

The state of copper, silver and indium in sphalerite studied by X-ray spectroscopy of synthetic crystals and natural minerals

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Sphalerite (Zn, Fe)S is a host mineral for a wide range of minor and trace elements including Ag and In. The concentration of Ag strongly correlates with the amount of In in the ore. In most samples of natural sphalerites In concentrations show a positive correlation with Cu which implies the coupled substitution mechanism $2\text{Zn}^{2+} \leftrightarrow \text{Cu}^+ + \text{In}^{3+}$. Based on similar chemical properties of Ag and Cu it can be suggested that the formation of a solid solution in Ag-In-bearing sphalerite corresponds to the scheme $2\text{Zn}^{2+} \leftrightarrow \text{Ag}^+ + \text{In}^{3+}$. X-ray absorption spectroscopy (XAS) was applied to determine the local atomic environment and the valence state of the admixtures of Cu, Ag, and In in synthetic and natural sphalerites.

Sphalerite crystals were synthesized using three methods: gas transport (In-Ag-bearing sphalerites, In-bearing sphalerite), salt-flux method (In-Cu-bearing sphalerites), and dry synthesis (In-Ag-bearing sphalerite). Natural samples were collected from La Florida mine, Spain (PE-6 and PE-8) and Picos de Europa deposit, Spain (CL-1). The phase compositions of sphalerite samples were confirmed by X-ray diffraction (XRD). The morphology of the crystals was studied by means of scanning electron microscopy (SEM/EDS). Chemical composition was determined via electron probe microanalysis (EPMA) and laser ablation inductively coupled mass spectrometry (LA-ICP-MS).

In accordance with XANES spectroscopy the studied elements are present in sphalerite in +3 (In), +2 (Cu), +1 (Ag, Cu), and 0 (Ag) “formal” oxidation states.

Results of the EXAFS spectroscopy study of synthetic crystals demonstrate that when Ag is the only admixture in sphalerite it occurs in the form of metal Ag^0 . In the presence of In the solid solution Ag^+ predominates over Ag^0 , In exists in the solid solution state as well. When sphalerite contains only Cu without any other admixtures, Cu occurs in the form of covellite (CuS) microinclusions. In Cu-In-bearing sphalerites both Cu and In are present in the solid solution state. Contrast to Ag and Cu, In alone forms the solid solution with sphalerite, according to the scheme: $3\text{Zn}^{2+} \leftrightarrow 2\text{In}^{3+} + \text{Y}$, where Y is a vacancy at cation position. In the samples of natural sphalerites the local atomic environment in the 1st coordination shell corresponds to tenorite (CuO).

In addition, X-ray emission spectra (XES) of Cu in covellite and some other Cu-bearing sulfides are presented and discussed.

Our data demonstrate that In, Cu and Ag present in sphalerite in the solid solution state, which is stabilized by charge compensation scheme $2\text{Zn}^{2+} \leftrightarrow \text{Me}^+ + \text{Me}^{3+}$.