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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 $2Zn^{2+} \leftrightarrow Cu^{+} + In^{3+}$; 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 ordering observed in In-(Cu)-rich ZnS domains was modeled as mixed sites in a cubic structure with $P\bar{4}3m$ symmetry and empirical formula $[(Cu,In,Zn)_3(Zn_{0.5}Fe_{0.5})]_4S_4$. This sphalerite modification is distinct from the cubic-tetragonal phase transition reported elsewhere for analogous, synthetic phases with abundant planar defects. The $Zn_{1.5}Fe_{0.5}CuInS_4$ nanophase described here potentially represents a Fe-bearing polymorph of Zn_2CuInS_4, considered as an end-member in the sakuraiite solid-solution series. At ≤50 mol% $CuInS_2$ in the ZnS-$CuInS_2$ system, incorporation of In via coupled In+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