INDIUM CRYSTAL CHEMISTRY: FROM THIN-FILM MATERIALS TO NATURAL BULK CHALCOGENIDES *

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Introduction

Indium is nowadays widely used in many technologic fields - electronics, solders, low melting-temperature alloys, etc. Discovered in 1863 and isolated four years later as a metal, indium became one of the most relevant scarce metals used in the production of new "high-tech devices" based on innovative nanotechnologies.

Suggestive examples of indium incorporation - along with other rare metals, gallium and tin - are 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 chalcopyrite-type compounds turned into promising materials for photovoltaic solar cells with increased efficiency - e.g., Cu(In,Ga)Se_2 (CIGS).

Consumption of indium is therefore expected to increase in years to come, focusing a special interest on its exploitation from polymetallic sulphide ores [2] – namely, the Iberian Pyrite Belt (IPB), a metallogenetic province crossing the south of Portugal and extending to Spain (fig.1) – and on the improvement of indium recovery and recycling technologies. Accordingly, it became opportune to *revise indium crystal chemistry*, starting with minerals (natural materials).

Crystal Chemistry of Indium

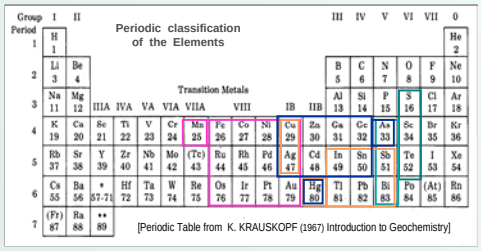
Indium (Z=49) has the electronic structure [Kr] $4d^{10}$ $5s^2$ $5p^1$ and *frequently assumes the trivalent state*, suggesting the inertness of $5s^2$ electron-pair. Like gallium and unlike tin, *indium seldom forms specific minerals*, exhibiting a *distinctly chalcophile behavior in the Earth's crust and occurring rather dispersed within polymetallic sulfide ores* (Table 1).

The sulphide *roquesite* (CuInS$_2$) was the first In-mineral to be described [5], followed [6] by *indite* (FeIn_2S_4) and *dzhalindite*, a tri-hydroxide with $In(OH)_6$ octahedra. The *recovery of indium* stands mostly on the *processing of zinc blende* - a cubic mineral typifying **tetrahedral sulphides** (fig.2) where cations fill half of the available tetrahedral sites in a cubic closest packing (*ccp*) of sulfur anions ($S^=$). The **crystal-chemical formula** is written $Zn^t[S^t]^c$, where t stands for tetrahedral coordination and c quotes the anion packing [7]. In is mainly carried in *solid solution or diadochic replacement*, not only by sphalerite, but also by **excess-metal Cu-rich "tetrahedral sulphides"** – *bornite*, $Cu_5{}^tFe^t[S_4{}^t]^c$ and *sakuraite*, $(Cu,Ag)_2{}^t(Zn,Fe)^t(In,Sn)^t[S_4{}^t]^c$, plus by complex sulfides of the **series tetrahedrite-tennantite** also structural derivatives from tetrahedral arrays (fig.3).

Synthetic indium selenides with excess metal were first reported fifty years ago - In_2Se [9]; since then, many **In-chalcogenides** have been synthesized – In_6Se_7, In_7Te_{10}, InTe and In_4Se_3 plus In_4Te_3, both with excess metal – and their structural characterization has revealed the occurrence of **polymetallic In-cations** [10,11] : $[In_2]^{4+}$ *dimmers* and/or $[In_3]^{5+}$ *trimers* (fig.4).

Table 1 – MORPHOTROPIC DOMAINS of CHALCOGENIDE MINERALS (Sulphides & Sulphosalts)

[chemical range for stable diadochic substitutions in minerals deduced from stable synthetic compounds]



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

CRYSTAL STRUCTURE-TYPES (*STPs*)

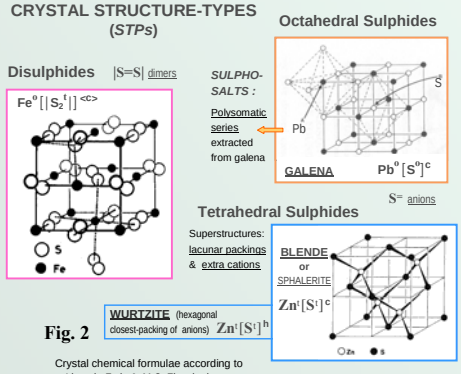


Fig. 2

Crystal chemical formulae according to J. Lima-de-Faria & M.O. Figueiredo (1976) *J. Solid St. Chem.* 16 7-12

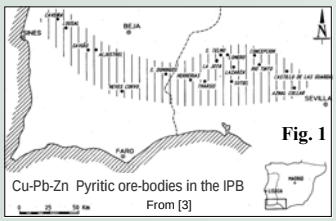


Fig. 1

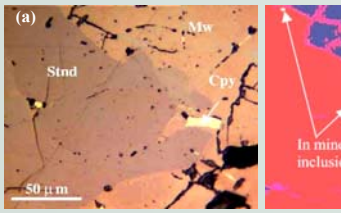
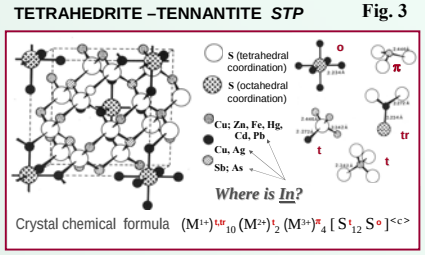


Fig. 5 – (a) Optical micrograph of a massive sulphide from Neves-Corvo deposit. Mw, mawsonite, $Cu_6Fe_2SnS_8$; Cpy, chalcopyrite, $CuFeS_2$; Stnd, stannoidite, $Cu_8(Fe,Zn)_3Sn_2S_{12}$.

(b) Part of (a) in reversed ion-image. In-carrier mineral inclusions are assigned [13].

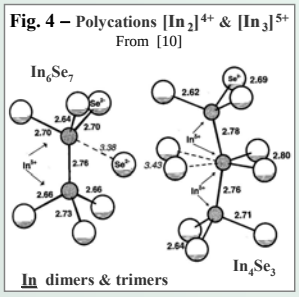
TETRAHEDRITE –TENNANTITE *STP*

Fig. 3



Structural hierarchy: an isolated tetrahedron inside a single tetrahedrite cage compared to a super-tetrahedral cluster cavity (yellow sphere) in a synthetic Cd (orange)–In (blue)–sulphide capable of hosting functional organic molecules in materials for optical devices [8].

Fig. 4 – Polycations $[In_2]^{4+}$ & $[In_3]^{5+}$ From [10]



Isolated In-ions

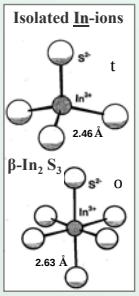
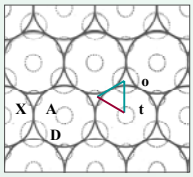


Fig. 6



Condensed-model standard sheet [14] for $A^t_2D^o[X]$: large circles, closest packing atoms (X); A, tetrahedral, and D, octahedral available interstices.

Ideal radii : $r_A = 0.225\, r_X$; $r_D = 0.414\, r_X$

In–S distances vary accordingly.

Table 2 – In-concentrations (ppm) in accessory minerals from massive copper sulphide ores of Neves-Corvo polymetallic deposit, southern Portugal [4].

Mineral , empirical formula	In
Bornite , $(Cu,Ag)_{4.93}\, Fe_{0.97}\, S_{4.10}$	not reported
Mawsonite, $Cu_{5.95}\, Fe_{2.01}\, Sn_{1.0}\, S_{8.05}$	300
Tennantite, $(Cu,Fe,Zn,Ag)_{11.8}\, (As,Bi)_{4.1}\, S_{13.2}$	27 400

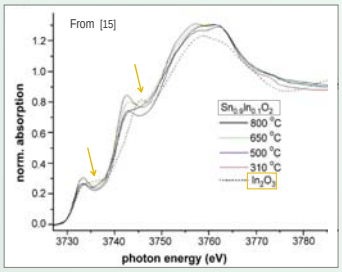
In at the Nanoscale in Polymetallic Sulphide Ores

Diadochic replacement of indium for zinc is common world-around in *sphalerite ores* but not so for the IPB polymetallic sulphide ores.

Replacements and *recrystallization* resulting from *a later copper-rich hydrothermal solution* often remove the primary texture in volcanogenic massive sulfides (VMS). For that reason, the *remobilization of chalcopyrite* and *tetrahedrite* is common in Neves-Corvo copper ores [12] and the resulting paragenesis involves promising indium carriers (Table 2). Encouraging results have already been published [13], showing exsolved indium minerals as minute grains within stannoidite (fig. 5, Table 2).

Mastering the nano-scale complexity in minerals is gaining well turned-out solutions through the use of *highly focused micro-beam analytical techniques* making use of either *particle beams* (electrons in EPMA, protons in micro-PIXE) or *photon beams* in "third generation" synchrotrons. These large-scale installations provide very suitable instrumental means of non-destructive research at the nanoscale and synchrotron radiation allows for *assessing at the binding situation* as successfully applied to indium-oxygen compounds.

Fig. 7 – In L_3-edge X-ray absorption spectra collected from synthetic Sn-In oxides compared to In_2O_3 [15]. Differences resulting from In being in the (3+) state are assigned by arrows.



Comments

It is worth noticing that the *cubic closest packing anionic array* configured by sulphur anions ($S^=$) in **chalcopyrite**, **bornite**, **mawsonite**, **stannoidite** and even **tetrahedrite-tennantite** is particularly *suitable to accommodate polymetallic cations by filling closely positioned interstitial sites.* This is clearly perceptible when looking at a sheet figuring out a single closest packed anionic layer with the available interstices located between this and the forthcoming anionic layer (fig.6): tetrahedral (t) and octahedral (o), in the proportion 2:1. Distances between interstices, [t–o] and [t–t], compare well with In-In distances in synthetic selenides.

Furthermore, once selenides and tellurides are stable synthetic compounds containing In-*polycations*, it is expectable that Se & Te may be favourably hosted by such anionic closest packing in the presence of indium in natural compounds. Accordingly, it is foreseen to undertake a nanoscale analysis of selected ore samples and pursue an X-ray absorption near-edge spectroscopy (XANES) study at In L_3-edge (fig.7) in order to assess In-binding in carrier chalcogenide minerals.

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