Crystal structures of chalcostibite (CuSbS$_2$) and emplectite (CuBiS$_2$): Structural relationship of stereochemical activity between chalcostibite and emplectite

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ABSTRACT

The crystal structures of chalcostibite CuSbS$_2$ (orthorhombic, space group Pnma, $a = 6.018(1)$, $b = 3.7958(6)$, and $c = 14.495(7)$ Å, $V = 331.1(1)$ Å$^3$, $Z = 4$, $R_1 = 0.040$, $wR_2 = 0.155$ for 533 reflections) and emplectite CuBiS$_2$ (orthorhombic, space group Pnma, $a = 6.134(1)$, $b = 3.9111(8)$, and $c = 14.548(8)$ Å, $V = 348.8(2)$ Å$^3$, $Z = 4$, $R_1 = 0.037$, $wR_2 = 0.112$ for 492 reflections) were redetermined using a four-circle diffractometer and graphite-monochromatized MoK$_\alpha$ radiation. These two crystal structures are composed of MS$_5$ square pyramids ($M$ = Sb and Bi) and nearly regular CuS$_8$ tetrahedra. The five $M$-S bond distances in the SbS$_5$ square pyramid in chalcostibite are always shorter than corresponding distances in the BiS$_8$ square pyramid in emplectite because the Sb atom is smaller than the Bi atom. The $c$ cell parameter increases appreciably from chalcostibite to emplectite not only because of increasing $M$-S bond distances in the MS$_5$ square pyramid, but also because of increasing Cu-S$_2$-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-S$_2$-Cu bond angles ascribed to weakened stereochemical activity of Bi 6$s^2$ 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.

INTRODUCTION

Chalcostibite CuSbS$_2$ and emplectite CuBiS$_2$ are isostructural (Hofmann 1933; Portheine and Nowacki 1975; Razmara et al. 1997). Their structures comprise square pyramids of Sb (or Bi) linked to form chains of Sb$_2$ (or Bi$_2$) along $b$ and CuS$_8$ tetrahedra forming chains of CuS$_4$ parallel to $b$ (Razmara et al. 1997). These two types of infinite chains are linked to form sheets that are perpendicular to $c$ (Portheine and Nowacki 1975; Razmara et al. 1997). These structures can be imagined as being made up of slices of the SnS$_3$-like structure parallel to (101) and (101–)SnS$_3$ (Portheine and Nowacki 1975; Razmara et al. 1997). Their structures comprise square pyramids of Sb (or Bi) linked to form chains of Sb$_2$ (or Bi$_2$) along $b$ and CuS$_8$ tetrahedra forming chains of CuS$_4$ tetrahedra (Hofmann 1933; Portheine and Nowacki 1975; Razmara et al. 1997). The main parts of the crystal structures of chalcostibite and emplectite that have been described previously (Portheine and Nowacki 1975; Razmara et al. 1997) are ascribed to inelastic linkages between the SbS$_2$ (or BiS$_2$) + CuS$_4$ chains parallel to $b$ (Razmara et al. 1997).

RESULTS AND DISCUSSION

The samples of chalcostibite and emplectite used in this study are from Rar el Anz, east of Casablanca, Morocco, and Kaefersteige, Schwarzwald, Germany. Chemical compositions of the crystals were analyzed quantitatively by electron microprobe (Superprobe JXA-8600; JEOL), with an acceleration voltage of 25 kV and a beam current of 10 nA. The natural and synthetic standards used were as follows: Cu metal (CuK$_\alpha$), stibnite (Sb$_2$O$_3$), Bi$_2$Te$_3$ (Bi$_4$), (BiMn)$_2$, and pyrite (SFe$_2$O$_4$). Microprobe analyses showed no marked deviation from ideal compositions. Trace metals (e.g., Ag, As, and Pb) were less than their detection limits of 0.1 wt%.

Single crystals suitable for intensity data collection were fixed on a glass capillary 0.1 mm in diameter and mounted on a four-circle diffractometer (CAD4; Enraf-Nonius B.V., Netherlands) using graphite-monochromatized MoK$_\alpha$ radiation ($\lambda = 0.71069$ Å). The unit-cell parameters were carefully measured and determined accurately from a least-squares fit to the corrected setting angles of 25 reflections between 10° ≤ $\theta$ ≤ 13° (Table 1). Diffraction data were collected at room temperature up to 0 = 30°. Data reduction, including background and Lorentz polarization correction, was carried out with the SDP program system (Enraf-Nonius 1983). An empirical absorption correction using the $\psi$-scan technique was applied. Structural refinements were performed with the SHELXL-97 program (Sheldrick 1997). Several refinement cycles were carried out using first isotropic, then anisotropic thermal displacement parameters. The final $R_1$ values converged to 0.040 for 533 unique reflections and 0.037 for 492 unique reflections. Table 2 summarizes crystallographic data and the details of the refinements. Tables 3 and 4 list atomic coordinates, atomic displacement parameters, and selected bond distances and angles.

EXPERIMENTAL METHODS

The main parts of the crystal structures of chalcostibite and emplectite that have been described previously (Portheine and Nowacki 1975; Razmara et al. 1997) are consistent with the results of the present refinements. However, the details of the interatomic bond distances and angles have been clarified.

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