

Crystal structures of chalcostibite (CuSbS₂) and emplectite (CuBiS₂): Structural relationship of stereochemical activity between chalcostibite and emplectite

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ABSTRACT

The crystal structures of chalcostibite CuSbS₂ (orthorhombic, space group *Pnma*, $a = 6.018(1)$, $b = 3.7958(6)$, and $c = 14.495(7)$ Å, $V = 331.1(1)$ Å³, $Z = 4$, $R1 = 0.040$, $wR2 = 0.155$ for 533 reflections) and emplectite CuBiS₂ (orthorhombic, space group *Pnma*, $a = 6.134(1)$, $b = 3.9111(8)$, and $c = 14.548(8)$ Å, $V = 348.8(2)$ Å³, $Z = 4$, $R1 = 0.037$, $wR2 = 0.112$ 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 ($M = \text{Sb}$ and Bi) and nearly regular CuS₄ tetrahedra. The five M -S bond distances in the 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 the Bi atom. The a cell parameter increases appreciably from chalcostibite to emplectite not only because of increasing M -S bond distances in the MS₅ square pyramid, but also because of increasing Cu-S2-Cu bond angles along **a**. The increase in the b cell parameter is caused mainly by increasing M -S bond distances along **b**. In contrast, the slight increase of the c cell parameter is largely brought about by decreasing Cu-S2-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 strongly associated with the positions of the lone-pair electrons in the unit cell.