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Structure Flexibility of the Cu_2ZnSnS_4 Absorber in Low-Cost Photovoltaic Cells: From the Stoichiometric to the Copper-Poor Compounds

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Supporting Information

ABSTRACT: Here we present for the very first time a single-crystal investigation of the Cu-poor Zn-rich derivative of Cu_2ZnSnS_4. Nowadays, this composition is considered as the one that delivers the best photovoltaic performances in the specific domain of Cu_2ZnSnS_4-based thin-film solar cells. The existence of this nonstoichiometric phase is definitely demonstrated here in an explicit and unequivocal manner on the basis of powder and single-crystal X-ray diffraction analyses coupled with electron microprobe analyses. Crystals are tetragonal, space group $I\bar{4}$, $Z = 2$, with $a = 5.43440(15)$ Å and $c = 10.8382(6)$ Å for Cu_2ZnSnS_4 and $a = 5.43006(5)$ Å and $c = 10.8222(2)$ Å for $Cu_{1.71}Zn_{1.18}Sn_{0.99}S_4$.

Chalcogenide thin-film solar cells are very promising to achieve grid parity for the production of photovoltaic electricity.[1] In that context, the CdTe- and $Cu(In,Ga)Se_2$ (CIGS)-based technologies have currently reached the industrial production level, even if many issues are still under discussion, giving rise to fundamental researches. Unfortunately, the chemical elements involved in these solar cells are toxic or scarce, and very expensive, which could impede further developments on a large scale.

One of the reasons for the "success story" of the CIGS thin-film solar cells is related to the huge flexibility of its chalcopyrite crystal structure.[2,3] This flexibility is a key point for multinary compounds because the growth of thin films is in essence a nonequilibrium process that goes along with slight local unhomogeneities in composition to be balanced by the structure type.

Namely, Cu_2ZnSnS_4-derived compounds (CZTS) have drawn much attention in recent years as potential absorber candidates for low-cost solar cells. A large set of thin-film deposition methods has been investigated,[4] yielding a dramatic increase of the solar energy conversion efficiency, up to about 10%.[5] The best solar cells always show deviations from the ideal stoichiometry of Cu_2ZnSnS_4 to Cu-poor, Zn-rich compositions.[6,7] However, the real nature of these nonstoichiometric phases is still unknown. Because the electronic behavior of a semiconductor is highly related to its crystal structure, it is of strong interest to investigate the nature of the compounds in the Cu−Zn−Sn−S system on a solid-state chemical point of view, to address issues such as phase domain limits, actual chemical compositions, and crystal structures.

So far, several crystal structures are reported in the literature for the Cu_2ZnSnS_4 composition. Namely, this compound belongs to the $Cu_2(Fe,Zn)SnS_4$ series, in which two natural minerals are known: stannite (iron-rich) and kësterite (zinc-rich).[8] Both minerals adopt a tetragonal symmetry with the $I\bar{4}2m$ and $I\bar{4}$ space groups for stannite and kësterite, respectively. The difference between the two structures comes from the distribution of the Cu and (Fe, Zn) atoms over the cationic sites. In any case, it is worth noticing that both stannite and kësterite structures are closely related to the chalcopyrite structure of $CuInSe_2$, where one In^{3+} cation is formally replaced by 0.5 $(Fe, Zn)^{2+}$ and 0.5 Sn^{4+} cations.

The first published single-crystal investigation of a synthetic iron-free compound (Cu_2ZnSnS_4) concluded that the stannite structural model better fits the experimental data than the kësterite model.[9] Later on, neutron powder diffraction experiments[10] as well as theoretical studies based on first-principles calculations[11,12] have demonstrated that Cu_2ZnSnS_4 adopts the kësterite structure. However, because the two structures are thermodynamically very close, we may suppose that the synthetic route can strongly impact the adopted structure. This would explain why published powder X-ray diffraction (PXRD) data can coincide either with the stannite structure,[13] with the kësterite structure[14] or with a disordered stannite structure in which Cu and Zn atoms are randomly distributed over their exclusive sites. In addition, all of these PXRD patterns are commonly indexed in tetragonal unit cells with c/a ratios very close to 2, leading to the nondiscrimination of several doublets (e.g., 220/204, 312/116). On the other hand, it is well-known that Cu^+ and Zn^{2+} ions exhibit very similar X-ray scattering factors, hindering any refinement of the Cu/Zn distribution over the crystallographic sites of CZTS compounds from the conventional powder patterns. So, the three structural models (kësterite, stannite, and disordered stannite) cannot be distinguished from X-ray diffraction experiments, which can explain the different structural models available in the literature. Herein, we present the (re)-investigation of the crystal structure of both a stoichiometric Cu_2ZnSnS_4 compound as well as a Cu-poor CZTS derivative based on accurate chemical analyses, single-crystal X-ray structure investigations, and PXRD measurements.

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The elemental composition of the samples (see experimental synthesis details in the Supporting Information, SI) is a critical point for this study, and many efforts have been made to ensure both accuracy and precision in these measurements. Practically, powders were embedded in epoxy and polished to get a perfect flat surface of the grains. Elemental analyses were performed using the Wavelength Dispersion Spectrometry technique (see details in the SI). The use of calibrated internal standards leads to very reliable results.

It is worth noticing for both samples that the individual spot analyses are very lightly dispersed around average compositions (see Figure 1), showing that the powders are highly homogeneous. The corresponding formulations are $Cu_{1.996(8)}Zn_{1.001(7)}Sn_{1.008(9)}S_{4.000(9)}$ (sample 1) and $Cu_{1.711(6)}Zn_{1.181(7)}Sn_{0.994(5)}S_{4.00(1)}$ (sample 2) for Cu_2ZnSnS_4 and $Cu_{1.6}Zn_{1.2}SnS_4$ targeted compositions, respectively. In order to check the precision of the obtained results, the statistic errors (3σ) based on the measured intensities of the individual lines of Cu, Zn, and Sn in the X-ray spectra are represented by polygons in Figure 1. The two compositions are clearly distinct, demonstrating for the very first time the existence of a nonstoichiometric compound in the CZTS system as a bulk material. The composition of a Cu-poor CZTS compound corresponds to Cu/(Zn + Sn) = 0.787 and Zn/Sn = 1.188. These ratios are very close to those of the CZTS compounds reported to give the best solar cell performances (i.e., Cu/(Zn + Sn) = 0.8 and Zn/Sn = 1.22).[15]

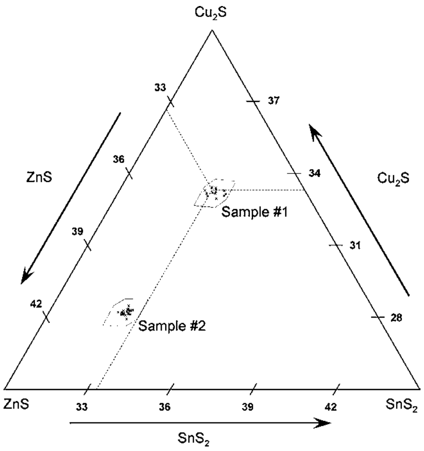

Figure 1. Elemental compositions of the studied samples in a pseudoternary diagram. Crosses correspond to the individual spots, and the dashed lines indicate the nominal Cu_2ZnSnS_4 composition. The polygon around the spots represents the statistic errors (3σ).

Single crystals suitable for diffraction were selected from the powder samples. The data collections were done on a Nonius diffractometer. The refinements were carried out with the help of the *JANA2006* program.[16] From the selected single crystal of the stoichiometric compound (sample 1), reliability factors of $R(\mathrm{obs})/R_w(\mathrm{obs})$ = 3.38/8.14 (for 389 unique observed reflections and 14 parameters) were obtained for the stannite structure, while the refinement converged to $R(\mathrm{obs})/R_w(\mathrm{obs})$ = 3.36/8.07 (684 unique observed reflections and 19 parameters) when the kësterite structural model was used. From these results, it is tricky to discriminate between the stannite and kësterite models. However, from a convincing neutron powder diffraction study, Schorr et al.[10] have definitely shown that Cu_2ZnSnS_4 adopts the kësterite structure. So, we decided naturally to keep this model for refinement. In that context, the cations are located on centrosymmetric positions, i.e., Cu(2a), Cu(2c), Zn(2d), and Sn(2b), with the whole structure being noncentrosymmetric because of the position of the S atoms (8e). Thus, the absolute configuration was checked by refining the inversion twin ratio. The *R* factors for the inverted structure are $R(\mathrm{obs})/R_w(\mathrm{obs})$ = 4.22/9.55, so we can definitively conclude that the structure of Cu_2ZnSnS_4 corresponds to that of $Cu_2(Fe,Zn)SnS_4$ already published by Hall et al.,[8] in which the position of the S atom is [0.7562(2), 0.2434(2), 0.12821(6)]. The quality of this single-crystal structure refinement is supported by the bond-valence calculation according to Brown and Altermatt.[17] Using the bond-valence coefficients of 1.81, 2.09, and 2.40 Å for Cu, Zn, and Sn atoms, respectively,[18] the bond-valence sums are found to be very close to the expected values for Cu^+, Zn^{2+}, and Sn^{4+}, i.e., 0.98, 2.09, and 3.86, respectively.

By analogy with the previous study on the stoichiometric compound, the single-crystal structure refinement for the nonstoichiometric compound (sample 2) was performed starting from the kësterite model (see comments about the stannite model in the SI). At the first step of the refinement, it was clear that the 2a crystallographic site was not fully occupied. In CZTS compounds, the charge balance is achieved with Cu^+, Zn^{2+}, and Sn^{4+} oxidation states. According to the chemical composition of sample 2, i.e., Cu/(Zn + Sn) < 1 and Zn/*Sn* > 1, copper vacancies were expected to be counterbalanced with Zn^{2+} cations in excess. Thus, two substitution processes could be envisioned: (i) two Cu^+ cations are replaced by one Zn^{2+} cation located at the 2a site, leading also to one vacancy on this site [formally $2Cu^+(2a) \leftrightarrow Zn^{2+}(2a) + V_{Cu}(2a)$]; (ii) one Cu^+ cation is removed from the 2a site, leading to one vacancy on this site, while one Cu^+ cation is replaced by one Zn^{2+} cation on the 2c site [formally $Cu^+(2a) + Cu^+(2c) \leftrightarrow Zn^{2+}(2c) + V_{Cu}(2a)$]. The second model is statistically much more favorable to ensure the charge balance around a specific S atom, which is 4-fold-coordinated with cations lying at the 2a, 2b, 2c, and 2d sites (see Figure SI-1 in the SI). Thus, the refinement was performed with Cu on the 2a site (partially occupied) and Cu/Zn on the 2c site (fully occupied), with the site occupancy factors (sof's) being constrained to fulfill the charge balance, i.e., $\mathrm{sof}(Cu_{2a}) + \mathrm{sof}(Zn_{2c}) = 1$ and $\mathrm{sof}(Cu_{2c}) + \mathrm{sof}(Zn_{2c}) = 1$. The *R* factors decrease from 4.24/9.95 to 3.87/8.83 (668 unique observed reflections and 19 parameters) when $\mathrm{sof}(Zn_{2c})$ increases from 0 to 0.058(4). In the final step, the enantiomer configuration was tested, leading to a better refinement [$R(\mathrm{obs})/R_w(\mathrm{obs})$ = 2.84/7.32], with the position of sulfur being [0.2437(2), 0.2438(2), 0.12773(7)]. The obtained crystallographic formula is then $Cu_{1.8847(8)}Zn_{1.0577(4)}SnS_4$, demonstrating that this compound is Cu-poor compared to Cu_2ZnSnS_4. Nevertheless, this composition is slightly different from that deduced from microprobe analysis, $Cu_{1.711(7)}Zn_{1.181(7)}Sn_{0.994(5)}S_{4.00(1)}$, likely because of the low sensitivity of the X-ray refinement of the sof's even if a possible deviation of the single-crystal composition from that of the bulk cannot be rebutted. All of the refinement results, atomic positions, sof's, and anisotropic atomic displacement parameters are given as SI.

Rietveld refinements (see experimental details in the SI) using the structures determined from the single-crystal investigations were performed using the *JANA2006* program.[16] The very good agreement between the observed and calculated patterns is clearly visible in Figure 2. These refinements show

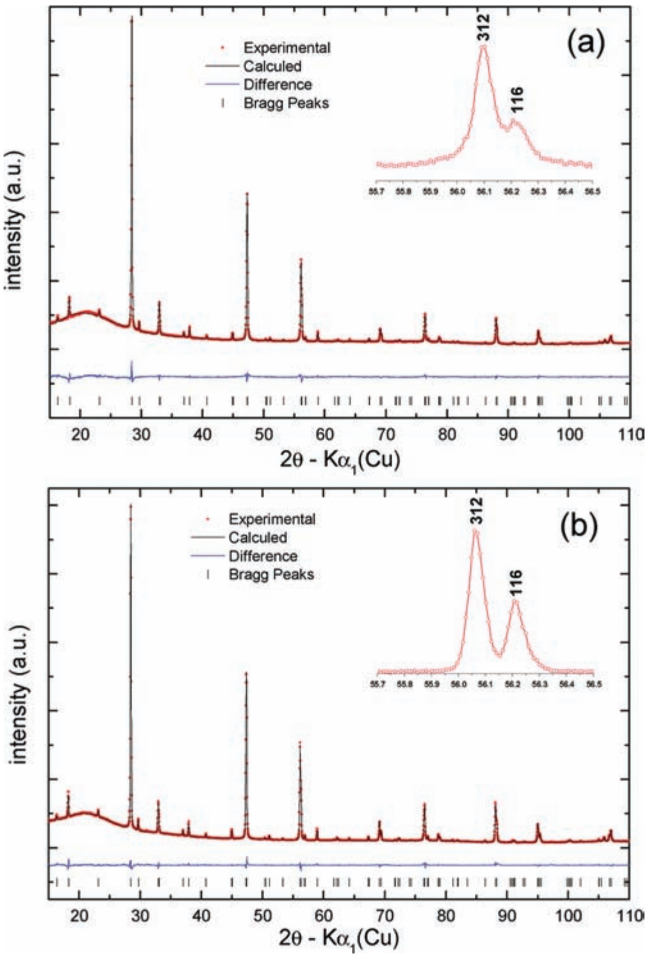

Figure 2. Rietveld refinement plots for samples 1 (a) and 2 (b). The insets evidenced the separation of the (312)/(116) doublets thanks to the high-resolution Bruker D8-diffractometer corresponding to c/a ratios of slightly less than 2 for both samples (see Table 1).

that the unit-cell parameters very slightly depend on the actual compositions of CZTS compounds (see Table 1). In the case of the stoichiometric compound (sample 1), the refined unit-cell parameters are found to be a little bit different from those available in the literature,[13,14] likely because of the small deviation from the nominal compositions in the other studies. The results of the Rietveld refinements are given in Table 1. From these refinements, the calculated densities are of 4.558 and 4.497 for Cu_2ZnSnS_4 and $Cu_{1.71}Zn_{1.18}Sn_{0.99}S_4$, respectively, which can be compared to the experimental ones, 4.57(4) and 4.43(5).

Table 1. Rietveld Refinement Results for Both Samples 1 and 2 (See Figure 2)[a]

	sample 1	sample 2
chemical composition	Cu_2ZnSnS_4	$Cu_{1.71}Zn_{1.18}Sn_{0.99}S_4$
R_{wp}	3.63	2.73
GOF	2.27	2.43
R/R_w(obs)	3.87/4.46	2.68/3.36
a (Å)	5.43440(15)	5.43006(5)
c (Å)	10.8382(6)	10.8222(2)
V (Å^3)	320.08(2)	319.098(7)
c/a	1.99437(12)	1.99302(4)

[a] The atomic positions are those determined from the single-crystal structure refinements.

For the first time, it was clearly demonstrated that the kësterite structure can accept some shifts from the standard Cu_2ZnSnS_4 composition. Nevertheless, at first sight, this structure seems to be much less flexible than the chalcopyrite structure in which a very high concentration in copper vacancies (up to 75%) can be observed.[3] This result could explain why the preparation of efficient CZTS-based solar cells is more complicated than using CIGS materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, data collection conditions, and refinement results for the single-crystal X-ray diffraction study of samples 1 and 2 and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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