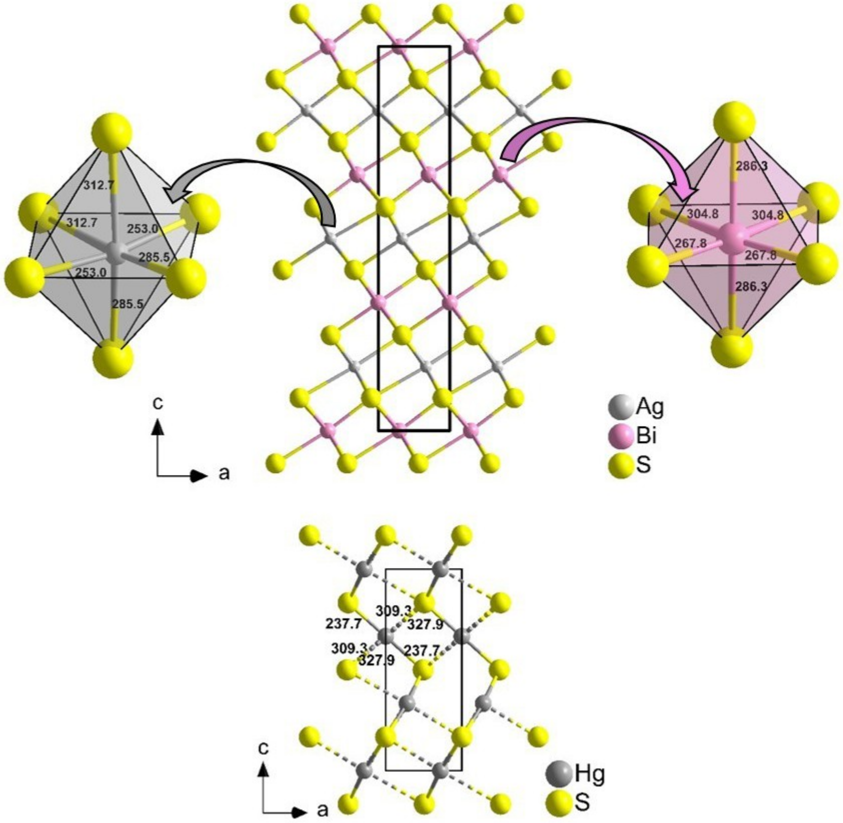

Figure 1. The trigonal crystal structure of matildite-type $AgBiS_2$ as compared to the cinnabar-type structure of HgS

[1] Geller, S.; Wernick, J. H. (1959) *Acta Crystallogr.* **12**, 46.

[2] Schleid, Th., Lauxmann, P.; Schneck, C. (1999) *Z. Kristallogr.* **16**, 95.