

# DETECTION OF ZnS PHASES IN CZTS THIN-FILMS BY EXAFS

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## ABSTRACT

Copper zinc tin sulfide (CZTS) is a promising Earth-abundant thin-film solar cell material; it has an appropriate band gap of ~1.45 eV and a high absorption coefficient. The most efficient CZTS cells tend to be slightly Zn-rich and Cu-poor. However, growing Zn-rich CZTS films can sometimes result in phase decomposition of CZTS into ZnS and Cu<sub>2</sub>SnS<sub>3</sub>, which is generally deleterious to solar cell performance. Cubic ZnS is difficult to detect by XRD, due to a similar diffraction pattern. We hypothesize that synchrotron-based extended X-ray absorption fine structure (EXAFS), which is sensitive to local chemical environment, may be able to determine the quantity of ZnS phase in CZTS films by detecting differences in the second-nearest neighbor shell of the Zn atoms. Films of varying stoichiometries, from Zn-rich to Cu-rich (Zn-poor) were examined using the EXAFS technique. Differences in the spectra as a function of Cu/Zn ratio are detected. Linear combination analysis suggests increasing ZnS signal as the CZTS films become more Zn-rich. We demonstrate that the sensitive technique of EXAFS could be used to quantify the amount of ZnS present and provide a guide to crystal growth of highly phase pure films.

## INTRODUCTION

Copper zinc tin sulfide (Cu<sub>2</sub>ZnSnS<sub>4</sub> or CZTS) is a promising Earth-abundant alternative to copper indium gallium diselenide (CIGS) [1]. One of the challenges impeding high efficiencies in these materials are small deviations in stoichiometry, which can result in recombination-active intrinsic point defect creation or, in extreme cases, decomposition into two or more phases [2]. Small deviations in stoichiometry have been linked to changes in performance of CZTS solar cells [3], and are a likely driver for the large difference between record small-area CIGS devices and full-size module efficiencies [4].

Studies show that the ideal region for highest performance cells is slightly Zn-rich and Cu-poor, compared to pure CZTS (Cu/Zn = 2) [3]. However, during thin-film growth in a Zn-rich regime, it may be difficult to control the development of a minority ZnS phase. Inhomogeneity due

to the presence of ZnS phases may contribute to lower efficiencies.

Detecting ZnS phases in CZTS using standard X-ray diffraction (XRD) techniques has been difficult because the two phases have similar XRD patterns. Kesterite CZTS shares multiple peaks with cubic ZnS and the ternary Cu<sub>2</sub>SnS<sub>3</sub> (CTS). Wurtzite ZnS, due to its hexagonal structure, is somewhat easier to distinguish, but only if certain peaks diffract. This renders standard XRD largely incapable of detecting differences between homogeneous and phase-decomposed films.

Upon analysis of the cubic ZnS and Kesterite CZTS crystal structures, we recognize key differences in the second-nearest neighbor shells of the Zn atoms of each structure. While the second-nearest neighbor shell of zinc in cubic ZnS is also comprised of Zn atoms, in Kesterite CZTS the second-nearest neighbor shell is comprised of Cu and Sn atoms [5,6]. X-ray absorption spectroscopy (XAS) probes the chemical state of a specific atomic species. The absorption spectrum is a function of the scattering amplitude of an excited photoelectron interacting with neighboring atoms, which scales strongly with the atomic mass (~Z<sup>4</sup>). This provides a probe of the short to mid-range chemical neighborhood (2-10 Å) around an excited atom. We hypothesize that a technique sensitive to the local chemical environment around Zn atoms, such as extended X-ray absorption fine structure (EXAFS), should enable one to discern between “pure” CZTS films and those with percents of phase decomposition and possibly native point defect concentrations.

## RESULTS

Sample Set 1 is comprised of two composition-graded films deposited by a thermal co-evaporation process, in a glass/Mo/CZTS stack. Three positions on each film were analyzed. One film is Zn-poor (1A, 1B, 1C) and the other Zn-rich (1D, 1E, 1F). Set 2 contains two films of CZTS grown by room-temperature RF co-sputtering of Cu<sub>2</sub>S, SnS<sub>2</sub> and ZnS and post-deposition sulfurization, in a glass/Mo/CZTS stack. Set 3 contains three films produced

Label	$\frac{[Cu]}{[Sn]+[Zn]}$	$\frac{[Zn]}{[Sn]}$	$\frac{[Cu]}{[Zn]}$	$\frac{[Cu]}{[Sn]}$	$\frac{[S]}{[Metal]}$
	1A	0.99	0.83	2.17	1.81
1B	1.03	0.92	2.14	1.98	1.00
1C	0.96	0.86	2.07	1.77	1.00
1D	0.92	1.03	1.81	1.86	1.02
1E	0.82	1.17	1.51	1.77	1.00
1F	0.83	1.51	1.38	2.09	0.96
2A	0.80	1.25	1.44	1.81	1.12
2B	0.88	1.12	1.67	1.87	1.03
3A	0.91	0.92	1.90	1.74	1.00
3B	0.92	1.04	1.81	1.88	0.98
3C	0.93	1.15	1.74	2.01	0.91

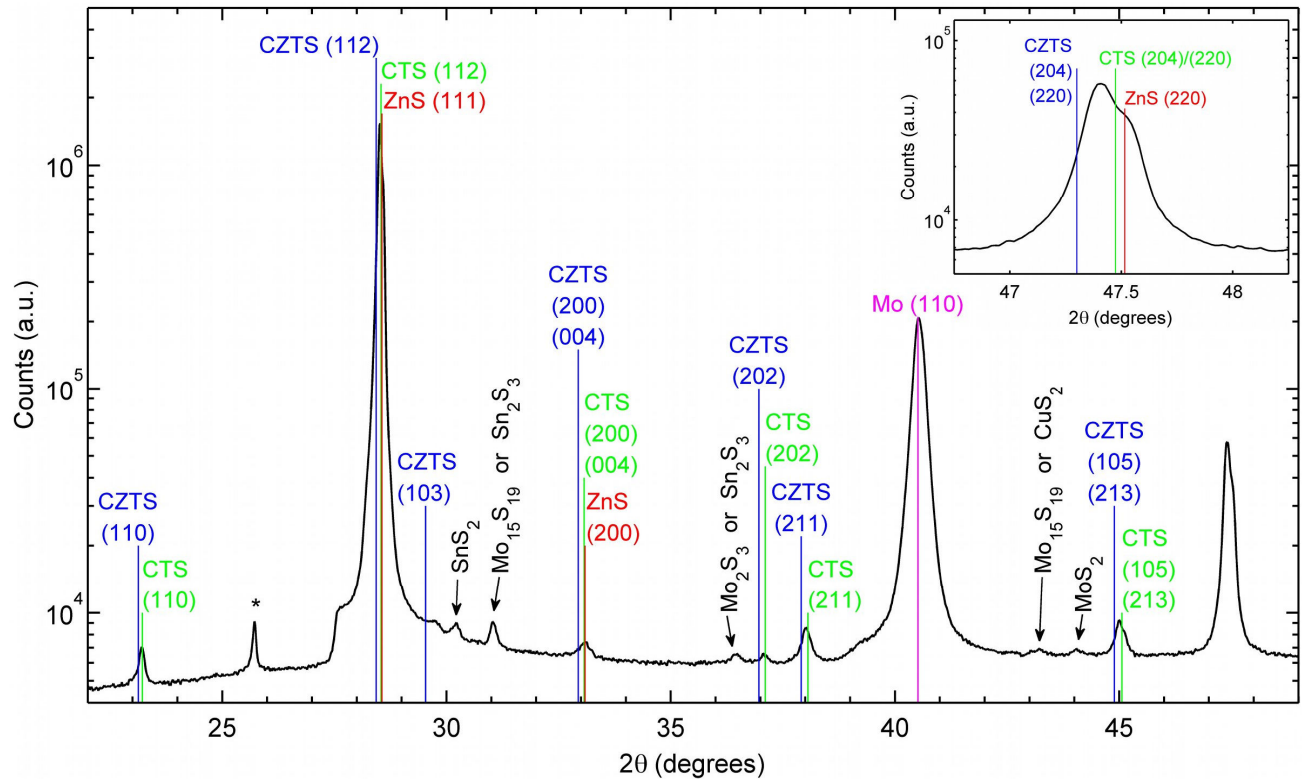
**Table 1. Eleven spots analyzed for stoichiometry. Sets 1 and 2 measured by calibrated WDS ( $\pm 2\%$  at.). Set 3 measured by EDS.**

by sulfurization of DC sputtered metallic precursors, grown in a glass/CZTS stack. The composition of each position, as measured by calibrated wavelength dispersive spectroscopy (WDS) or energy dispersive spectroscopy (EDS), is listed in Table 1.

XRD of the Zn-rich film from Set 1 (1D, 1E, 1F) were taken using Cu-K $\alpha$  radiation in the Bragg-Brentano configuration. Figure 1 also shows reference peaks for cubic ZnS, CZTS, and CTS, demonstrating the difficulty in identifying the ZnS phase using XRD peaks alone.

EXAFS was performed at beamline 9-BM-B at the Advanced Photon Source at Argonne National Laboratory using bending-magnet radiation. EXAFS was performed at the Zn X-ray absorption edge on the films and a ZnS reference standard. The photon flux at the Zn edge is  $\sim 10^{10}$  photons/sec with a spot size of  $1 \text{ mm}^2$ . Figure 2 shows the normalized absorption spectra at the Zn-K $\alpha$  edge for Set 1 and the ZnS standard. Subtracting the background absorption signal isolates the perturbed scattering signal,  $\chi(E)$  according to equation 1 [7],

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E)} \sim \frac{\mu(E) - \mu_0(E)}{\Delta\mu(E_0)}, \quad (1)$$



**Figure 1. Observed XRD peaks for the Set 1 Zn-rich film. Reference peaks for cubic ZnS, CZTS, and CTS are shown [6]. The main peaks for CZTS, CTS, and cubic ZnS are closely spaced, making it difficult to use XRD to evaluate the phase composition of CZTS films. Peak labeled "\*" is a CZTS 112 Cu-K $\beta$  peak.**

where  $\mu_0(E)$  is the background, or the expected absorption of an isolated Zn atom and  $\Delta\mu(E_0)$  is the edge step, or normalizing factor.

Using Equation 2 [7], the energy axis in Figure 2 is replotted in wavenumber, or k-space (Figure 3)

$$k^2 = \frac{2m_e(E - E_0)}{h}, \quad (2)$$

where  $k$  = wavenumber ( $\text{\AA}^{-1}$ ),  $m_e$  = mass of electron and  $E_0$  = absorption edge energy. Differences in the EXAFS spectra can now be seen and are noted primarily at  $k = \sim 4.5 \text{\AA}^{-1}$  and  $k = \sim 6.5 \text{\AA}^{-1}$ .

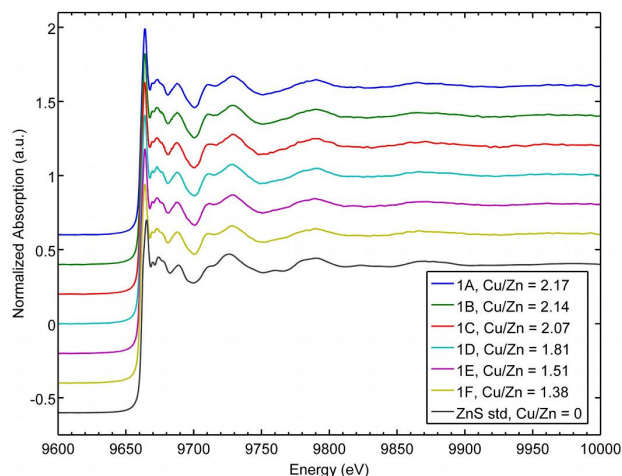


Figure 2. Normalized absorption at the Zn-K $\alpha$  edge for Set 1 and ZnS standard.

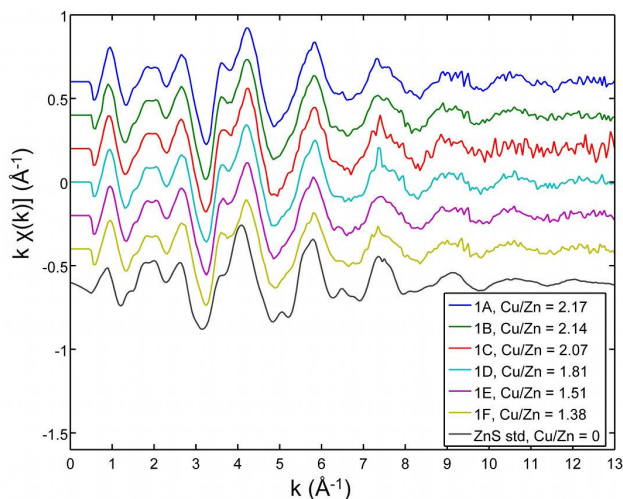


Figure 3. k-space data ( $k$ -weight = 1) for Set 1 and ZnS standard. Changes in spectra are noted at  $k = \sim 4.5 \text{\AA}^{-1}$  and  $k = \sim 6.5 \text{\AA}^{-1}$ .

## ANALYSIS

Of all films, Sample 1B is closest to stoichiometrically pure CZTS. It is also slightly Zn-poor, which may reduce the probability of ZnS formation in the film. Thus the Zn atoms in this film should only participate in the CZTS phase. From the calculated phase diagram [5], we expect the appearance of a ZnS minority phase as film composition becomes more Zn-rich. Thus, we could expect the EXAFS spectra of Zn-rich CZTS samples to be comprised of a linear combination of the EXAFS spectra of 'pure CZTS,' taken to be Sample 1B, and the ZnS standard.

A linear combination analysis (LCA) using a least squares fitting method was performed using k-space EXAFS spectra from all samples, from  $k = 2$ - $12 \text{\AA}^{-1}$  and  $k$ -weight = 1. Examining results only from Set 1, the LCA shows a trend of increasing contribution of ZnS EXAFS component as samples become more Zn-rich (Cu/Zn ratio decreases below 2.0). Alternatively, the contribution of the ZnS EXAFS component decreases as Zn-rich films approach stoichiometry (Cu/Zn ratio = 2.0). Figure 4 shows the 'CZTS' fraction, as described by the near-stoichiometric Sample 1B, as a function of the Cu/Zn ratio of the various films. The fractional values in this figure are not absolute fractions of CZTS phase or ZnS phase in the films.

In Zn-poor films (Cu/Zn ratio > 2.0), the expected trend is unknown and results may depend on the kinetic limitations of the film growth process and the likelihood of formation of ZnS phase in a Zn-poor environment. The lattice

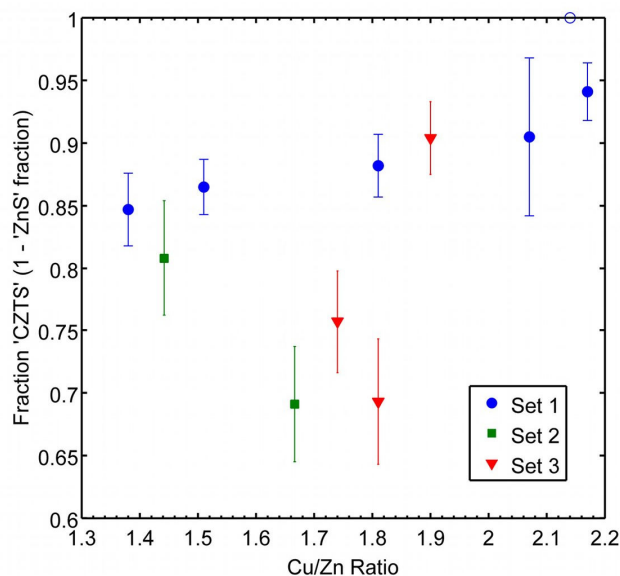


Figure 4. LCA results for all nominally CZTS films, Set 1 shows a trend of increasing contribution of 'CZTS' EXAFS spectra as Zn-rich films tend towards stoichiometry (increasing Cu/Zn ratio to 2). Open circle represents the near-stoichiometric film 1B, used as the 'CZTS' reference EXAFS spectra.

constants of ZnS, CTS, and CZTS are closely matched, thus formation of ZnS in a Zn-poor film may be possible under non-equilibrium conditions.

Results from Set 2 and 3 do not fit the trend observed in Set 1. Different growth methods may influence the amount of ZnS formed in Zn-rich films. Variables such as substrate temperature, annealing temperature, annealing time, and sulfur overpressure may all impact the favorability of ZnS growth. These results suggest that the degree of off-stoichiometry is not the dominant or only contributor to ZnS minority phase formation.

### SUMMARY

We demonstrate that EXAFS succeeds where XRD fails, as a useful tool for discerning phase inhomogeneities in CZTS films. We focus primarily on ZnS as a secondary phase, which has proven difficult to detect by traditional characterization techniques, even in CZTS films that appear phase-pure. We have shown significant differences in EXAFS spectra with varying amounts of Zn and Cu in the CZTS films. The observed trend shows that as the Zn atomic percentage increases, more ZnS phase will form and contribute to the ZnS signal observed in EXAFS spectra. However, this trend cannot be generalized to all CZTS films grown under any condition. Further work will focus on quantifying the amount of secondary ZnS phase in EXAFS spectra. In order to do so, a confirmed pure CZTS standard will be obtained, so that its EXAFS spectrum may be used in the LCA. Direct and quantitative detection of secondary phases provides a pathway to optimize growth of high-quality CZTS films for solar energy conversion.

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### REFERENCES

- [1] C. Wadia, A.P. Alivisatos, D.M. Kammen, "Materials Availability Expands the Opportunity for Large-Scale Photovoltaics Deployment", *Environ. Sci. Technol.* **43**, 2009, pp. 2072-2077.
- [2] A. Rockett, "The Electronic effects of point defects in  $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ ", *Thin Solid Films* **361-362**, 2000, pp. 330-337.
- [3] H. Katagiri, K Jimbo, M. Tahara et al., "The influence of the composition ratio on CZTS-based thin film solar cells", *Mater. Res. Soc. Symp. Proc.* **1165**, 2009, M04-01.
- [4] U. Malm, M. Edoff, "Simulating Material Inhomogeneities and Defects in CIGS Thin-film Solar Cells", *Prog. Photovolt: Res. Appl.* **17**, 2009, pp. 306-314.
- [5] S. Chen, X.G. Gong, A. Walsh, S. Wei, "Defect physics of the kesterite thin-film solar cell absorber  $\text{Cu}_2\text{ZnSnS}_4$ ", *Appl. Phys. Lett.* **96**, 2010, 021902.
- [6] PDF # 01-075-4122 (Kesterite CZTS), PDF # 01-089-4714 (tetragonal CTS), PDF # 00-005-0566 (cubic ZnS), PDF # 00-023-0677 ( $\text{SnS}_2$ ), PDF # 00-014-0619 ( $\text{Sn}_2\text{S}_3$ ), PDF # 00-037-1492 ( $\text{MoS}_2$ ), PDF # 00-040-0973 ( $\text{Mo}_2\text{S}_3$ ), PDF # 01-073-5260 ( $\text{Mo}_{15}\text{S}_{19}$ ), PDF # 00-042-1120 (Mo), PDF # 04-004-6505 ( $\text{CuS}_2$ ), International Centre for Diffraction Data, Newtown Square, PA, 2010.
- [7] J.J. Rehr and R.C. Albers, "Theoretical approaches to x-ray absorption fine structure", *Rev. Mod. Phys.* **72**, 2000, pp. 621-654.