

Indium incorporation in synthetic sphalerite: examination via powder diffraction and XANES spectroscopy

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Indium, used in several high technology applications, is hosted mainly in sulfidic ores (e.g. sphalerite) and is regarded as strategic or critical metal [1]. Hydrometallurgical recovery rates of In from sphalerite-bearing ores depend on efficient leaching technologies. Standardised sphalerite samples are required to model and understand the leaching behaviour, and finally to optimize the leaching procedure as a crucial step to maximise the In extraction.

Sphalerite samples that are potentially beneficial as In-leaching standards were sintered in a melt-freeze procedure from homogenized ZnS powders with 0.05 to 10 wt.% In as dopant in a toroidal high pressure cell at $p = 8$ GPa and up to $T = 1800$ K. This treatment also removes wurtzitic stacking faults from the sphalerite ZnS (sp-ZnS) yielding a defect-free ZnS(In) reference material. Phase composition and microstructure parameters, especially the recovery of stacking faults, were deduced from X-ray diffraction via full powder pattern fitting of a dedicated stacking fault model.

In-L₃ X-ray Absorption Near Edge Structure (XANES) spectroscopy is used to reveal the atomic structure of In in sp-ZnS by comparing sample spectra and spectra of In-bearing minerals as references (fingerprint). Usually, In is incorporated together with copper in the sp-ZnS structure, replacing zinc atoms via coupled substitution [2]. XANES spectra of In doped sp-ZnS indicate that incorporation of In without concurrent Cu uptake is possible. Up to ~0.1 wt.%, In is tetrahedrally coordinated with S demonstrated by the similarity of sample spectra with the roquesite (CuInS₂) spectrum as reference for [InS₄] tetrahedra. Beyond 0.1 wt.%, additionally, octahedrally coordinated In is observed. The leaching behaviour of In-doped Cu-free ZnS reference materials is evaluated in biological leaching experiments with respect to the In coordination in ZnS in order to get a deeper understanding of ecological In-leaching.

[1] EU Commission (2014). [2] Johan (1988) *Mineral Petrol* **39**, 211-229.