

The binding state of indium and tin in natural sulphides: first results of a comparative study by X-ray absorption spectroscopy at the L-edge

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One electron makes the difference between the outer shell of In and Sn, two scarce metals with very distinct crystal chemical behaviour in the Earth's crust: indium is clearly chalcophile, very seldom forming specific minerals and occurring mainly dispersed within excess-metal polymetallic sulphides, while tin is markedly lithophile and currently present as stannic oxide.

Indium is nowadays widely used in many technologic fields (low melting-temperature alloys, solders and various «high-tech» devices like liquid crystal displays (LCD), organic light emitting diodes (OLED), transparent flexible thin-films of ionic amorphous oxide semiconductors (IAOS), photovoltaic cells with increased efficiency based on Cu(In,Ga)Se₂ (CIGS)). As a consequence, indium consumption is expected to increase in the near future, centring a special interest on the improvement of its exploitation from polymetallic sulphide ores, along with its recycling technology.

Indium recovery stands mostly on zinc extraction from the natural cubic sulphide – sphalerite, the prototype of so-called «tetrahedral structures» where metal ions fill half of the available tetrahedral sites within the cubic closest packing of sulphur anions. Such anionic array is thus particularly suitable to accommodate poly-cations in close edge-sharing tetrahedral sites [1,2], as occurs in excess-metal copper sulphides (e.g., bornite, ideally Cu₅FeS₄), recognized to be relevant In-carrier minerals in many polymetallic sulphide ore deposits. A similar situation holds for the tetrahedral [Sn₂S₆] cluster in special meso-structured semiconductors [3].

X-ray absorption spectroscopy at the L-edges (arising from *s,p* → *d* transitions) is a suitable methodology for probing unoccupied density of states and *s-p* orbital hybridization [4]. Accordingly, a comparative study of In and Sn by X-ray absorption near-edge spectroscopy (XANES) at the L₃-edge was undertaken at the ESRF (European Synchrotron Radiation Facility in Grenoble/France) using the instrumental set-up of beamline ID21.

Beyond two edge shoulders ascribed to 2*s* → 5*p* transitions that were also observed in the In L₃-edge spectra of wurtzite-type indium nitride [5], a third weak white line was noticed at lower energy (3,730 eV) in the XANES spectra collected from a polymetallic ore sample. An identical pattern of pre-edge details was detected in Sn L₃-edge XANES spectra collected at the same irradiated point – an expectable result in view of earlier data [5]. However, a single intense «white line» at 3,730 eV was noticed in a faint In L₃-edge XANES spectra collected at another point of the same ore sample but the impossibility of clearly identifying the nanoscale phase hosting indium has hindered a full interpretation of X-ray absorption data. Further work is in progress focusing on coexisting indium and tin.

Acknowledgements: Work developed through the project PTDC/CTE-GIN/67027/2006 financed by the Portuguese Foundation for Science & Technology (MCTES). Financial support of EU to perform the experiments at the ESRF.

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Sulfur speciation in silicates: an X-ray absorption spectroscopy study

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There is still ambiguity on sulfur speciation in some silicate minerals, especially for minerals that are characterized by cages in its structure (like sodalite group minerals). Several minerals from different localities like

- lazurite ((Na,Ca)₈[(S,SO₄,Cl₂)|Al₆Si₆O₂₄]),
- hackmanite (Na₈[Al₆Si₆O₂₄](Cl₂,S),
- afghanite ((Na,Ca,K)₈[(Cl₂,SO₄,CO₃)₃|Al₆Si₆O₂₄]x0.5H₂O),
- nosean (Na₈[SO₄|Al₆Si₆O₂₄]),
- hauyne ((Na,Ca)₄₋₈[Al₆Si₆(O,S)₂₄](SO₄,Cl)₁₋₂) and
- davynite ((Na,K)₆Ca₂[(Cl₂,SO₄)₂|Al₆Si₆O₂₄])

have been investigated by x-ray absorption spectroscopy at the sulfur K-edge in order to get information on sulfur valence and molecular structure.

The measurements have been performed at the X-ray Beamline for Environmental Studies (SUL-X) of the synchrotron radiation source ANKA in Karlsruhe in normal focus and partly in microfocus to separate signals from minerals when they are inter-grown with other sulfur containing phases.

The X-ray absorption near edge structure (XANES) spectra are classified with respect to pre-edge features and edge structures. Hackmanites for example show a sharp pre-edge at the lowest energy so far recognized in S K-edge x-ray absorption spectra [1]. Lazurites are characterized by a sulfate resonance and spectral features that indicate reduced sulfur species. Ultramarine color pigments show two types of spectra, both indicate reduced reduced sulfur species, too.

Besides the above mentioned minerals and color pigments helvine (Mn₄Be₃[S|(SiO₄)₃]), vishnevite ((Na,K)₈[(SO₄,CO₃)|Al₆Si₆O₂₄]x2H₂O) and other non-tectosilicates like ellestadite (Ca₅(SiO₄,PO₄,SO₄)₃(F,OH,Cl)) have been included in the study.

The results will be compared with non-silicate compounds and minerals where sulfur is the main constituent, like elemental sulfur, iron sulfides and different sulfites and sulfates.

A first attempt to gain structural information on sulfur in silicate minerals using S K-edge Extended Fine structure (EXAFS) spectroscopy will also be discussed.

[1] Goettlicher, J. et al. (2010) *Deutsche Tagung für Forschung mit Synchrotronstrahlung, Neutronen und Ionenstrahlen an Großgeräten SNI 2010*. Berlin, Freie Universität.