Local Atomic Structure and Analysis of Secondary Phases in Non-Stoichiometric $\text{Cu}_2\text{ZnSnS}_4$ Using X-ray Absorption Fine Structure Spectroscopy

R.A. Colina-Ruiz^a, J. Mustre de León^a, J.S. Lezama-Pacheco^b, F. Caballero-Briones^c, M. Acosta-Alejandro^d, F.J. Espinosa-Faller^{e,*}

^a *Departamento de Física Aplicada, CINVESTAV Unidad Mérida, Mérida, Yucatán 97310, México.*

^b *Department of Earth System Science, Stanford University, Stanford, California 94305, USA.*

^c *Instituto Politécnico Nacional, Materials and Technologies for Energy, Health and Environment (GESMAT), CICATA Altamira. Km 14.5 Carretera Tampico-Puerto Industrial Altamira, 89600 Altamira, México*

^d *Universidad Juárez Autónoma de Tabasco, Cunduacán, Tabasco, 86690, México.*

^e *Universidad Marista de Mérida, Mérida, Yucatán 97310, México.*

* Corresponding author.

E-mail address: fjespinosa@marista.edu.mx (F.J. Espinosa-Faller)

ABSTRACT: The local atomic structure in non-stoichiometric $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films was investigated using X-ray absorption fine structure spectroscopy (XAFS). From the XAFS spectra we infer the presence of disorder in the Cu-Zn plane suggesting that this characteristic might be intrinsic of non-stoichiometric CZTS. This disorder increases with the $\text{Cu}/(\text{Zn}+\text{Sn})$ ratio. Structural parameters derived from fits to the data show a contraction in the Cu-S bond length and an expansion in the Sn-S bond length, compared to distances obtained from diffraction, for all samples. X-ray absorption near edge spectroscopy (XANES) indicates presence of secondary phases not observed by X-ray diffraction. In Cu-poor samples, ZnS and SnS were identified as secondary phases. The amount of those phases correlates with the Cu deficit and were quantified by a linear combination fit of the XANES of standard materials. This work provides direct evidence of intrinsic disorder in CZTS, which must be considered to generate a realistic atomic structural model, in addition to lattice relaxations and secondary phases.

KEYWORDS:

$\text{Cu}_2\text{ZnSnS}_4$; Thin films; XAFS; Crystal structure; Secondary phases; Disorder.

1. INTRODUCTION

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is currently considered as a prime ingredient for thin film solar cells, catalysts and sensors as it is composed of earth abundant non-toxic elements [1–4]. CZTS is considered a promising candidate for the absorbing layer in solar cells due to its direct bandgap of ~ 1.5 eV, a high absorption coefficient ($>10^4 \text{ cm}^{-1}$) and its native p-type conductivity [5,6]. The most efficient CZTS solar cells (9.2%) have been produced with a Cu-poor and Zn-rich composition ($\text{Cu}/(\text{Zn}+\text{Sn}) = 0.88$, $\text{Zn}/\text{Sn} = 1.18$) [7,8]. Still, higher efficiencies (12.6%) have

been achieved by substitution of S by Se. [9]. Copper is expected to generate shallow acceptor levels where Zn atoms form antisite defects (Zn_{Cu}) [10,11]. Structurally, this generates not only local lattice relaxations around antisite atoms and vacancies but also local fluctuations in composition that might extend several unit cells breaking the expected crystallographic periodicity and homogeneity. This would result in variations of the electronic properties of the material at the local level [12]. Structural disorder in stoichiometric CZTS has been previously reported indicating the presence of antisites and disorder in the cationic Cu/Zn planes [13–15]. In principle CZTS can crystallize either in Kesterite or Stannite structures, however, first principles calculations show that Kesterite has a lower energy of formation [16]. Hence, one has a higher probability of obtaining the Kesterite phase when the material is grown and/or annealed at high temperatures. Crystallographically, the Kesterite structure has space group I-4 with lattice parameters [17,18] $a = b = 5.428 \text{ \AA}$ and $c = 10.846 \text{ \AA}$, as shown in Fig. 1.

Fig. 1. Kesterite structure of CZTS, where Cu is shown in red, Zn in gray, Sn in green and S in yellow.

As perfectly crystalline CZTS might not be adequate as a photovoltaic material, it is important to characterize non-stoichiometric material. Moreover, theoretical studies indicate that the Kesterite structure forms within a narrow chemical potential range. Consequently, under non-stoichiometric growth conditions, the precipitation of secondary phases like Cu_2S , CuS , ZnS , SnS , SnS_2 and Cu_2SnS_3 is expected [10,11,19]. Consequently, the actual atomic structure of a material that can be useful for photovoltaic applications might differ in substantial manner from the ideal crystalline structure.

The Kesterite structure of CZTS consists of alternating layers of Cu/Sn (located at $z = 0, 1/2$, and 1) and Cu/Zn (located at $z = 1/4$ and $3/4$) with alternating atoms at the corners and the center of the ab plane being held together with S layers formed by two S atoms (at $z = 1/8, 3/8, 5/8$, and $7/8$). The S atoms are located at the centers of Cu(2)-Sn-Zn tetrahedral. We note that the S atoms are slightly displaced from the $(1/4, 1/4, 1/8)$ positions to accommodate the Sn ion, which is larger than Cu and Zn [20,21]. The principal structural variant of Kesterite, Stannite, is formed by alternating Cu planes with Sn/Zn planes. This phase is slightly higher in energy (~ 2.8 meV/atom) with respect to Kesterite so it should not form under high temperature processing and annealing [22]. The nearest neighbor environment for all metal atoms consists of 4 sulfur atoms at $2.350 \text{ \AA}$ forming a tetrahedron. For Zn (Sn) atoms, second neighbors are composed of 4 Cu atoms at $3.840 \text{ \AA}$ coming from the Cu/Zn (Cu/Sn) planes and 8 Cu/Sn (Cu/Zn) atoms at $3.836 \text{ \AA}$ placed at neighboring planes. For Cu atoms, the second neighbor environment is more complex, consisting of 4 Zn/Sn atoms at $3.840 \text{ \AA}$ (corresponding to the Cu/Zn and Cu/Sn planes) and 8 Cu/Sn or Cu/Zn neighbors from neighboring planes at $3.836 \text{ \AA}$. The third neighbor shell is composed of sulfur atoms located at a distance of $4.4 \text{ \AA}$.

In order to reveal the actual atomic structure of complex materials, one uses as a starting point the crystallographic description. Average atomic positions within a unit cell are modified using information obtained from local atomic structure techniques such as X-ray absorption fine structure spectroscopy (XAFS) which identify deviations from it. It is important to determine the actual local atomic structure of the material, which differs from the average crystallographic structure, and also the presence of secondary residual phases. Both aspects are crucial to determine the actual electronic structure of the material and provide an understanding of the advantage of the non-stoichiometric material as a component of a solar cell.

In this paper, we address the local atomic structure environment around all atoms in non-stoichiometric CZTS samples. Local deviations from the crystallographic structure provide insights into the structural effects of the Cu deficit/surplus in the short-range order and its consequences for the long-range order in the atomic structure. For local structure analysis, XAFS provides a one-dimensional atom specific pair distribution function, coming from the Fourier transform of the X-ray absorption spectra. Oscillations in the XAFS spectra are due to photoelectron backscattering from neighboring atoms that generate an interference pattern relating the X-ray absorption spectra to the local atomic structure. XAFS is normally used to obtain neighbor distances from a specific absorbing atom species with a precision between 0.01 and 0.03 Å. In addition, it can be used to obtain the pairwise Debye-Waller factor and the identity and number of neighboring atoms if large deviations from the crystallographic description of the structure are present, albeit the precision in the number of atoms lies between 10% and 30% [21].

2. EXPERIMENTAL AND ANALYTICAL PROCEDURES

Samples were prepared in a two-step process [23–25]. First, a stack of ZnS, Sn and Cu layers were deposited by vacuum thermal evaporation over soda lime glass at a substrate temperature of 150 °C. Thicknesses of the layers were measured by a quartz crystal monitor and were adjusted to provide the required composition. Four samples were prepared in this way and were labeled as C64, C85, C91 and C106. Such naming scheme is related with the composition of Cu of the samples and it is used herein as a simple identifier. A stack of ZnS/Sn/Cu of 396/350/254 nm was deposited for sample C64. For samples C85, C91 and C102, the thicknesses of the layers were 368/355/277, 340/361/299, 313/369/318 nm respectively. Base pressure was $<10^{-5}$ Torr and raw materials were 99.99 % pure ZnS pieces, 99.999 % pure Cu pellets, 99.998 % pure Sn pellets and sulfur powder 99.9 % pure. In a second step, each multilayer was subject to a sulfurization process. The multilayer was mounted in a graphite box with a sulfur powder pellet. The sulfurization process started at room temperature (~ 24 °C), increasing the temperature at a rate of 10 °C/min until it reached 250 °C. This temperature was then held constant for 30 min. At this temperature, a combination of the metallic sulfur compounds was obtained. After this step, a second ramp in temperature was performed at a rate of 10 °C/min until the graphite box reached 510 °C. Previous work reports that CZTS forms within about 3 minutes above 500 °C [26,27] and at temperatures above 550°C the loss of Sn and Zn becomes considerable [25,28]. Hence, the graphite box was held at 510 °C for 30 minutes in order to minimize Sn and Zn losses and to allow diffusion, in order to obtain crystalline samples [29] (Zhang 2013). After sulfurization, the sample was left to cool freely to room temperature. A chemical etch of 30 sec. in a solution of 5% KCN was finally performed to remove any copper sulfide excess [30–32]. Details of the growth procedure will be published elsewhere [33].

Elemental concentration was determined by energy dispersive X-ray analysis (EDS) in a Jeol JSM-7600F electron microscope in high vacuum mode with an accelerating voltage of 25 kV and covering an area of 250 x 170 μm^2 . X-ray diffraction measurements were performed in a Siemens D5000 diffractometer fitted with a Cu anode. All diffraction peaks were indexed and the GSAS [34,35] code was used to obtain the lattice parameter. XAFS measurements for Cu, Zn and Sn were carried out in fluorescence mode using a 30-element Ge solid-state detector at beam line 4-1 at the Stanford Synchrotron Radiation Lightsource (SSRL). Samples were mounted in a liquid nitrogen cryostat for measurements at ~ 80 K. Sulfur XAFS was measured at room temperature at beamline 4-3 of SSRL configured in low energy mode using a 4-element Ge detector. Beam intensity was monitored with an ionization chamber, and the absorption spectra were obtained by plotting the ratio between the fluorescence of the sample and the incident beam intensity. Corrections for detector deadtime were performed using standard procedures. For beamline 4-1, a liquid nitrogen cooled Si (200) double crystal monochromator was used to select the energy of the incident X-ray beam in an unfocused energy range from 5500 eV to 38000 eV necessary for the measurements at the Cu, Zn and Sn K-edge. Harmonic rejection was accomplished by changing the relative alignment of the monochromator until the flux was reduced to 50% of its maximum level. For beamline 4-3, a liquid nitrogen cooled Si (111) double crystal monochromator was used for measurements at the S K-edge (2472 eV). Harmonic rejection was accomplished using a Rh coated mirror in the beam path. Energy calibration was performed using the first inflection point in K-edge spectra of Cu, Zn and Sn foils and sodium thiosulfate powder as 8979 eV, 9659 eV, 29200 eV and 2472.02 eV respectively. E_0 was set to the calibration energy such that the photoelectron wave vector is $k = \sqrt{(2m/\hbar^2)(E - E_0)}$ [36].

Data reduction and analysis were performed in a standard manner, with the use of the IFEFFIT, ARTEMIS and ATHENA data analysis programs [37]. Data were normalized setting the value of a second order polynomial fit over the pre-edge to zero and a third order polynomial over the region above the edge to unity at E_0 . XAFS were extracted as the difference between the normalized spectra and an adjustable spline function over the edge. The knots of this spline were determined by minimizing the low frequency residuals ($R < 1.0 \text{ \AA}$) in the Fourier transform modulus of each absorption spectra. Theoretical scattering amplitude and phases were calculated using the ab-initio code FEFF8 [38].

Structural parameters were obtained via nonlinear least squares curve fitting in momentum space (k) with data weighted by k^2 , using a Hanning window function, in the range $2.75 \text{ \AA}^{-1}$ - $12.75 \text{ \AA}^{-1}$. The fits included three coordination shells and we considered fitting paths with amplitudes over 10% using mainly single scattering paths (SSP) and double scattering paths (DSP) to get high quality fits and not to exceed the maximum limit of independent fitting parameter in our model. For Cu K-edge and Zn K-edge fits, 4 SSP and 3 DSP were taken, for Sn-K edge were considered 3 SSP and 1 DSP, finally at the S K-edge we performed fits with 5 SSP and 1 DSP. The fit quality was estimated from the value of the R-factor, a measure of the goodness of fit relative to the theoretical model (a good value of R-factor is < 0.02 [37]).

3. RESULTS AND DISCUSSION

3.1 EDS

The composition of the samples as measured by EDS is shown in Table 1. For the Cu poor samples (C64, C85 and C91) the ratio between Cu and Zn+Sn increases from 0.64 to 0.91 while the relation Zn/Sn decreases from 1.64 to 1.0. The metal rates Cu/Zn and Cu/Sn increases as the

copper content increases. Sulfur excess is observed, confirming previous reports for samples annealed in an S atmosphere [6,24]. The ratio between sulfur and metal concentration decreases from 1.23 to 1.12. For the Cu richest sample (C102), a different ratio between metals is observed. The excess of Cu ($\text{Cu}/(\text{Zn}+\text{Sn}) = 1.02$) is accompanied with a reduction in Zn and an excess Sn as shown in the metals ratios $\text{Zn}/\text{Sn} = 0.8$ and $\text{Cu}/\text{Zn} = 2.30$. This result could indicate that the Cu/Zn plane is rich in copper (Cu_{Zn}) while the Cu/Sn plane is compensating with an excess Sn (Sn_{Zn}) [21]. The composition ratios indicate deviations from stoichiometry that reflect either defects in the structure or formation of secondary phases. It is important to note that sample C85 with a $\text{Cu}/(\text{Zn}+\text{Sn})$ ratio of 0.85, Zn/Sn of 1.10 and Cu/Sn of 1.79 has a composition close to the highest efficiency CZTS solar cell recently reported by Sun et al. [8] with ratios $\text{Cu}/(\text{Zn}+\text{Sn}) = 0.88$ and $\text{Zn}/\text{Sn} = 1.18$. As sample C85 is poor in Cu concentration, it is expected the formation of antisite defects Zn_{Cu} which form shallow acceptors [10]. In addition to this discussion we note that morphologically, samples have an average grain size of $\sim 1.0 \mu\text{m}$ and bandgaps that vary from 1.39 to 1.47 eV, consistent with other reports [1,39–41].

Table 1. Sample composition and lattice parameters.

	Samples			
Relations	C64	C85	C91	C102
$\text{Cu}/(\text{Zn}+\text{Sn})$	0.64	0.85	0.91	1.02
Zn/Sn	1.64	1.10	1.00	0.80
Cu/Zn	1.03	1.62	1.83	2.30
Cu/Sn	1.69	1.79	1.83	1.84
S/Metals	1.23	1.18	1.12	1.19
Lattice parameters				
$a=b$	5.427(2)	5.4291(2)	5.4338(1)	5.4280(1)
c	10.8280(7)	10.8352(6)	10.8458(4)	10.8336(4)
$c/2a$	0.9976	0.9979	0.9980	0.9979
Cell volume	318.87(3)	319.37(1)	320.24(2)	319.19(2)

3.2 XRD

The diffraction pattern of the CZTS samples is shown in Fig. 2. We note that the intensity is presented in a logarithmic scale to better appreciate low intensity superstructure reflections of the Kesterite structure. All peaks were indexed and correspond to the Kesterite structure [18,42]. The sharpness of the peaks is indicative of the good crystallinity of the samples. The observed non-monotonic decreasing background of samples C91 and C102 is indicative of either an amorphous contribution from the soda-lime substrate or coming from diffuse scattering generated by disorder in the samples [43]. Analysis of the diffraction patterns using the GSAS software indicates that all peaks positions and intensities correspond to the CZTS Kesterite structure. Lattice parameters are reported in Table 1, where a trend in increasing cell volume is observed, except for sample C102 where a small reduction is observed. It is important to mention that the diffraction pattern of ZnS in the zinc-blende structure matches the main reflections of the Kesterite, so from the diffraction pattern alone one cannot rule out the presence of this phase [44].

Fig 2. X-ray diffraction pattern of samples C64 (a), C85 (b), C91 (c) and C102 (d). Bragg peaks are indexed with the structure of CZTS.

3.3 XANES

X-ray Absorption Near Edge Structure (XANES) spectra in the K-edge of Cu, Zn, Sn and S are presented in Fig. 3. XANES is sensitive to changes in the local electronic states around the absorbing species [45]. In the K-edge absorption process, the initial state is a K-shell (1s electron), while the final state is a photoelectron corresponding to an unoccupied state with *p*-symmetry with respect to the absorbing atom. XANES has been used to obtain information about the oxidation state of the absorbing species [46]. It can also be used to signal the presence of secondary phases by shifting positions and/or intensities of peaks near the absorption edge [47]. For the Cu K-edge (Fig. 3a) the absence of any significant change in the absorption edge energy or developing features in the near edge spectra discards the presence of significant amounts of

Cu related secondary phases. A small decrease in the intensity of the main absorption peak at ca. 8985 eV with Cu content indicates a decrease in the unoccupied electronic states around Cu probably due to a reduction in point defects, as more copper is included in the structure (see inset) [11,38]. The Zn K-edge XANES (Fig. 3b) presents an interesting feature. A shoulder to the left of the main absorption peak at Ca. 9665 eV is developed (see inset). This shoulder indicates the presence of unoccupied electronic states which most likely arise from the presence of a secondary phase that contains Zn or a changing environment around Zn [47,48].

We observe that the shoulder decreases as the amount of Cu increases, being the sample with less Cu (C64) the one that presents the shoulder with the largest intensity. Fig. 3c presents the Sn K-edge XANES. We observe a distinct behavior for sample C64, departing from the three other samples by an increased intensity and a shift in the absorption edge. From the inset we can identify the presence of SnS as a secondary phase in sample C64. For samples C85, C91 and C102, the Sn XANES show no difference, indicating that the Sn electronic local environment is not being sensitive to changes in sample composition. The sulfur XANES (Fig. 3d) is perhaps the most complex due to the fact that all metals are nearest neighbors of S, consequently, the sulfur XANES can be very informative about secondary phases although its interpretation becomes more difficult. The inset shows the XANES of SnS and ZnS, the most likely secondary phases in the samples. We note the presence of SnS for sample C64 by the increased intensity of the second and third peak. This result confirms the information obtained from the Sn XANES. The presence of ZnS can be identified by the relative amplitude of the pre-edge peak at ~2470 eV and the edge peak at ~2472 eV. As the amount of Cu increases, the pre-edge peak increases, while the edge peak decreases. When the pre-edge peak is smaller than the edge peak, significant

amounts of ZnS are present in the samples [48]. This indicates that as the relative amount of Cu increases, the presence of ZnS decreases.

Fig. 3. Normalized XANES spectra of (a) Cu K-edge, (b) Zn K-edge, (c) Sn K-edge and (d) S K-edge. Inset of (a) shows the region of the main XANES peak of all samples. For (b), (c) and (d), insets compare the XANES spectra of sample C91 with standards.

Changes in the sulfur XANES caused by secondary phases can be quantified by the superposition of reference XANES with a linear combination fit. We performed fits of the XANES of the samples with ZnS and SnS standards, taking as internal reference sample C91 in the range 2470-2480 eV. These fits indicate that the amount of ZnS in samples C64, C85 and C102 is $14\% \pm 3\%$, $6\% \pm 2\%$ and $1\% \pm 1\%$ respectively; while the amount of SnS is $11\% \pm 1\%$, $4\% \pm 1\%$ and $2\% \pm 0.3\%$ respectively. Fig. 4 shows the linear combination fit of the XANES.

The quality of XANES fits can be quantified with the R-factor [37]. For sample C64, $R=0.0098$ while for samples C85 and C102, $R=0.0099$. These values are below the recommended limit value for a reasonable fit at $R=0.02$. These results indicate that Cu-poor and Zn-rich samples tend to generate ZnS together with some SnS as indicated by the XANES. It is important to stress that XRD spectra provide no evidence of SnS secondary phases. This can be explained if the secondary phase particle size is below the diffraction limit, a characteristic that has been observed in other systems [49].

Fig. 4. Linear combination fit of the XANES for samples C64, C85 and C102 with ZnS and SnS standards with sample C91 as reference.

3.4 EXAFS

Raw data in the extended X-ray absorption fine structure (EXAFS) region is presented in Fig. 5. A decrease in the amplitude of the oscillations with Cu concentration is observed. This is more prominent for the Cu and Zn EXAFS in the region between $5 \text{ \AA}^{-1}$ and $10 \text{ \AA}^{-1}$, indicating a larger Debye-Waller factor. The Debye-Waller factor in EXAFS contains a thermal disorder component and a static disorder component. The decrease in amplitude corresponds to static disorder, since all measurements were performed at the same temperature.

Qualitatively, we note from Fig. 5 that disorder around Cu and Zn is not accompanied with a corresponding disorder in the Sn and S EXAFS. This observation suggests that disorder in Cu-Zn planes is not accompanied with disorder in the Cu-Sn planes. This characteristic was first reported by S. Schorr [50] based on neutron diffraction data for stoichiometric CZTS synthesized by the Bridgman technique. Thus, disorder in the Cu-Zn planes is not a specific characteristic of non-stoichiometric CZTS but it is intrinsic to CZTS.

Fig. 5. EXAFS spectra of all elements for samples C64 (blue), C85 (black), C91 (green) and C112 (red).

The Fourier Transform Magnitude (FTM) of the EXAFS is shown in Fig. 6. It represents a pseudo radial distribution function with peaks representing atomic density around the absorbing species. The peak positions are shifted towards lower distances than the actual bond distances (R) due to a phase change (ϕ) in the photoelectron backscattering phenomena inherent to the EXAFS technique that depends on the nature of the neighboring atoms [36]. Disorder is reflected in a diminished amplitude for the first, second and third neighbors at $R - \phi \sim 1.8 \text{ \AA}$, $3.2 \text{ \AA}$ and $4.0 \text{ \AA}$ respectively. For the metal atoms, the general tendency is a reduction of the amplitude of the peaks with the copper concentration, being more evident at larger distances. This indicates that there is increased disorder at the local atomic scale as the sample contains more copper. For the Zn FTM we observe a change in the relative amplitude between the peaks at $3.2 \text{ \AA}$ and $4 \text{ \AA}$

(second and third neighbors) while for the other metals (Sn, Cu) the ratio of amplitudes is relatively constant. In the Zn FTM the first and third neighbors of the CZTS structure correspond to sulfur atoms, while second neighbors are Cu and Sn atoms. Considering the presence of a relatively small quantity of ZnS as a secondary phase for the samples with less copper, the reduction of the relative amplitude could be caused by a combined reduction in the amount of ZnS and disorder. Based on this argument, samples C91 and C102 show only disorder inherent to CZTS. The sulfur FTM contains as first neighbors all metal atoms. Decreasing amplitude is observed for samples C91 and C102. This confirms what we observed before. Samples with less presence of secondary phases, i.e. with more Cu, exhibit more disorder at the local scale.

Fig. 6. Fourier transform moduli of the k^2 -weighted EXAFS spectra for (a) Cu, (b) Zn, (c) Sn, and (d) S.

Numerical parameters from fits to the data are presented in Table 2. Fig. 7 presents the Fourier transform magnitude of the data, the fit and the individual contributions from the neighboring atoms up to the third nearest neighbor.

From numerical fits, we observe that the nearest neighbor distance around Cu atoms (Cu-S) for all samples is contracted with respect to the crystallographically derived distance by $\sim 0.036(4)$ Å, while for Sn atoms (Sn-S) it is expanded by $\sim 0.070(4)$ Å, this is expected due to the different atomic radii of the metallic atoms involved. From the Zn atom any difference in nearest neighbor distance from the crystallographically derived distance is within the error of the measurement (0.006 Å). This behavior, where nearest neighbor bond distances are contracted/expanded from the crystallographic description of the lattice have been observed before in other systems [51]. In general, the long range order obtained from crystallographic techniques describes the average structure where local deviations are averaged. In this case the contraction from the two Cu atoms in the structure is averaged with the expansion from the Sn atom. From the S K-edge we observe a large difference between the pairwise Debye-Waller factors between S-Sn (~ 0.03 Å) and S-Cu/Zn (~ 0.11 Å). This is not mirrored in the individual Cu/Zn/Sn-S confirming a difference of ~ 0.04 Å between the distance S-Cu and S-Zn that is absorbed in the Debye-Waller factor when measured from the sulfur atoms. The behavior of the Debye-Waller factors is an indicator of disorder around specific atoms in the structure. From the Cu atoms, the tendency is that the Cu-Sn has a smaller Debye-Waller factor than the Cu-Zn (although this variation lies within the estimated uncertainties of this parameter); also from the Zn atoms the Debye-Waller factor of the Zn-Cu increases with the Cu concentration in the samples. These tendencies reflect what was observed when comparing the amplitudes of the EXAFS signal and FT in Fig. 5 and Fig. 6. While for the Zn-S neighbors, the Debye-Waller factor remains similar for all samples, the

Debye-Waller factor for Zn-Sn and Zn-Cu (second neighbors) increases with the Cu content, although inherent disorder also increases the errors in the fit.

For sample C85, being close to the up to date optimal composition for CZTS solar cells, we observe a better local atomic ordering with respect to samples with higher Cu/(Zn+Sn) ratios (C91 and C102) reflected in a higher amplitude of its XAFS FTM. The FTM amplitude of sample C85 is close to sample C64, indicating that at least up to a Cu/(Zn+Sn) ratio of 0.85, there is no appreciable increase in local disorder.

Fig. 7. Curve-fit results showing the total fit (red line) in the upper portion of each data plot and the contribution of each shell to the fit (lower portion, inverted) for Cu, Zn, Sn, and S-K edges (from top to bottom).

Table 2. Structural parameters from fits to the EXAFS data^a

	C64	C85	C91	C102
Cu – 4S	$R_F = 2.314(4) \text{ \AA}$	$R_F = 2.316(6) \text{ \AA}$	$R_F = 2.316(5) \text{ \AA}$	$R_F = 2.309(5) \text{ \AA}$
$R_C = 2.350 \text{ \AA}$	$\sigma = 0.06(2) \text{ \AA}$	$\sigma = 0.06(3) \text{ \AA}$	$\sigma = 0.07(3) \text{ \AA}$	$\sigma = 0.08(3) \text{ \AA}$
Cu – 4Sn	$R_F = 3.86(1) \text{ \AA}$	$R_F = 3.88(2) \text{ \AA}$	$R_F = 3.89(3) \text{ \AA}$	$R_F = 3.86(4) \text{ \AA}$
$R_C = 3.84 \text{ \AA}$	$\sigma = 0.09(3) \text{ \AA}$	$\sigma = 0.11(5) \text{ \AA}$	$\sigma = 0.10(5) \text{ \AA}$	$\sigma = 0.09(3) \text{ \AA}$
Cu – 8Cu/Zn	$R_F = 3.87(1) \text{ \AA}$	$R_F = 3.89(2) \text{ \AA}$	$R_F = 3.89(2) \text{ \AA}$	$R_F = 3.89(3) \text{ \AA}$
$R_C = 3.84 \text{ \AA}$	$\sigma = 0.13(4) \text{ \AA}$	$\sigma = 0.14(5) \text{ \AA}$	$\sigma = 0.15(6) \text{ \AA}$	$\sigma = 0.13(4) \text{ \AA}$
Cu – 12S	$R_F = 4.49(1) \text{ \AA}$	$R_F = 4.47(2) \text{ \AA}$	$R_F = 4.46(2) \text{ \AA}$	$R_F = 4.44(2) \text{ \AA}$
$R_C = 4.50 \text{ \AA}$	$\sigma = 0.11(4) \text{ \AA}$	$\sigma = 0.12(5) \text{ \AA}$	$\sigma = 0.12(6) \text{ \AA}$	$\sigma = 0.14(4) \text{ \AA}$
Zn – 4S	$R_F = 2.349(6) \text{ \AA}$	$R_F = 2.346(6) \text{ \AA}$	$R_F = 2.351(6) \text{ \AA}$	$R_F = 2.349(6) \text{ \AA}$
$R_C = 2.350 \text{ \AA}$	$\sigma = 0.06(3) \text{ \AA}$	$\sigma = 0.06(2) \text{ \AA}$	$\sigma = 0.06(2) \text{ \AA}$	$\sigma = 0.07(3) \text{ \AA}$
Zn – 4Sn	$R_F = 3.85(2) \text{ \AA}$	$R_F = 3.85(3) \text{ \AA}$	$R_F = 3.87(3) \text{ \AA}$	$R_F = 3.87(3) \text{ \AA}$
$R_C = 3.84 \text{ \AA}$	$\sigma = 0.07(4) \text{ \AA}$	$\sigma = 0.09(6) \text{ \AA}$	$\sigma = 0.09(5) \text{ \AA}$	$\sigma = 0.11(6) \text{ \AA}$
Zn – 8Cu	$R_F = 3.86(1) \text{ \AA}$	$R_F = 3.86(1) \text{ \AA}$	$R_F = 3.87(2) \text{ \AA}$	$R_F = 3.89(2) \text{ \AA}$
$R_C = 3.84 \text{ \AA}$	$\sigma = 0.07(4) \text{ \AA}$	$\sigma = 0.09(4) \text{ \AA}$	$\sigma = 0.11(5) \text{ \AA}$	$\sigma = 0.14(7) \text{ \AA}$
Zn – 12S	$R_F = 4.49(1) \text{ \AA}$	$R_F = 4.48(1) \text{ \AA}$	$R_F = 4.49(2) \text{ \AA}$	$R_F = 4.47(2) \text{ \AA}$
$R_C = 4.50 \text{ \AA}$	$\sigma = 0.09(4) \text{ \AA}$	$\sigma = 0.09(4) \text{ \AA}$	$\sigma = 0.10(4) \text{ \AA}$	$\sigma = 0.12(6) \text{ \AA}$
Sn – 4S	$R_F = 2.420(4) \text{ \AA}$	$R_F = 2.412(4) \text{ \AA}$	$R_F = 2.411(4) \text{ \AA}$	$R_F = 2.416(3) \text{ \AA}$
$R_C = 2.350 \text{ \AA}$	$\sigma = 0.05(2) \text{ \AA}$	$\sigma = 0.05(2) \text{ \AA}$	$\sigma = 0.05(2) \text{ \AA}$	$\sigma = 0.06(2) \text{ \AA}$
Sn - 8Cu/Zn	$R_F = 3.870(7) \text{ \AA}$	$R_F = 3.855(9) \text{ \AA}$	$R_F = 3.855(8) \text{ \AA}$	$R_F = 3.861(8) \text{ \AA}$
$R_C = 3.84 \text{ \AA}$	$\sigma = 0.12(3) \text{ \AA}$	$\sigma = 0.13(3) \text{ \AA}$	$\sigma = 0.13(3) \text{ \AA}$	$\sigma = 0.14(3) \text{ \AA}$
Sn – 12S	$R_F = 4.46(2) \text{ \AA}$	$R_F = 4.43(2) \text{ \AA}$	$R_F = 4.42(2) \text{ \AA}$	$R_F = 4.43(2) \text{ \AA}$
$R_C = 4.50 \text{ \AA}$	$\sigma = 0.10(4) \text{ \AA}$	$\sigma = 0.11(5) \text{ \AA}$	$\sigma = 0.11(5) \text{ \AA}$	$\sigma = 0.12(5) \text{ \AA}$
S - 3Cu/Zn	$R_F = 2.324(8) \text{ \AA}$	$R_F = 2.320(9) \text{ \AA}$	$R_F = 2.317(9) \text{ \AA}$	$R_F = 2.315(8) \text{ \AA}$

$R_C = 2.350 \text{ \AA}$	$\sigma = 0.11(4) \text{ \AA}$	$\sigma = 0.11(5) \text{ \AA}$	$\sigma = 0.11(5) \text{ \AA}$	$\sigma = 0.11(5) \text{ \AA}$
S – 1Sn	$R_F = 2.409(5) \text{ \AA}$	$R_F = 2.407(5) \text{ \AA}$	$R_F = 2.403(5) \text{ \AA}$	$R_F = 2.403(5) \text{ \AA}$
$R_C = 2.350 \text{ \AA}$	$\sigma = 0.03(2) \text{ \AA}$	$\sigma = 0.02(2) \text{ \AA}$	$\sigma = 0.02(2) \text{ \AA}$	$\sigma = 0.03(3) \text{ \AA}$
S – 12S	$R_F = 3.81(2) \text{ \AA}$	$R_F = 3.81(2) \text{ \AA}$	$R_F = 3.81(2) \text{ \AA}$	$R_F = 3.81(2) \text{ \AA}$
$R_C = 3.84 \text{ \AA}$	$\sigma = 0.12(3) \text{ \AA}$	$\sigma = 0.12(3) \text{ \AA}$	$\sigma = 0.12(6) \text{ \AA}$	$\sigma = 0.12(3) \text{ \AA}$
S - 9Cu/Zn	$R_F = 4.43(6) \text{ \AA}$	$R_F = 4.42(8) \text{ \AA}$	$R_F = 4.38(8) \text{ \AA}$	$R_F = 4.43(6) \text{ \AA}$
$R_C = 4.50 \text{ \AA}$	$\sigma = 0.18(9) \text{ \AA}$	$\sigma = 0.18(9) \text{ \AA}$	$\sigma = 0.19(9) \text{ \AA}$	$\sigma = 0.22(9) \text{ \AA}$
S – 3Sn	$R_F = 4.8(2) \text{ \AA}$	$R_F = 4.9(2) \text{ \AA}$	$R_F = 4.9(2) \text{ \AA}$	$R_F = 4.2(1) \text{ \AA}$
$R_C = 4.50 \text{ \AA}$	$\sigma = 0.2(2) \text{ \AA}$	$\sigma = 0.2(2) \text{ \AA}$	$\sigma = 0.2(2) \text{ \AA}$	$\sigma = 0.2(2) \text{ \AA}$

^aN = number of neighbors, R_{Cy} = reference crystallographic distance, R_{Fit} = distance from curve fits to the EXAFS, and σ = pairwise Debye-Waller factor.

4. CONCLUSIONS

In this work, we have shown the presence of secondary phases in CZTS. These phases cannot be detected by traditional diffraction techniques, as either the diffraction peaks overlap with the peaks of CZTS (as in the case of ZnS) or are present in regions of sizes below the diffraction limit (SnS). Consequently we have shown the importance of XANES as a technique that can be used to reveal the actual atomic structure of a complex material. Moreover, as it does not rely on long range order it can detect the presence of amorphous phases.

Copper poor samples have the tendency to segregate ZnS (and other phases that might be present, including SnS). The presence of secondary phases diminishes as the amount of copper increases, approaching the stoichiometric composition.

EXAFS spectra exhibit significant amplitude changes between samples, especially at the Zn and Cu K-edges, indicating differences in the local structural order as the Cu/(Zn+Sn) ratio varies. This finding implies the presence of disorder in the Cu-Zn planes not present in the Cu-Sn

planes. From the FTM of the EXAFS it is also observed, in a qualitative manner that as the amount of copper increases, disorder in the local atomic scale including up to third neighbors increments. Such an effect probably originates from differences in atomic radii between Cu/Zn and Sn in the structure, thus generating local deviations in atomic positions, as seen from fits to the data. For samples with a ratio of Cu/(Zn+Sn) of 0.64 and 0.85 we observed a better local atomic order than for samples with higher ratios, indicating that local distortions play a significant role in this material.

Fits to the EXAFS data show a contraction in the Cu-S bond length and an expansion of the Sn-S bond length with respect to the average crystallographic structure for all samples. A small difference for the Zn-S bond length was also observed. These results imply that disorder in these materials originates from displacements of atoms from their crystallographic positions, this being an important point for evaluating structural disorder in stoichiometric and non-stoichiometric CZTS.

We stress that the reliable prediction of electronic properties, related for example to the photovoltaic performance, needs to be based on realistic atomic structural models that take into account the presence of secondary phases, deviations from the average crystalline structure and intrinsic disorder as found in this study.

ACKNOWLEDGMENTS

This work was supported by CONACYT, México, through grant N°169108 and by SIP-IPN 20161804/0291 project. For SEM and XRD measurements we thank LANNBIO-CINVESTAV México through grant FOMIX-YUCATAN 2008-108160 and CONACYT LAB-2009-01 N°123913. The authors thank Dora A. Huerta-Quintanilla, Daniel H. Aguilar-Treviño and Wilian

Cauch-Ruiz for technical support. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515.

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EXAFS EVIDENCE

Disordered Structure