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Crystal Chemistry Investigations on Photovoltaic Chalcogenides

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1 Introduction

Photovoltaics (abbreviated PV hereafter) is a generic term to describe the direct conversion of light (very often from the sun) into electricity. Basically, a photovoltaic solar cell is a *pn* junction (semiconducting materials) in which photons are absorbed and give rise to electron-hole pairs. These carriers are collected on both sides of the cell leading to a photovoltage and a photocurrent in the outside circuit, thus available to operate devices. The market is, by far, still dominated by the silicon-based technology¹ although emerging materials are of interest. Among them, copper-based chalcogenides have strong potential applications specifically for thin film solar cells (i.e. low amount of active materials) due to their high light absorption coefficient² and their band gap tunability^{3,4}.

To date, solar cells based on Cu(In,Ga)Se₂ (CIGSe) and CdTe have high energy conversion efficiency^{5,6}. However, some of the chemical elements involved in these materials suffer from either scarcity or toxicity issues. Thus compounds derived from Cu₂ZnSnS₄ (CZTS) have been proposed as alternative absorbers⁷. On the other hand, as the efficiency of a solar cell based on a single *pn* junction is intrinsically limited to about 30% (known as Shockley–Queisser limit⁸), the concept of tandem solar cell has been proposed⁹ to overpass this limit. In such devices, more of the solar spectrum can be absorbed; the photons of lowest and highest energy are absorbed in the bottom cell (band gap of about 1.1 eV) and in the top cell (*E_g* around 1.7 eV), respectively. In this scenario, Cu(In,Ga)S₂ (CIGS) compounds receive a strong incentive to be used as absorber in the top cell, the bottom one being based on Si technology.

Whatever, before launching of a new product on the market, fundamental knowledge on the chemical and physical properties of materials have to be amassed. In particular, to optimize opto-electronic properties, the relationship between crystal structure (long and short ranges) and materials properties have to be clarified. In this context, we have thoroughly studied CZTS and CIGS compounds through a crystal chemistry approach. Indeed, the crystal structure is the key venue to rationalize and move forwards. In this chapter, we have selected two specific topics: the study of the cationic disorder in CZTS materials and the investigation of the phase equilibria in the Cu₂S - In₂S₃ - Ga₂S₃ pseudo-ternary system. Our aim is clearly to highlight the capital importance of X-ray diffraction techniques (especially on single crystals) and Nuclear Magnetic Resonance (NMR) spectroscopy in the in-depth characterization of solid materials.

2 Experimental

In the two thorough crystal chemistry investigations presented here, the use of highly pure and very well characterized samples is of high importance. Thus the experimental procedures (synthesis and chemical analyses) are key steps and are briefly described hereafter. In addition, few words are given to contextualize the inputs of the single crystal resonant X-ray diffraction and of the solid state NMR spectroscopy.

2.1 Synthesis

The studied compounds in the Cu₂S-ZnS-SnS and Cu₂S-In₂S₃-Ga₂S₃ systems were synthesized by ceramic route which consists of a high temperature reaction between the precursors in evacuated quartz ampoules. Namely, pure elements or binary sulfides are weighted in an appropriate ratio and pressed into pellets (when possible), and introduced in a silica tube. Once sealed under vacuum, the mixture is heated up to 750-900°C for periods ranging from 2-3 days to 1-2 weeks. Afterwards the samples may be homogenized by grinding, pressed into pellets again and annealed at the same

temperature. At this step, samples can be slow cooled or quenched in water. This synthesis route was adapted from the one proposed by Bernardini¹⁰ and Schorr¹¹. In a number of cases, iodine is added to favor crystal growth and get crystals large enough (typically 10-20 microns in each dimension) for single crystal X-ray studies.

2.2 Elemental chemical analyses

The Energy Dispersive X-ray (EDX) analyses were done using a scanning electron microscope (JEOL 5800 LV) with an accelerating voltage of 20 kV. As the elemental composition is a crucial point as part of this study particularly, careful analyses were systematically carried out on polished sections of the powders imbedded in epoxy. The elemental percentages were calculated using internal calibration in order to achieve both accurate and precise results. The standards were: Cu metal (Cu-K α), InAs (In-L α), GaP (Ga-K α), ZnS (Zn-K α), SnO₂ (Sn-L α), FeS₂ (S-K α). Collected EDX data were systematically validated by checking the charge balance equilibrium with Cu⁺, In³⁺, Ga³⁺, Zn²⁺, Sn⁴⁺ and S²⁻ ions. In the case of the CIGS derivatives the stoichiometric compound (Cu_{1.005(5)}In_{0.483(4)}Ga_{0.512(3)}S_{2.000(9)}), well characterized by Powder X-ray diffraction (PXRD) and electron microprobe analysis, was used as a secondary standard.

2.3 Conventional X-ray diffraction in laboratory

Powder X-ray diffraction measurements were carried out a Bruker D8-Advance diffractometer in a Bragg-Brentano geometry using monochromatic radiation Cu(K-L₃, $\lambda = 1.540598 \text{ \AA}$) and a LynxEye detector. Powder patterns were recorded in the 8-100° 2 θ -range, 2 θ -step = 0.008°. The full pattern matching and Rietveld analyses were performed thanks to Jana2006 program¹².

For the single crystal structure determinations, data collections were done on a Brüker Kappa CCD instrument, using graphite monochromated Mo KL_{2,3} radiation (0.71073 $\text{\AA}$) with the ρ - and ω -scan techniques. The recorded images were processed with the set of programs of Nonius. The structures were refined using also Jana2006 program.

2.4 Single crystal resonant X-ray diffraction

In X-ray diffraction experiments, scattering comes from the interaction of the impinging light with electrons of matter. The power of such scattering by a given atom depends on its atomic scattering factor f which is a complex term, $f = f_o + f' + if''$. The non-resonant factor f_o is related to the atomic number of the corresponding atom and is energy independent but decreases when the scattering angle ($\sin(\theta)/\lambda$) increases. On the contrary, the f' and f'' terms, known as the resonant factors, are quite independent of the scattering angle but hugely dependent on the X-ray photon energy near the edge of the scattered atom (see Figure 3.1). In conventional X-ray diffraction experiment, very often the contributions of f' and f'' remain very low compared to that of f_o . In those conditions neighbor elements in the periodic table have very close atomic scattering factors and appear to be roughly identical in X-ray diffraction analyses. This situation occurs in CZTS compounds for copper and zinc (identical electronic configurations for Zn²⁺ and Cu⁺ cations). Thus, Cu/Zn distribution in the crystal structure of CZTS compounds is hard to address by conventional X-ray diffraction. In contrast, resonant X-ray diffraction (i.e. close to absorption edge of one of the constituent element) is known to enhance the contrast between elements which are close in the periodic table¹³. This method requires finely tuned photon energy which is readily available at synchrotron facilities. Let us notice that neutron diffraction could also be employed as reported by Schorr¹⁴.

Figure 3.1: Calculated f' and f'' scattering factors for copper and zinc close to their $K\alpha$ absorption edges (Dispano software with Sasaki data).

In CZTS compounds, the single crystal X-ray resonant diffraction technique has been used to investigate the copper-zinc distribution (see below). Practically, single crystals were picked up from powders and sorted out via preliminary diffraction data collection at the laboratory to check their quality. The best ones were selected for resonant diffraction investigations on the CRISTAL beamline at the Soleil French synchrotron. In order to increase the contrast between Cu and Zn data, sets were collected just below both the Cu $K\alpha$ and Zn $K\alpha$ absorption edges, at $\lambda = 1.3825$ (2) Å and $\lambda = 1.2844$ (2) Å, respectively. An extra data set was collected far from the absorption edges at $\lambda = 0.66842$ (4) Å. All crystal structure refinements were performed using JANA2006¹² using the anomalous scattering factor values from Sasaki data given by the Dispano program¹⁵. More details about these experiments can be found in the original paper¹⁶.

2.5 Solid state NMR spectroscopy

The ^{119}Sn spectra were acquired on Bruker Avance III 300 MHz (7 T) spectrometer using a 4 mm CP-MAS probe. This set up appears as a good compromise since the use of low magnetic field avoids the too large spreading of spectra due to chemical shift anisotropy. Moreover, the T_1 relaxation time, then the recycle time, which can be quite long for $1/2$ spin nucleus in crystalline compound is lowered. Finally, the large volume of 4 mm rotor allows to reduce the number of scan while keeping a high MAS speed.

Spectra were acquired by using a full shifted echo acquisition ($\pi/2 - 1.9 \text{ ms} - \pi - \text{acq}$) to obtain a pure absorption mode line shape (then, an absolute criterion for adjusting phases of the spectra). The radio frequency strength was 80 kHz. The MAS frequency was set to 14 kHz and the recycle delay to 120 s. Spectra were referenced to Me_4Sn using Ph_4Sn as a secondary reference (-121.15 ppm). Note that when line broadening occurs, the use of CPMG (Carr – Purcell – Meiboom - Gill) approach^{17,18} followed by spectral reconstruction can be beneficial to save spectrometer time¹⁹.

3 Cationic disorder in CZTS materials

As aforementioned, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) material has been proposed as suitable absorber for thin film solar cell successively by Ito², Nakayama²⁰ and Katagiri⁷. During the last 2 decades, the efficiency of CZTSSe-based solar cells dramatically increased but the world record of 12.6 %²¹ reached a ceiling and is far below the best performance of its CIGSe counterpart⁵.

Formally, several intrinsic limitations of CZTS materials have been found such as cationic disorder^{22–24}, shift from the nominal stoichiometry due to the volatility of SnS ²⁵ and the formation of secondary phases²⁶ to account the far from expected PV performances. That is why we engaged in the more-in-depth investigation of the crystal chemistry of the cationic disorder in CSTS bulk materials to try to shed light on its behavior in solar cell.

The crystal structure of the CZTS compounds derives from that of natural kesterite, $\text{Cu}_2(\text{Zn,Fe})\text{SnS}_4$, in the $\bar{I}4$ space group²⁷ for low Fe/Zn ratios. For Fe-rich compounds an alternative stannite crystal structure can occur, corresponding

to the more symmetric $\bar{I}42m$ space group²⁷. These two crystal structures are very similar; the main difference originates from the ordering of the metal atoms. In kesterite, the $z=0$ and $z=1/2$ layers are comprised of well-ordered Cu and Sn, whereas mixed (Zn,Fe) sites are found on the $z=1/4$ and $z=3/4$ layers ($2c$ and $2d$ Wyckoff positions of the $\bar{I}4$ space group). In the alternate stannite structure, mixed (Fe,Zn) sites are found in the $z=0$ and $z=1/2$ layers, while copper is located on a unique crystallographic position ($4d$ of the $\bar{I}42m$ space group) at the $z=1/4$ and $z=3/4$ (see Figure 3.2). The occurrence of both kesterite and stannite crystal structures in the case of the synthetic CZTSSe compounds has been mentioned in the literature^{14,27,28}. Our goal is to go further and investigate the relationship between the synthesis conditions and the Cu/Zn disorder in such materials.

Comment: You should mention here that Cu/Zn disorder was shown experimentally for the first time by neutron diffraction on CZTS (reference 14). I consider that important because it was not Jonathan Scragg who found Cu/Zn disorder. I would suggest that you insert one or two sentences about Cu/Zn disorder in kesterites before you start with "our goal".

Figure 3.2: Unit cell content for the kesterite (a) and stannite (b) minerals²⁷ (Wyckoff positions of metal atoms are given).

The CZTSSe materials have been thoroughly investigated through theoretical calculations specifically to determine the nature of defects (and their concentration) which could explain their semiconducting properties^{29,30}. These studies demonstrated that at the thermodynamic equilibrium for the stoichiometric $\text{Cu}_2\text{ZnSnS}_4$ composition, many defects in high concentration may exist in this material. Nevertheless, its p-type behavior is correlated to Cu'_{Zn} antisites, the concentration of isolated $\text{Zn}^{\bullet}_{\text{Cu}}$ donor defects being strongly limited thanks to the concomitant and competing formation of neutral $[\text{V}'_{\text{Cu}} + \text{Zn}^{\bullet}_{\text{Cu}}]$ complexes (Kröger–Vink notation³¹).

On the other hand, best performances are observed so far for Cu-poor/Zn-rich composition for which, on a chemical point of view, two main substitutions can occur:

- the A-type where 2 copper atoms are replaced by 1 zinc atom as aforementioned ($2\text{Cu}^{\times}_{\text{Cu}} \rightarrow \text{V}'_{\text{Cu}} + \text{Zn}^{\bullet}_{\text{Cu}}$)
- the B-type where 2 copper atoms and 1 tin atom are simultaneously replaced by 3 zinc atoms ($2\text{Cu}^{\times}_{\text{Cu}} + \text{Sn}^{\times}_{\text{Sn}} \rightarrow 2\text{Zn}^{\bullet}_{\text{Cu}} + \text{Zn}^{\bullet}_{\text{Sn}}$).

The two corresponding substitution lines are drawn in the Cu_2S - ZnS - SnS_2 pseudo-ternary diagram displayed in Figure 3.3.

Figure 3.4: Unit cell content for $\text{Cu}_2\text{ZnSnS}_4$ with disordered-kesterite structure, in space group $\bar{4}2m$.

This study has shown that the resonant effect at Cu and Zn absorption edges is large enough to enhance the contrast between Cu and Zn and to give a direct evidence of the disordered-kesterite structure for $\text{Cu}_2\text{ZnSnS}_4$ in the case of a quenched sample. The same investigation was done on a sample which was very slowly cooled from 750°C down to the room temperature, with the same results. At the long range scale (i.e. average structure obtained from diffraction experiments), $\text{Cu}_2\text{ZnSnS}_4$ adopts consequently the disordered-kesterite structure, regardless the thermal history of the sample. Nevertheless, experimental evidences exist that show that slow cooled samples could exhibit a lower Cu-Zn disorder^{37,38}. This prompted us to investigate the ordering at short range scale (local order) via solid state NMR spectroscopy, indeed a very complementary technique to diffraction for that purpose.

3.2 Solid state NMR

Solid state NMR was successfully applied to structural characterization of a large variety of CZTSSe compounds^{19,36,39}, as well as related materials like $\text{Li}_2\text{ZnSnS}_4$ or Cu_2SnS_3 ^{40,41}. The ^{65}Cu , ^{67}Zn , ^{119}Sn and ^{77}Se nuclei have been used to probe the local structure of CZTSSe compounds. ^{65}Cu static NMR was shown to be a quick and very efficient way to identify the kesterite structure (versus the stannite one) from the spectral signature of the two crystallographic sites, $2a$ and $2c$ for Cu atoms^{36,42}. Although more demanding, ^{67}Zn MAS NMR appeared as a valuable tool to prove the presence of B-type substitutions in Cu-poor Zn-rich CZTS materials⁴³. ^{77}Se MAS NMR has suggested the random distribution of S and Se in mixed S/Se compounds³⁹. Finally, the ^{119}Sn MAS NMR signature of the defect complexes associated with the A-type substitution was used to show their propensity to segregate⁴³.

For all of the 4 nuclei, the modification of the local environment (geometry and chemistry) by Cu/Zn disorder leads to line broadening reflecting the distribution of chemical shift. For the two quadrupolar nuclei ^{65}Cu and ^{67}Zn , an additional broadening comes from the distribution of electric field gradient (EFG). As a non quadrupolar nucleus, ^{119}Sn is not subject to EFG. Moreover, under MAS condition, the broadening of the ^{119}Sn NMR lines is only governed by the distribution of isotropic chemical shift. In addition, as a heavy nucleus, the chemical shift of ^{119}Sn is very sensitive to its local environment i.e. up to its second sphere of coordination. Thus, ^{119}Sn appears as the nucleus of choice to probe the Cu/Zn disorder in kesterite structure.

The ^{119}Sn MAS NMR spectrum of the quenched stoichiometric $\text{Cu}_2\text{ZnSnS}_4$ sample (Figure 3.5) exhibits a single line showing an unusual asymmetric broadening which is the signature of the occurrence of Cu/Zn disorder. On the contrary, for its slowly cooled variant, the narrower line width indicates a strong reduction of the level of Cu/Zn disorder. However, even carefully slow-cooled, stoichiometric $\text{Cu}_2\text{ZnSnS}_4$ samples cannot reach the full Cu/Zn ordering expected at thermodynamic equilibrium as pointed out by the existence of a low intensity tail at low frequency (from -130 to -160 ppm). This situation dramatically changes for Cu-poor Zn-rich CZTS materials where A-type substitution ($2\text{Cu}_{\text{Cu}}^{\times} \rightarrow \text{V}_{\text{Cu}}' + \text{Zn}_{\text{Cu}}'$) was shown to be able to decrease the level of Cu/Zn disorder. This is illustrated in Figure 3.5 where the ^{119}Sn MAS NMR spectrum of the slow cooled Cu-poor Zn-rich CZTS sample no longer shows the low frequency tail, and where the ^{119}Sn NMR line of the quenched Cu-poor Zn-rich CZTS sample shows only moderate broadening. Using

^{119}Sn NMR characterization, the segregation of $[\text{V}'_{\text{Cu}} + \text{Zn}^{\bullet}_{\text{Cu}}]$ defect complexes and their role on Cu/Zn disorder have also been proven in pure selenide⁴² or mixed S/Se CZTSSe compounds synthesized from colloidal or ceramic routes^{19,39}.

Figure 3.5: ^{119}Sn NMR MAS (14 kHz) spectra of quenched or slow cooled samples of $\text{Cu}_2\text{ZnSnS}_4$ and Cu-poor Zn-rich CZTS. Asterisks indicate the signal from Sn nuclei experiencing the presence of Cu vacancies at the 2a site. The arrow points out the tail demonstrating that slow cooled $\text{Cu}_2\text{ZnSnS}_4$ compounds are not fully ordered.

3.3 Concluding remarks on CZTS

The aim of the above section was to illustrate the use of two very powerful techniques to investigate the Cu/Zn disorder in CZTS phases. For the studied samples, whatever the thermal treatment, the CZTS samples remain highly disordered at long range, i.e. at the X-ray diffraction scale, while there are evidences of local cationic Cu/Zn ordering at short range, i.e. at the NMR scale, this last observation being more pronounced in the slow cooled sample than the quenched one. It is worth noticing that the use of the NMR spectroscopy requires pure and well characterized samples in a significant amount (ca. 100 mg). Anyway, NMR can help a lot in the material characterization even for thin film for which area and thickness have to be large enough. Investigations devoted to the Cu/Zn disorder in CZTS materials are today still in progress to refine the image of disorder in these phases and their impact on properties^{44–46}. In parallel, others materials for thin film solar cells are studied in Nantes (France) and others laboratories, especially materials with different requisites for application in tandem solar cells. In this context, let us consider now the $\text{Cu}_2\text{S}-\text{In}_2\text{S}_3-\text{Ga}_2\text{S}_3$ system.

4 Phase equilibria in $\text{Cu}_2\text{S} - \text{In}_2\text{S}_3 - \text{Ga}_2\text{S}_3$ pseudo-ternary system

A promising way to improve conversion efficiencies beyond the limit for a single junction is by combining a silicon cell with a wide-bandgap absorber material in a tandem solar cell⁴⁷. In that framework, copper indium gallium sulfide (CIGS) compounds, with the chalcopyrite crystal structure, appear to be good candidates since their band gap can be easily tuned between 1.5 up to 2.4 eV by adjusting the Ga/(In+Ga) ratio. Up to now, the CIGS-based solar cells have efficiencies far below those of their selenide counterparts (CIGSe). One important feature of the selenides compared to sulfides originates from their ability to accommodate copper deficiencies without major crystal structure changes⁴⁸. Although the CIGS compounds have been already studied through a solid state chemistry approach^{49–51} and through thermal analyses^{52,53}, no systematic investigation on the copper-poor limits of the chalcopyrite phase domain is reported in the literature. Here, we present an overall study of the whole $\text{Cu}_2\text{S}-\text{In}_2\text{S}_3-\text{Ga}_2\text{S}_3$ pseudo-ternary system through a chemical crystallography approach on bulk materials.

In these compounds, the charge balance is quite well fulfilled with normal valence for the cations, that is Cu(I), In(III), Ga(III) and S(-II). In copper deficient compounds, the charge balance is achieved when 3 copper atoms are replaced by 1 trivalent atom leading to the formation of 2 vacancies which is illustrated by the general formulation Cu_1 .

$z(\text{In}_{1-x}\text{Ga}_x)_{1+z/3}\text{S}_2$ where $0 \leq x \leq 1$ and $0 \leq z \leq 0.75$. For examples, the value $z = 0$ corresponds to the so called stoichiometric $\text{Cu}(\text{In,Ga})\text{S}_2$ compounds and the thiospinel CuIn_5S_8 can be represented by $\text{Cu}_{0.25}\text{In}_{1.25}\text{S}_2$, i.e. $z = 0.75$. Then, the all compositions in the copper-poor region of the Cu_2S - In_2S_3 - Ga_2S_3 system can be written with the formulation $\text{Cu}_{1-z}(\text{In}_{1-x}\text{Ga}_x)_{1+z/3}\text{S}_2$ where x is the $\text{Ga}/(\text{In}+\text{Ga})$ ratio while z is the copper deficiency from the stoichiometric composition (see Figure 3.6).

Figure 3.6: Cu_2S - In_2S_3 - Ga_2S_3 pseudo-ternary diagram. The general composition of the studied samples is $\text{Cu}_{1-z}(\text{In}_{1-x}\text{Ga}_x)_{1+z/3}\text{S}_2$, where x is the $\text{Ga}/(\text{In}+\text{Ga})$ ratio and z the copper deficiency compared to $\text{Cu}(\text{In,Ga})\text{S}_2$.

4.1 Stoichiometric compounds $\text{Cu}(\text{In,Ga})\text{S}_2$

Several papers report on the crystal structure of the stoichiometric CIGS series from powder X-ray diffraction analyses^{50,54,55}. This series is claimed to be a solid solution from CuInS_2 ($x = 0$) to CuGaS_2 ($x = 1$) with the chalcopyrite structure (see Figure 3.7). Copper and indium atoms are located on 2 distinct crystallographic sites and gallium progressively replaces indium with a random distribution on the $4b$ site. For the pure gallium compound, the very low difference between X-ray scattering factors of Cu and Ga atoms could prevent definitive conclusions about possible cation disorder especially from X-ray powder diffraction technique.

Figure 3.7: Representation of the unit cell content of the chalcopyrite crystal structure of CuInS_2 (space group $\bar{1}42d$).

We have investigated the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ series through single crystal X-ray diffraction that is known as a powerful technique to evaluate very tiny structural modifications that can occur especially for the gallium pure derivative. For that purpose, crystals were picked from powders with nominal compositions of $x = 0, 0.25, 0.50$ and 1 . Table 1 gives some of the refinement results for these 4 crystals.

From this study, it is clear that the indium-rich compounds crystallize in the chalcopyrite structure with the $\bar{I}42d$ space group in which Cu and (In,Ga) are respectively located on $4a$ (0,0,0) and $4b$ (0,0,1/2) Wyckoff positions while sulfur atoms are on the $8d$ position ($x \approx 0.25, 1/4, 1/8$). In this structure, the atomic radii of copper and the trivalent metals (In,Ga) are different enough to lead to a clear segregation of both atoms on the two distinct crystallographic sites ($4a$ and $4b$). On the other hand, for the indium-free compound (CuGaS_2), a mixing of copper and gallium is likely due to their very similar atomic radii. If such atomic mixing would occur, the crystal structure would be modified. In the $\bar{I}42d$ space group, the hhl reflections with $2h+l = 2n+1$ are forbidden (intensities are exactly equal to 0) due to the presence of the d glide plane (further reading about such distinction rules [ref]). Thus, the systematic absence of such reflections is the signature of the chalcopyrite structure. Special attention was paid to these reflections in the case of CuGaS_2 . They are all found to be below the standard $I/\sigma(I) = 3$ threshold meaning they are so weak and so noisy that they can be considered as absent reflections, confirming the $\bar{I}42d$ space group for CuGaS_2 and, thus, the chalcopyrite structure. It is worth noting that such analysis cannot be done from powder diffraction pattern because the corresponding hhl reflections are still of very low intensities even if there was a structural modification from the chalcopyrite structure (see section 4.3).

Table 1: Unit cell volume (V), x atomic coordinate of sulfur ($x(\text{S})$), equivalent atomic displacement parameters (U_{eq}) for the stoichiometric $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ series. The structural refinements have been done from single crystal XRD data in the chalcopyrite structure ($\bar{I}42d$ space group).

Ga/(Ga+In) (XRD)	V ($\text{\AA}^3$)	$x(\text{S})$	$U_{\text{eq}}(\text{Cu})$ ($\text{\AA}^2$)	$U_{\text{eq}}(\text{In/Ga})$ ($\text{\AA}^2$)	$U_{\text{eq}}(\text{S})$ ($\text{\AA}^2$)	$R_{\text{obs}} / wR_{\text{obs}}$	Fourier-diff ($\text{e}/\text{\AA}^3$)
0	339.3	0.22984(15)	0.02020(12)	0.01203(7)	0.0113(2)	1.58/4.41	0.44/-0.34
0.305(1)	326.7	0.2372(3)	0.0209(2)	0.01239(11)	0.0150(6)	3.10/5.67	0.91/-0.99
0.495(13)	319.8	0.2429(3)	0.0207(2)	0.01274(14)	0.0157(15)	3.27/ 7.14	2.12 / -1.97
1	301.3	0.2556(3)	0.0162(2)	0.00964(14)	0.009(2)	1.85/4.82	1.01/-1.03

When Ga is substituted for In, the unit cell volume decreases (see Figure 3.8a), consistent with the fact that the Ga-S bonds are shorter than the In-S ones. In addition, the position of the sulfur atom is slightly shifted towards $x \approx 0.25$. Consequently, the Cu-S bond length is roughly constant (Figure 3.8b) meaning that the bond valence of copper is also constant, very close to 1, along the series. The chalcopyrite structure is flexible enough to accommodate quite large metal(III)-S bond distance variation from $2.46 \text{ \AA}$ in CuInS_2 to $2.29 \text{ \AA}$ in CuGaS_2 . It is worth noting that in these sulfides, the Metal-S bond distances cannot not be well evaluated from ionic radii, the concept of bond valence^{56,57} is much more suited.

Figure 3.8: Evolution of the unit cell volume (a) and the Cu-S bond distance (b) in the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{S}_2$ series from single crystal X-ray diffraction analyses.

4.2 CuInS_2 - In_2S_3 system

In the literature, the Cu_2S - In_2S_3 pseudo-binary system ($\text{Cu}_{1-z}\text{In}_{1+z/3}\text{S}_2$) has been well investigated. Here again, charge balance is maintained in the formula through the decrease of Cu(I) (minus z value) and the corresponding increase of In(III) (plus $z/3$ value). The first published results indicate a large 2-phase region between CuInS_2 and CuIn_5S_8 ⁵⁸. A tentative temperature-composition phase diagram in the Cu_2S - In_2S_3 system, published by Binsma⁴⁹, also shows the absence of a single phase in a large composition range between CuInS_2 (chalcopyrite) and CuIn_5S_8 (thiospinel) at room temperature. This large 2-phase feature has recently been confirmed and the limit of the chalcopyrite phase domain has been found in the range of $0 \leq z \leq 0.09$ (see Figure 3.9)⁵⁹. Additionally, slightly copper-rich (relative to CuInS_2) samples were shown to comprise stoichiometric CuInS_2 and binary copper sulfides.

Figure 3.9: Phase diagram on the Cu_2S - CuIn_5S_8 line showing the large 2-phase domain between $\text{Cu}_{0.91}\text{In}_{1.03}\text{S}_2$ with the chalcopyrite structure and CuIn_5S_8 (equivalent to $\text{Cu}_{0.25}\text{In}_{1.25}\text{S}_2$) with the thiospinel structure.

It is worth noting that, unlike for copper-indium selenides (CISe) compounds, the specific composition of CuIn_3X_5 definitely does not exist for sulfides ($\text{X}=\text{S}$). Thus, if CIS thin films are prepared in copper-poor conditions, to avoid the formation of copper sulfide, it is very likely that the film will contain the cubic thiospinel CuIn_5S_8 compound. In the crystal structure of this compound, copper atoms share two distinct tetrahedral sites with a part of indium atoms (4a and 4c sites) while the remaining indium atoms are located on the 16e octahedral site in the $F\bar{4}3m$ cubic space group⁶⁰. The

crystal structure difference between chalcopyrite and thiospinel gives rise to very different electronic properties. For instance, the CuIn_5S_8 compound is found to be a n-type semiconductor and to be detrimental to the PV application⁶¹.

From a sample with target composition of $\text{Cu}_{0.70}\text{In}_{1.10}\text{S}_2$ (i.e. $z = 0.30$) a single crystal of the thiospinel phase was used for X-ray diffraction experiment. The obtained crystal structure is very close to that given in the literature but with a slight difference on the distribution of copper and indium atoms on the $4a$ and $4c$ tetrahedral sites ($F\bar{4}3m$ space group). The copper/indium site occupancy factors (s.o.f.) are $4a$ 0.30/0.70 and $4c$ 0.70/0.30, instead of $4a$ 0.52/0.48 and $4c$ 0.48/0.52 as published by Gastaldi⁶⁰. This discrepancy may originate from distinguishable synthesis conditions.

4.3 CuGaS_2 - Ga_2S_3 system

From the literature, it is clear that the copper-gallium sulfides (CGS) behave very differently than the copper indium ones^{62–64}. First, the compounds of interest ($\text{Cu}_{1-z}\text{Ga}_{1+z/3}\text{S}_2$ with $0 \leq z \leq 0.75$) all adopt a tetragonal crystal structure in which copper and gallium are in tetrahedral environments (while In may accept Td and Oh chemical environments). Copper and gallium are hard to be distinguished by conventional X-ray diffraction, this feature could explain some discrepancies into the literature about the actual crystal structure of these compounds. Then we decided to re-investigate the CuGaS_2 - CuGa_5S_8 system especially through the single crystal X-ray diffraction technique. The tetragonal symmetry for all the studied crystals is confirmed. On the other hand, for a slight copper-poor CGS compound (target composition of $\text{Cu}_{0.90}\text{Ga}_{1.03}\text{S}_2$) it was found that several hhl reflections with the condition $2h+l = 2n+1$ are to be definitely classified as observed reflections since their intensities are larger than 3 times their standard deviations (see Table 2). Thus the $I\bar{2}d$ space group has to be discarded for this crystal. The structure was then refined with the stannite model, space group $I\bar{4}2m$, in which copper and gallium share the $4d$ crystallographic position. In order to ensure the charge equilibrium, the copper deficiency (mainly located on the $2a$ position) is compensated by a gallium excess on $4d$. The crystal structure parameters are gathered in Table 3. The refined composition is $\text{Cu}_{0.874}\text{Ga}_{1.042}\text{S}_2$.

Table 2: Some of the strongest forbidden reflections in the $I\bar{4}2d$ space group for a crystal with composition close to $\text{Cu}_{0.90}\text{Ga}_{1.03}\text{S}_2$. These reflections cannot definitely be considered as absent reflections.

h	k	l	I	$\sigma(I)$	$I/\sigma(I)$
1	1	4	266.8	6.5	41.0
0	0	6	326.8	12.6	25.8
1	1	4	346.1	15.4	22.4
0	0	6	355.6	16.8	21.2
-2	2	6	223.8	11.5	19.5

Table 3: Main structural parameters for a crystal with refined composition of $\text{Cu}_{0.874}\text{Ga}_{1.042}\text{S}_2$ in the $I\bar{4}2m$ space group (#121). Residual factors $R(\text{obs})/R(\text{all}) = 2.07/3.92$, goodness of fit = 1.15, Fourier-difference largest peaks: 0.50/-0.69 $\text{e}/\text{\AA}^3$, reflections obs/all 241/368, 16 refined parameters. In order to fulfill the charge balance equilibrium, the normalized occupancies (ai) of copper and gallium are restrained according to the equation $\text{ai}[\text{Cu}(4d)] = 1 - \text{ai}[\text{Cu}(2a)] - 3 * \text{ai}[\text{Ga}(2b)] - 3 * \text{ai}[\text{Ga}(4d)]$, where $\text{ai} = \text{sofsite multiplicity/general multiplicity}$. In the $I\bar{4}2m$ space group, the general multiplicity is 16.

Atom	Wyckoff site	s.o.f.	x	y	z	$U_{\text{eq}}(\text{\AA}^2)$
Cu	2a	0.839(3)	0	0	0	0.0182(2)
Ga	2b	1	0.5	0.5	0	0.00900(14)
Ga	4d	0.5419(14)	0.5	0	0.25	0.01183(15)
Cu	4d	0.455(-)	0.5	0	0.25	0.01183(-)
S	8i	1	0.74772(7)	0.25228(-)	0.12432(4)	0.00986(18)

For very copper-poor compositions, i.e. $z = 0.60$ (CuGa_3S_5) and $z = 0.75$ (CuGa_5S_8) the powder diffraction patterns clearly show the presence of 002 and 110 reflections with their intensities increasing with copper deficiency (Figure 3.10). The structure of these compounds have been refined with the stannite model already proposed by Maeda⁶³. Additional samples have been prepared with intermediate compositions z in the range of 0.60-0.75. They are found to be of

pure phases meaning that a solid solution occurs in the composition range $z = 0.60 - 0.75$. Because copper and gallium have very close crystallographic behavior, the Cu/Ga distribution on the cationic sites of the stannite structure can vary in a large range according the composition as soon as the charge equilibrium is achieved: $3\text{Cu}^+ \Leftrightarrow \text{Ga}^{3+} + 2\text{V}_{\text{Cu}}$.

In the case of intermediate copper-poor target compositions ($0.10 < z < 0.60$), the corresponding powder patterns can be indexed with two unit-cells, close to that of $\text{Cu}_{0.90}\text{Ga}_{1.03}\text{S}_2$ ($z = 0.10$) and $\text{Cu}_{0.40}\text{Ga}_{1.20}\text{S}_2$ ($z = 0.60$), see Figure 3.11). It is worth nothing that this 2-phase feature disappears if the sample is quenched from 800°C to room temperature at the end of the synthesis procedure.

Figure 3.10: Powder X-ray diffraction pattern of CuGaS_2 (with chalcopyrite structure) and 2 very copper-poor CGS compounds with $z = 0.60$ and 0.70 (with stannite structure). The labelled reflections are forbidden in the chalcopyrite structure.

Figure 3.11: Powder X-ray diffraction pattern of slight Cu-poor ($z=0.10$) Cu-poor ($z=0.30$) and very Cu-poor ($z=0.60$) CGS samples. The 2-phase nature of the sample with intermediate composition is emphasized in the low- 2θ zoom (see inset).

4.4 Copper-poor CIGS compounds

Let us consider now the $\text{Cu}_2\text{S} - \text{In}_2\text{S}_3 - \text{Ga}_2\text{S}_3$ ternary system where CIGS samples are copper-poor and contain both indium and gallium as trivalent element, corresponding to the general formulation: $\text{Cu}_{1-z}(\text{In}_{1-x}\text{Ga}_x)_{1+z/3}\text{S}_2$, with $0 < x < 1$ and $0 < z \leq 0.60$. So far, no information about these compositions are reported in the literature. From the observation of powder-ray diffraction patterns, the main conclusion is that all these prepared materials were no pure-phase. In other words, as soon as the target composition is copper-poor, the obtained powdered sample is, at least, formed of two phases sample. Hence, for the targeted $\text{Cu}_{0.70}(\text{In}_{0.70}\text{Ga}_{0.30})_{1.10}\text{S}_2$ ($x = 0.30$, $z = 0.30$) composition, two compounds can be detected on the backscattered electron SEM image (Figure 3.12). From the EDX analyses, the actual compositions of the 2 phases

in equilibrium are $\text{Cu}_{0.96(4)}\text{In}_{0.61(3)}\text{Ga}_{0.39(1)}\text{S}_{2.00(2)}$ ($x = 0.39$, $z = 0.04$) and $\text{Cu}_{0.41(2)}\text{In}_{0.93(3)}\text{Ga}_{0.26(1)}\text{S}_{2.00(1)}$ ($x = 0.26$, $z = 0.59$). It is worth noticing that the almost stoichiometric $\text{Cu}(\text{In,Ga})\text{S}_2$ phase contains more (less) gallium (indium) than the copper-poor one. The 2-phase nature of $\text{Cu}_{0.3}(\text{In}_{0.7}\text{Ga}_{0.3})_{1+z/3}\text{S}_2$ samples ($z = 0, 0.21, 0.30, 0.60$) was confirmed by powder XRD analyses. Figure 3.13 gives the X-ray diffraction patterns of samples with target compositions of $\text{Cu}_{0.79}(\text{In}_{0.70}\text{Ga}_{0.30})_{1.07}\text{S}_2$ ($x = 0.30$, $z = 0.21$) and $\text{Cu}_{0.70}(\text{In}_{0.70}\text{Ga}_{0.30})_{1.10}\text{S}_2$ ($x = 0.30$, $z = 0.30$) compared to those of the single phase samples with compositions close to $\text{Cu}(\text{In}_{0.70}\text{Ga}_{0.30})\text{S}_2$ (chalcopyrite crystal structure) and $\text{Cu}_{0.40}(\text{In}_{0.70}\text{Ga}_{0.30})_{1.20}\text{S}_2$ (trigonal structure, see next section). One can definitely conclude that there is a large miscibility gap for $0.04 < z < 0.60$ for mixed In/Ga CIGS compounds.

Figure 3.12: SEM backscattered electron micrograph of sample with target composition of $x=0.30$ and $z=0.30$ showing the equilibrium between an almost stoichiometric phase ($\text{Cu}_{0.96}\text{In}_{0.61}\text{Ga}_{0.39}\text{S}_2$ in dark grey) and a very copper poor one ($\text{Cu}_{0.41}\text{In}_{0.93}\text{Ga}_{0.26}\text{S}_2$ in light grey).

Figure 3.13: Powder X-ray diffraction pattern of CIGS samples with target compositions of $z=0, 0.21, 0.30$ and 0.60 . The $z=0$ pattern can be indexed in the chalcopyrite crystal structure while the $z=0.60$ pattern corresponds to a trigonal phase. The samples with intermediate compositions are clearly a mixing of these two phases.

4.5 Very copper-poor In/Ga phases

As already mentioned attempts to synthesize $\text{Cu}_{1-z}(\text{In}_{1-x}\text{Ga}_x)_{1+z/3}\text{S}_2$ compounds systematically lead to multi-phase-samples for $z > 0.1$ with the formation of very copper-poor new CIGS compounds. To solve the structure of these new quaternary compounds, four suitable crystals were picked up in powdered samples with the targeted $\text{Cu}_{0.7}(\text{In}_{0.7}\text{Ga}_{0.3})_{1.1}\text{S}_2$ ($z=0.3$, $x=0.3$), $\text{Cu}_{0.4}(\text{In}_{0.7}\text{Ga}_{0.3})_{1.2}\text{S}_2$ ($z=0.6$, $x=0.3$) and $\text{Cu}_{0.4}(\text{In}_{0.5}\text{Ga}_{0.5})_{1.2}\text{S}_2$ ($z=0.6$, $x=0.5$) compositions⁶⁵. Four layered

structure-types, depicted in Figure 3.14, were then identified and named CIGS₄, CIGS₅, CIGS₆ and CIGS₇. In the CIGS_n notations, *n* corresponds to the number of anionic layers of the slab. Two consecutive slabs are separated by a van der Waals gap. The EDX analyses concluded to Cu_{0.32}In_{1.74}Ga_{0.84}S₄ (CIGS₄-type), Cu_{0.65}In_{1.75}Ga_{1.4}S₅ (CIGS₅-type), Cu_{1.44}In_{2.77}Ga_{0.76}S₆ (CIGS₆-type) and Cu_{1.1}In_{2.49}Ga_{1.8}S₇ (CIGS₇-type) chemical compositions. All the structures exhibit a 2D-character with layers built upon (InS₆) octahedra sharing edges on which condense on both side 1, 2 or 3 layers made of (MS₄) tetrahedra (M = Cu, In, Ga) sharing corner. This generic formulae can then be written (M_(Td))_{n-2}(In_(Oh))S_n. Cell parameters for all compounds are given in Table 4.

For all structures, the octahedral sites (Oh) are exclusively and fully occupied by indium atoms. Contrarily, tetrahedral sites (Td) can be partially vacant and a mixed occupancy is often observed. Interatomic distances match with those reported in the literature for phases with similar chemical environments^{49,63,66}. As expected, the In-S bond distances in octahedral site (~2.6 Å) are larger than the In-S bonds in tetrahedral environment (~2.4 Å) that are larger than Cu(Ga)-S ones (~2.3 Å). The presence of cationic vacancies leads systematically to a slight shortening of the mean cation-sulfur bond distances compared to the expected ones. The vacancy rate of Td sites never exceeds 20% except for CIGS₇ in which a mixed site (In-Cu) exhibits a vacancy rate of 50%. It is also worth noticing that indium atoms in tetrahedral sites are preferentially located at the van de Waals gap frontier, probably for steric reasons.

CIGS₄, CIGS₅ and CIGS₆ structure-types with Td_(Cu,In,Ga,□)-Oh_(In)-Td_(Cu,In,Ga,□), (Td_(In,Ga)-Td_(Cu,Ga,□)-Oh_(In)-Td_(Cu,In)) and (Td_(Cu,Ga)-Td_(Ga,In,□)-Oh_(In)-Td_(Cu,Ga)-Td_(Ga,In,□)) sequences are isostructural to ZnIn₂S₄-type I, Zn₂In₂S₅-type IIa and Zn₃In₂S₆, respectively⁶⁷. The CIGS₅ stacking type has been also already observed for Ag_{1.25}Ga_{2.5}In_{3.75}S₁₀⁶⁸. Conversely CIGS₇ (Td_(In,Ga)-Td_(Cu,In,□)-Td_(Ga,□)-Oh_(In)-Td_(In,Ga)-Td_(Cu)) exhibits an unprecedented layered stacking.

Figure 3.14: Polyhedra representation of the structure for Cu_{0.32}In_{1.74}Ga_{0.84}S₄ (CIGS₄) Cu_{0.65}In_{1.75}Ga_{1.4}S₅ (CIGS₅), Cu_{1.44}In_{2.77}Ga_{0.76}S₆ and Cu_{1.1}In_{2.49}Ga_{1.8}S₇ compounds.

Table 4: Cell parameters for CIGS_n phases

	CIGS ₄	CIGS ₅	CIGS ₆	CIGS ₇
a (Å)	3.8203(6)	3.7898(2)	3.8506(2)	3.7933(3)
c (Å)	12.182(2)	30.664(3)	18.704(2)	21.540(14)
S G	P-3m1	P63mc	P-3m1	P3m1

Due to the strong structural similarity in between $(M_{(Td)})_{n-2}In_{(Oh)}S_n$ blocks and on the other hand to the 2D character of these building entities, intergrowths and stacking faults could exist. In fact, the quality of the single crystals was often poor and the proposed structural models (CIGS₄, CIGS₅, CIGS₆ and CIGS₇) should probably be considered as average structures. Due the multiple possibilities to distribute cations over tetrahedral sites, these materials are subject to chemical composition deviations (In/Ga) which open up an avenue for the stabilization of new materials. To illustrate this purpose, in Figure 3.15, the HAADF-STEM image of a faulted crystal and its corresponding [100] electron diffraction pattern are shown. The streaking of diffraction spots observed along c^* -axis testify of a strong structural disorder. In addition, the Z-contrast image (HAADF-STEM) figures out intergrowths. The In-based octahedral layers appear as brighter spots rows and tetrahedral (MS₄) ones like gray rows. The van der Waals gap is imaged as a dark area. The number of tetrahedral layers on each side of the In-based layers can be then easily counted and the different members of the series $(M_{(Td)})_{n-2}(In_{(Oh)})S_n$ can thus be identified (see annotations in Figure 3.15).

Figure 3.15: HAADF-STEM image of a faulted crystal highlighting the propensity of $(M_{(Td)})_{n-2}(In_{(Oh)})S_n$ materials to contain intergrowth defects (the structure-type, according to the CIGS_n notation is given for each slab). The van der Waals gaps are imaged as dark contrast lines. The inset gives the corresponding [100] electron diffraction pattern.

4.6 CIGS phase diagram

Taking into account all the above presented results (combined with data from literature), we can now propose a ternary phase diagram for the $Cu_2S-In_2S_3-Ga_2S_3$ system⁵⁹ limited to the copper-poor side of the stoichiometric line $CuInS_2-CuGaS_2$ (see Figure 3.16). As detailed above, except for the indium-free compounds (i.e. $Cu_{1-z}Ga_{1+z/3}S_2$) the tetragonal structure (either chalcopyrite or stannite) with only tetrahedral cationic environments definitely does not exist for copper-poor compositions. For such target compositions, the obtained samples are made of at least two phases: a phase close to stoichiometry $Cu(In,Ga)S_2$ is systematically in equilibrium with a very copper-poor one. The main structural feature of these very-copper poor phases is the distribution of indium both on tetrahedral and octahedral sites while Cu and Ga remain with tetrahedral coordination⁶⁵.

As already indicated, the aim of this investigation on CIGS sulfide materials was their potential application as top cell in a silicon based tandem solar cell. Although this concept is quite simple, the gain in energy conversion efficiency

compared to the silicon based single junction needs to have a high efficient top cell with efficiencies close to 20%⁶⁹. This target is very challenging taking into account that for CIGS material the performance rapidly drops when the bandgap increases⁷⁰. Even though cell efficiencies up to 10% have been achieved with pure sulfide CIGS based solar cells for quite a long time⁷¹, the record is, nowadays, just above 15%⁷² which is far below the efficiencies for the selenide CIGSe counterpart materials (> 23%). We have investigated crystal chemistry issues which can be correlated to this large difference between sulfide and selenide. The proposed ternary phase diagram definitely shows that mixed In/Ga copper-poor CIGS materials do not exist with a tetragonal symmetry (in contrast with selenide derivatives). In other words, as soon as the prepared composition is Cu-poor, the resulting sample corresponds to the equilibrium of an almost stoichiometric phase and very copper-poor phases with other crystal structures. Thus, in the case of thin films preparation, the control of the synthesis conditions has to be very precise to obtain single phase materials.

Figure 3.16: CIGS ternary phase diagram. The single phase domains (according EDX and PXRD analyzes) are indicated in blue. The hatched area indicates the poly-phase domain. The high gallium content domain has not been studied, except the indium free CGS line.

5 Summary

Due to the very strong dependence of properties of a material with its composition and its structural arrangement, much attention has to be devoted to its characterization. Indeed, for solid state chemists, crystal chemistry is the essence of their work. Once the long range ordering of atoms is determined, physical characteristics can be anticipated, and change in composition may be envisioned if needed to achieve desired properties. For sure, materials contain naturally intrinsic defects which may drastically impact their properties. These defects are in so low concentration that they request specific techniques to be identified and quantified (out of the scope of a crystal chemistry investigation). Nevertheless, crystal X-ray analyses can be appropriate to account defect in larger concentration, specifically when crystal sites are randomly occupied. If scattering factor are quite different, regular single crystal analyses are sufficient. On the contrary, resonant X-ray (or neutron) diffraction may be requested to distinguish ions with identical (or almost identical) electronic configuration but this requires facility access to a synchrotron radiation (or neutron) source. Nevertheless, let us mention that much information can be extracted from a careful crystal analysis with a conventional X-ray diffraction source in laboratory if characteristics of chemical species are taken into account, e.g. their oxidation states, their preferential chemical environment or their ionic radius. NMR is a powerful complementary technique to X-ray diffraction to get local information. Whatever, when both techniques are coupled, a better characterization of the materials is achievable that can be extrapolated to thin films and photovoltaic devices.

As illustrations of the above general description of the crystal chemistry approach, this chapter is dealing with the investigation of two compounds which can be used as absorber in thin film solar cells. In the case of CZTS material, we have shown how advanced characterization techniques (resonant single crystal X-ray diffraction and solid state NMR

spectroscopy) can help to understand the complex Cu/Zn distribution. Additionally, this study has shown that copper-poor CZTS compounds are less prone to Cu/Zn disorder than the stoichiometric $\text{Cu}_2\text{ZnSnS}_4$. This point can be correlated to the better photovoltaic performances obtained with such copper-poor CZTS absorbers. On the other hand, the investigation of the $\text{Cu}_2\text{S-In}_2\text{S}_3\text{-Ga}_2\text{S}_3$ system pseudo-ternary system illustrates the importance of careful structural determinations coupled to precise chemical composition analyses in order to evaluate the ability of such compounds to accommodate with copper deficiencies. For compositions of interest for tandem solar cells (i.e. $\text{Ga}/(\text{Ga}+\text{In})$ close to 0.3) the single phase stability domain is shown to be very narrow. The consequence is that for thin film preparations, the control of the synthesis conditions has to be very precise to obtain single phase materials.

According to the literature, both for CZTS and CIGS compounds, selenides lead always to better photovoltaic efficiencies than the sulfide counterparts. This fact is likely correlated to the higher structural flexibility of selenides which can keep the tetrahedral metal coordination in a wide copper-composition range.

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