

Crystal structures of chalcostibite (CuSbS₂) and emplectite (CuBiS₂)

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Crystal structures of chalcostibite CuSbS₂ (orthorhombic, space group Pnma, $a = 6.018(1)$ Å, $b = 3.7958(6)$ Å, $c = 14.495(7)$ Å, $V = 331.1(1)$ Å³, $Z = 4$, $R_1 = 0.040$, $wR_2 = 0.155$ for 533 reflections) and emplectite CuBiS₂ (orthorhombic, space group Pnma, $a = 6.134(1)$ Å, $b = 3.9111(8)$ Å, $c = 14.548(8)$ Å, $V = 348.8(2)$ Å³, $Z = 4$, $R_1 = 0.037$, $wR_2 = 0.112$ for 492 reflections) were redetermined using a four-circle diffractometer and graphite-monochromatized MoK α radiation. These two crystal structures are composed of MS₅ square pyramids (M = Sb and Bi) and nearly regular CuS₄ tetrahedra. The five M-S bond distances in SbS₅ square pyramid in chalcostibite are always shorter than corresponding distances in the BiS₅ square pyramid in emplectite because the Sb atom is smaller than that of the Bi atom. The a cell parameter increases appreciably from chalcostibite to emplectite not only because of increasing M-S bond distances in MS₅ square pyramid, but also increasing Cu-S(2)-Cu bond angles along the a axis. The increase of b cell parameter is caused mainly by increasing M-S bond distances along the b axis. In contrast, slight increase of the c cell parameter is largely brought about by decreasing Cu-S(2)-Cu bond angles ascribed to weakened stereochemical activity of Bi 6s² lone pair electrons. The anisotropic change of unit cell parameters from chalcostibite to emplectite is associated strongly with directions of lone pair electrons in the unit cell.