Stacking disorder and polytypism in enargite and luzonite

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ABSTRACT

Microstructures of enargite and luzonite (Cu3AsS4) were studied using high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED). Enargite and luzonite are intergrown at the atomic level in samples from Recsk, Hungary. Both minerals typically contain faults along the planes of their close-packed layers. Comparisons of electron micrographs and images simulated for several types of fault models indicate that the planar defects can be interpreted as stacking faults in the regular cubic (luzonite) or hexagonal (enargite) sequence of close-packed layers. In addition to disordered layer sequences, two long-period, rhombohedral polytypes—9R, (21), and 24R, (311111)—occur in enargite. The presence of defect-free luzonite and enargite indicates that both minerals grew directly from the hydrothermal solution. The disordered structures represent transitional structural states between luzonite and enargite and probably reflect the effects of fluctuating conditions during hydrothermal deposition.

INTRODUCTION

Enargite and luzonite are polytypes of Cu3AsS4; they occur intergrown in many ore deposits. We wished to determine the microstructural and chemical characteristics of their intergrowths, because a better knowledge of these polytypic sulﬁdes is useful for the understanding of conditions and processes that control ore formation in a hydrothermal environment. The structure-types of enargite and luzonite are widespread in nature and important in materials science. Luzonite crystallizes in a sphalerite-type, cubic close-packed (ccp) structure, whereas enargite has a wurtzite-type, hexagonal close-packed (hcp) structure. Luzonite is tetragonal (space group I42m, a = 0.533, c = 1.057 nm; Maruno and Nowacki 1967) and enargite is orthorhombic (space group Pmn21, a = 0.7401, b = 0.6436, c = 0.6154 nm; Adiwidjaja and Löhn 1970).

The similarities and differences between the two structures are best seen from a direction parallel to the close-packed layers (Fig. 1). The metal atoms are tetrahedrally coordinated by S in both structures; in Figure 1 the S tetrahedra project as isosceles triangles. Because the apices of all metal-ﬁlled tetrahedra point along the same direction, the two structures are non-centrosymmetric. Cu and As atoms occupy the metal positions in an ordered fashion. Half of the metal-atom columns that are parallel to <110>110 or <100>1m contain only Cu atoms (marked X), and in half of them As and Cu atoms alternate (marked Y). The stacking sequences of S and metal layers that are parallel to (112)110 and (001)1m can be conveniently described using the ABC notation for close-packed structures. If capital letters denote the positions of S atoms and lowercase letters represent metal atoms (in enargite and luzonite, As is considered a metal), the stacking sequence of luzonite is AbBeCaAbBeCa . . . , and the stacking in enargite is AbBaAbBa . . . .

Sb can substitute for As in the enargite structure by up to about 20 mol% Cu3SbS4 (Springer 1969); whereas a complete solid solution series exists between the ccp luzonite (Cu3AsS4) and famatinite (Cu3SbS4) (Gaines 1957; Lévy 1967; Kanazawa 1984).

Polysynthetic twinning is common in luzonite (Gaines 1957; Lévy 1967; Sugaki et al. 1982), and some enargite crystals show characteristic striations under the optical microscope (Sztrokay 1944). Our preliminary TEM studies (Pósfai 1991) indicated that samples from several localities (including Reck, Hungary; Quiruvilca, Peru; Cosihuiriachic, Mexico) contain disordered luzonite and disordered enargite crystals.

The goal of the present paper is to study the nature of structural disorder by identifying the atomic structure of defects. A characterization of relationships between microstructures and compositions is given in another paper (Pósfai and Buseck 1998).

EXPERIMENTAL METHODS

We studied samples from the Lahóca Hill mine at Reck, Mátra Mountains, Hungary. This locality is sometimes referred to as Mátrabánya (Springer 1969) or Parád (Lévy 1967) in the mineralogical literature. Enargite and luzonite occur together in the metasomatized ore bodies; enargite is dark brown or black and forms elongated, prismatic crystals. Luzonite occurs in pinkish gray masses. Macroscopic and optical characteristics of the two min-