Phase relationships in the system ZnS-CuInS$_2$: Insights from a nanoscale study of indium-bearing sphalerite

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**Abstract**

Micrometer- to submicrometer-scale indium-rich domains are preserved within sphalerite included in hornfels-hosted pyrrhotite from the Dulong polymetallic skarn, Yunnan, China. The nano-mineralogy of the ZnS-bearing blebs was investigated using scanning transmission electron microscopy on thinned foils extracted in situ from pyrrhotite. Indium incorporation in sphalerite occurs via the coupled substitution $2\text{Zn}^{2+} \leftrightarrow \text{Cu}^{+} + \text{In}^{3+}$; the results thus allow insights into phase relationships in the system ZnS-CuInS$_2$ in which solubility limits are debated with respect to a cubic to tetragonal phase transition. The highest concentrations of In are measured in basket-weave domains from the smallest ZnS blebs or from un-patterned areas in coarser, irregular ZnS inclusions in pyrrhotite. Indium-rich domains contain 17–49 mol% CuInS$_2$, whereas In-poor sphalerite contains <5 mol% CuInS$_2$. Atomic-scale metal order–ordering observed in In-(Cu)-rich ZnS domains was modeled as mixed sites in a cubic structure with $P\bar{4}m3m$ symmetry and empirical formula $[(\text{Cu},\text{In},\text{Zn})_3(\text{Zn}_{0.5}\text{Fe}_{0.5})]_4\text{S}_4$. This sphalerite modification is distinct from the cubic-tetragonal phase transition reported elsewhere for analogous, synthetic phases with abundant planar defects. The $\text{Zn}_1\text{Fe}_{0.5}\text{CuInS}_4$ nanophase described here potentially represents a Fe-bearing polymorph of $\text{Zn}_2\text{CuInS}_4$, considered as an end-member in the sakuraiite solid-solution series. At $\leq$50 mol% CuInS$_2$ in the ZnS-CuInS$_2$ system, incorporation of In via coupled In$^+\text{Cu}$ substitution is promoted within a cubic ZnS phase with lower symmetry than sphalerite rather than into the spatially coexisting chalcopyrite of tetragonal symmetry. Solid-state diffusion accounts for phase re-equilibration resulting in the basket-weave textures typical of In-(Cu)-rich domains in the smallest blebs, whereas fluid percolation assists grain coarsening in the irregular inclusions. The results show evidence for the existence of a more complex phase transition than previously recognized from experimental studies, and, intriguingly, also to a potential eutectic in the system ZnS-CuInS$_2$. Pyrrhotite-bearing hornfels in skarns may concentrate In and other critical metals hosted in sphalerite and related sulfides due to the efficient scavenging from fluid by these minerals and the subsequent preservation of those included phases by sealing within the pyrrhotite matrix.

**Keywords:** Sphalerite, indium, system ZnS-CuInS$_2$, HAADF STEM

**Introduction**

Sphalerite is the dominant source of indium, a critical element of economic interest due to expanding applications in photoconductors, semi-conductors, and other advanced technologies (e.g., Werner et al. 2017). Knowledge about how critical metals occur in nature is of importance for identifying new resources and optimizing recovery from existing operations. This is particularly relevant in the case of In, which seldom forms independent minerals.

Zinc sulfide (ZnS) crystallizes as close-packed structures, of which the most common are the cubic $3C$ and hexagonal $2H$ structures in sphalerite, (Zn,Fe)S, and its polymorph wurtzite, respectively (Pósfai and Buseck 1997, and references therein; Table 1). These are referred to as ZnS$_{3C}$ and ZnS$_{2H}$ hereafter. Indium is a chalcophile element, almost exclusively occurring in sulfides (Cook et al. 2011a) and, in most base metal sulfide ores, will be preferentially partitioned into sphalerite over coexisting Cu-Fe-sulfides (George et al. 2016). Unlike isovalent substitutions, e.g., Zn$^{2+} \leftrightarrow \text{Fe}^{2+}$, incorporation of trivalent atoms such as In$^+$ requires a coupled substitution, of which the most common is: $2\text{Zn}^{2+} \leftrightarrow \text{Cu}^{+} + \text{In}^{3+}$ (e.g., Cook et al. 2012). Other substitution mechanisms have, however, been proposed based on measured inter-element correlations, including those involving available monovalent ions (e.g., Ag$^{+}$), and Sn commonly considered of tetravalent charge. Such substitutions are more complex and stipulate the presence of vacancies (□) or different oxidation