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Introduction

Indium became one of the most relevant scarce metals used in the last decades to produce new "high-tech devices" based on innovative nanotechnologies - liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) and the recently introduced transparent flexible thin-films (TFTs) [1], manufactured with ionic amorphous oxide semi-conductors (IAOs) within the systems In-Sn-O (ITO) and In-Ga-Zn-O (IGZO). Since the early 1970s, ternary semi-conducting compounds of chalcopyrite-type turned also into promising materials for photovoltaic solar cells with increased efficiency - e.g., Cu(In,Ga)Se₂ (CIGS).

Indium is a typical chalcophile element seldom forming specific minerals and occurring dispersed within polymetallic natural sulphides, particularly tetrahedral sulphides with excess metal [2]. The average content of indium in the Earth's crust is very low but its consumption is expected to increase in the next years, thus focusing a special interest on improving recovery and recycling technologies and finding new exploitation sites from promising polymetallic sulfide ores - e.g., the Iberian Pyrite Belt [3] (fig.1). Understanding *indium crystal chemistry* has become a demanding task and this work is a contribution to interpret its *binding state in natural chalcogenides* using *synchrotron radiation X-ray absorption spectroscopy*.

MAIN CRYSTAL STRUCTURE-TYPES (STP) of NATURAL CHALCOGENIDES (Minerals)

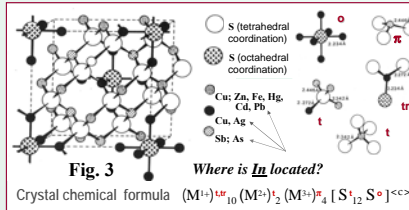
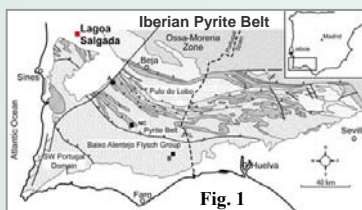
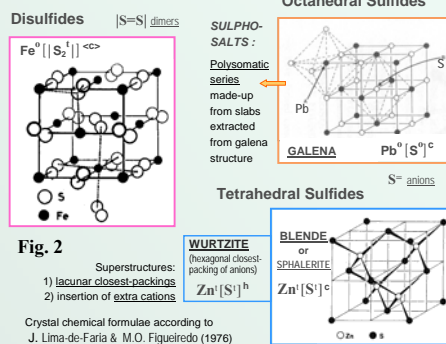


Fig. 4 - [In_2]⁴⁺ & [In_3]⁵⁺ Polycations [8]

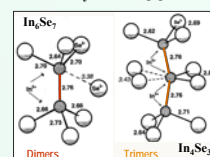


Table 1 - CHEMISTRY of CHALCOGENIDE MINERALS (MORPHOTROPIC DOMAINS, that is, chemical range for diadochic substitutions in minerals deduced from stable synthetic compounds)

Group	I	II	Transition Metals										III	IV	V	VI	VII	0
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be																Ne
3	Na	Mg																Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	(Fr)	Ra	**															

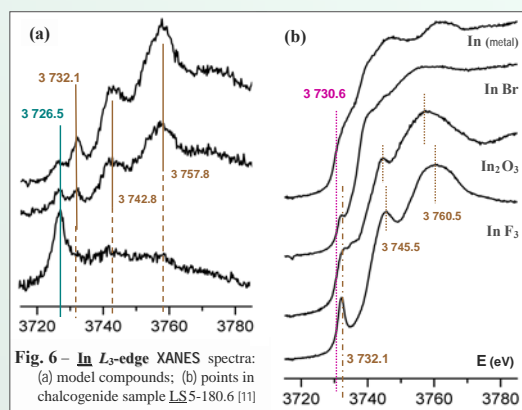
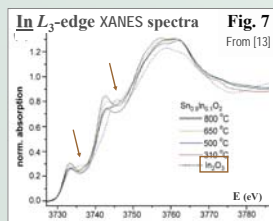
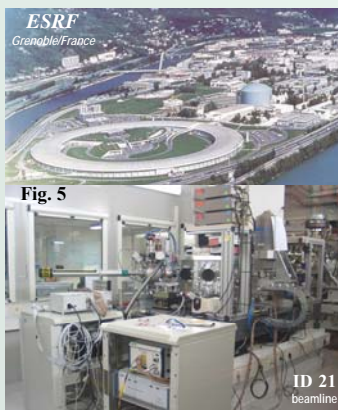
[Periodic Table from K. KRAUSKOPF (1967) Introduction to Geochemistry]

Pyrite Tetrahedral structures Galena-plus-sulphosalts / Anions (blende, wurtzite & allied)

Experimental

The X-ray absorption spectroscopy experiment at In L_3 -edge was carried out using the instrumental set-up of ID-21 beamline [10] (fig. 5) at the ESRF (European Synchrotron Radiation Facility).

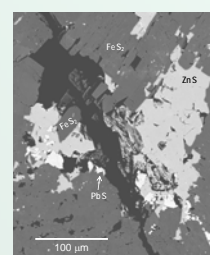
A polymetallic chalcogenide ore (In ~ 90ppm) from Lagoa Salgada [11] was irradiated, along with metallic indium and model compounds displaying distinct bonding situations of indium to other ligands (oxygen and halides). XANES spectra were collected in fluorescence yield mode using a photodiode detector mounted in the horizontal plane perpendicular to the X-ray beam, irradiating directly the rough sample fragments with a beam-size of 1x0.3µm². A fixed-exit Si(111) monochromator was used for the energy scans, assuring an energy resolution of 0.4 eV at the In L_3 -edge.



Results

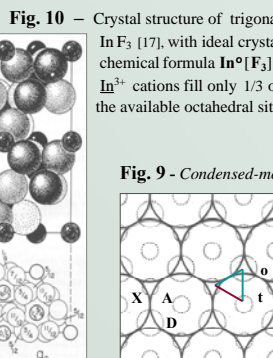
X-ray absorption spectra reflect the local symmetry and chemical bonding of the absorbing element and the band character of the compound through the position of the edge jump and the details that follow; the presence of a "white line" indicates unoccupied electronic states [12].

Beyond a white line at 3732.1 eV (fig. 6a), also displayed by InF₃ XANES spectrum (fig. 6b), the spectra collected from the chalcogenide ore show an extra white-line at 3726.5 eV plus details also observed in the spectra of the metal and model compounds In₂O₃ & InF₃. Although the In L_3 -edge spectra from the oxide (fig. 7) was already studied in the context of ITO thin-films [13] and the spectra from the metal was discussed a few years ago [14], further study is clearly required to fully interpret the spectra collected from natural chalcogenides (fig. 6a) which are quite distinct from the XANES spectra of synthetic spinel-type In₂S₃ [15].



Final Comments

The closest packing array built up by S²⁻ anions in most chalcogenide minerals present in ore sample LS5-180.6 (fig. 8) - chalcopyrite, sphalerite, tetrahedrite-tennantite, galena - is very suitable to lodge polymetallic cations by filling closely located interstitial sites, as illustrated by the condensed model sheet of a single anionic layer figuring out the interstices available between successive layers (fig. 9). Considering that InF₃ is also a closest-packed compound, despite hexagonal (fig. 10), it is not to exclude that interactions may occur between neighbor In cations, thus accounting for singularities of the observed white lines. Further study is in progress to explore this hypothesis.



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