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**Resolving the Effects of Compositional Change on Structures in $\text{Cu}_2\text{ZnSnS}_4$ Nanocrystals
by X-ray Absorption Fine Structure**

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Draft

Abstract

Renewable energy sources, and solar energy in particular, are a high impact research topic in the push for sustainable, long-term energy alternatives to fossil fuels. $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is one of the attractive, cost-effective materials that meets these needs. The quaternary nature makes the structure prone to defects and crystal alignment disorder. Some of these defects create advantageous electronic effects through antisite substitutions of Zn for Cu, $\text{Zn}_{\text{Cu}}^\bullet$. Others, such as Sn for Zn replacements, are detrimental. Synchrotron-based X-ray absorbance fine structure (XAFS) analysis was used to identify specific patterns in the antisite contributions to the structure of low- cost CZTS films that produced the highest photoresponse in each of our samples. Correlations were found between the Cu/(Zn+Sn) ratio and advantageous antisite formations, though at the cost of increased alignment disorder. Similarly, the Zn/Sn ratio showed relationships between both advantageous and disadvantageous antisite and vacancy pairs. Variations in the local surroundings for each metal center were confirmed through X-ray absorption near-edge structures (XANES). Extended X-ray absorption fine structures (EXAFS), verified through FEFF fitting of the EXAFS, confirmed the patterns in crystal alignment disorder, and the effects each antisite had on the overall crystal structure. The precision and unique nature of such synchrotron techniques offers opportunities to identify these trends at each metal center, providing guidance to balance negative and positive structural components during fabrication. Each minor change in stoichiometry has been shown to affect several interactions within the structure.

Keywords: $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) nanocrystals; antisites between Cu and Zn; crystal lattice site vacancy; crystal site symmetry; X-ray absorption near-edge structures (XANES); Extended X-ray absorption fine structures (EXAFS); Synchrotron radiation source

Introduction

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is a strong prospective light-absorbing materials candidate for future commercialization of thin-film solar cells. Made of inexpensive, earth-abundant materials, this p-type semiconductor has great potential for producing high efficiency and low cost solar cells.¹ Current CZTS-based devices have reached laboratory efficiencies of 12.6%, but require additional efforts to maximize light absorption, and carrier management to improve fill factor.²⁻³ In addition, the energy-intensive processes required to fabricate high efficiency CZTS films makes them very costly, both in terms of energy usage and in terms of environmental impact.³ The eventual incorporation of these devices into mainstream usage requires better characterization of the structure of the absorber layer, to better employ high photocurrent producing films of optimized structure. In particular, a focus on microstructural changes will lead to enhancements of the electron mobility and a reduction in geminate recombination within the device. Only through analysis of these microstructural changes can the maximization of the photoresponse be achieved.⁴⁻⁵

Each synthetic method for producing CZTS has different characteristic structural relationships. Its quaternary nature often makes for complex associations and randomness in the crystal structure that can create both advantageous and disadvantageous microstructures and substructures within the film.⁶ Previous work has shown maximal photoresponse within small compositional ranges, though the exact range appears to be dependent on the method of synthesis.^{5,7-9} Using a facile, low-temperature solvothermal method, the maximal photocurrent range appears to be relatively large. This occurs due to the increased number of antisite substitutions and disordered sites associated with low-temperature fabrication. Such a trade-off between cost-effective fabrication, and highly controlled structural congruency, necessitates the intense probing of the various structures that produce high photoresponse.¹⁰⁻¹¹ Focusing on those permutations with high short circuit current will allow for the selecting and controlling of specific structures in high-performing layers that will compliment and extend the charge carrier management through the device, ultimately leading to better open circuit potentials, and useful device efficiencies.

Synchrotron radiation (SR) is an especially potent tool for probing small structural changes at the atomic level.¹²⁻¹⁴ SR provides X-rays of high brilliance, in a highly focussed beam.¹⁴⁻¹⁵ Combined with the ability to specifically target individual metal centers, SR allows

for the detection of small changes to the substructure and atomic alignment of local regions of the CZTS films.¹⁶ Previous work has identified many different defect structures that form in CZTS films, and how they contribute to the overall photoresponse of the layer.^{7,9} These defects, including antisite substitutions and atomic vacancies, are associated with stoichiometric regions that correspond with different photoresponses. Using X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS), the changes in antisite structure within the narrow stoichiometric band that produces high photoresponse can be isolated for many different stoichiometries.^{13,17} These are particularly important when dealing with low-cost fabrications.

CZTS NCs that are produced without high-temperature or high-energy post-processing steps tend to contain deviations from the perfect crystal, as shown in Figure 1.⁹

Figure 1. The CZTS crystal structure as A) a perfectly stoichiometric kesterite structure and B) a kesterite structure exhibiting two Zn_{Cu} antisite substitutions, denoted with a red circle, and a Cu vacancy, denoted with a purple circle.

The antisite substitutions shown in Fig. 1B (red circle) occur when an atom, Zn as shown, occupies a crystal position that is typically filled with a different atom. Vacancies, as shown in Fig. 1B (purple circle), also can occur. These deviations from the ‘perfect’ crystal contribute to the disorder in the films. In some cases, these antisites can create beneficial effects on the overall photoresponse, whereas others contribute to lattice strain and disorder, both of which can hinder the photoresponse. Through exact fabrication, specific metal ratios were synthesized within a stoichiometric range that produces the highest photoresponse, and the antisite structures of each were characterized. Further work is required in the step-wise optimization of the CZTS NCs, for eventual fabrication of low-cost solar cells based on a CZTS light-absorber layer.

Experimental

Nanocrystal Fabrication. CZTS Nanocrystals (NCs) were synthesized via a previously reported one-pot solvothermal method.¹⁸ This method produced NCs with high photoresponses, provided the Cu/(Zn+Sn) ratio was between 0.9 and 1.0, and the Zn/Sn ratio was between 0.9 and 1.1. Herein, the elemental compositions are purposely tuned within these regions to produce minor variations in the metal ratios while maintaining maximum photoresponse. Cu-, Zn, and Sn-metal precursor salts (Sigma-Aldrich) were dissolved in benzyl alcohol (BA) at 160 °C for 2 minutes. The temperature was raised to 180 °C, and 0.2 M thiourea (Sigma-Aldrich, ≥99.0%) in BA was added, followed by 0.1 M 2-mercapto-5-n-propylpyrimidine in BA. This mixture was held at temperature for 10 minutes. Resultant NCs were washed in acetone three times, and centrifuged from solution at 12.0×10^3 times gravity using a Thermo Scientific Sorveall Legend Micro 21 centrifuge.

Sample composition was determined using Energy Dispersive X-ray spectroscopy (EDX). A Hitachi S-4500 field emission microscope with a 100 kV EDX system was used. Samples were stored under argon in sealed containers until examined at the synchrotron facilities.

Synchrotron Analysis. XAFS measurements were performed at the CLS@APS 20-BM beamline at the Advanced Photon Source (APS) in the Argonne National Laboratory in Argonne, IL. The stored NCs were encapsulated in Kapton tape to a thickness that produced a strong edge jump ($\Delta\mu_0 > 0.5$). Multiple measurements were collected at room temperature for each sample to ensure reproducibility of fine structure oscillations, reduce artifacts, and improve the resolution. The Cu, Zn, and Sn K-edges were probed using an unfocussed beam, which has a spot size of 30 mm x 1 mm, and an energy resolution of about 2 eV. It should be noted that the observed deviations are expected to be very small relative to the photon resolution and 1s lifetime of each of the elements; therefore, multiple passes were made at each sample, and multiple locations within each sample were scanned, to ensure reproducibility, and averaged to improve the resolution. A Si (111) monochromator with a harmonic rejection mirror, and vertical slit height of 3.5 mm were used for the Cu and Zn edges. The mirror was removed, and the vertical slit height was reduced to 400 μm , for the Sn edge. Data was collected in transmission mode using ionization chamber detection, and samples placed 45° to the incident photons. The incident

chamber was filled with 100% N₂ when measuring the Cu and Zn edges, and 100% Ar for the Sn edge. The transmission and reference chambers were filled with 90% N₂, and 10% Ar by weight throughout. For the Cu and Zn K-edge measurements, the incident beam was detuned 15% at 9.8 keV, and a harmonic rejection (HR) mirror was placed at a grazing angle within the beam to reflect the fundamental energy towards the sample, while reflecting any harmonic X-rays away. For the Sn K-edge, the beam was detuned 15% at 29.5 keV. The HR mirror was not required during Sn measurements.

Data processing was carried out using the Athena software package.¹⁹ Spectra were normalized to unity against the incident photon flux, I_0 , and calibrated against a reference foil (EXAFS Materials Inc.) using the first inflection point of the derivative spectra.¹³ Derivative spectra were then smoothed using a 7 point, 4th order Savitzky-Golay algorithm. The standards used included a 7.5 μm thick copper foil, a 10 μm Zn foil, and a 50 μm Sn foil. The treated data was transferred to k-space, using a range of 3 – 12 for Cu, and 3 – 14 for Zn and Sn data. These were then fit using the Artemis software package, and using the FEFF8.2 computational software.¹⁹ Fittings were based around a kesterite-phase CZTS unit cell (JCPDS card 26-0575) at room temperature, as calculated from the crystallographic information file generated using VESTA.²⁰ Coordination number was fixed according to the theoretical value from the kesterite crystal structure. The amplitude reduction factor was fixed at 0.70 for the Cu K-edge, 0.90 for the Zn K-edge, and 1.04 for the Sn K-edge EXAFS fitting, with each determined by measuring the metal reference foil and fitting the metal-metal bond distance.²¹ Energy corrections to the measured energy threshold were applied uniformly to all atoms within a fit to ensure phase transferability between the experimental and theoretical EXAFS signal. Interatomic distance and thermal vibrations were allowed to adjust separately, to allow for expected antisites within the structure. In this manner, the total free running parameters for the fittings were reduced, allowing for the extended multi-shell fitting.

Throughout the manuscript, defects are indicated by Kröger-Vink notation, which uses the notation M_S^C , where M represents the atomic species or vacancy (denoted “V” for vacancy) that currently occupies the lattice site in question, S represents the atom that should occupy the site if it were a perfect crystal lattice, and C represents the charge difference at that location that results from the defect indicated by M and S. A negative charge difference is indicated by a ' (apostrophe) symbol, and each positive by a • symbol.

Results and Discussion

Composition. The compositional integrity of the CZTS layer ultimately determines the effectiveness of the absorbing layer. This integrity is comprised of the ratios of the elements present, of their local arrangement about each other, and of the extent to which that arrangement is facsimiled through a long-range film. CZTS NC-based films of similar composition were tested to determine the extent to which compositional integrity hinders electron flow. Intense focus was paid to the effects of minor changes in the Cu and Zn content. This was used to refine the composition of the NCs, and limit resistance within the absorber layer.

Samples were analyzed via EDX to quantify the composition. Results are summarized in Table 1.

Table 1: Elemental ratios for each sample as determined through EDX averages of 25 films. The range for the Cu ratio is shown in Samples 1 through 3, while the range for the Zn ratio is shown in Samples 3 through 5. These have been separated by dashed lines. Deviation within the presented ratios was calculated to ± 0.02 .

Sample	Final Ratio (Cu : Zn : Sn : S)	$\frac{Cu}{(Zn + Sn)}$	$\frac{Zn}{Sn}$
1	1.8 : 1.0 : 1.0 : 4.4	0.89	1.0
2	2.0 : 1.0 : 1.0 : 4.5	0.99	1.0
3	1.9 : 1.0 : 1.0 : 4.4	0.95	1.0
4	2.0 : 1.1 : 1.0 : 4.4	0.95	1.1
5	1.8 : 0.9 : 1.0 : 4.5	0.95	0.9

Each of the samples presented show small metal ratio deviations relative to each other. These ratio changes were consistently measured across each of the 25 films that made up each sample set; however, photoelectrochemical measurements were unable to detect a deviation in the resulting photoresponse. Each NC-based film consistently produced $0.148 \pm 0.007 \text{ mA/cm}^2$. Measurements for each sample can be found in Fig. S1 in Supplementary Material. As such, the deviations in metal ratio can be attributed to local antisites or vacancies within the film, as opposed to deviations pervasive throughout. The nature of these local structures will have a more significant impact on the solid-solid interface of the final device, and requires characterization in order to optimize the CZTS layer for use in full devices. Two trends were

observed via the presented ratios. Samples 1, 2, and 3 hold the Zn/Sn ratio constant within error, while altering the Cu/(Zn+Sn) ratio. Samples 3, 4, and 5 hold a constant Cu/(Zn+Sn) ratio, while varying the Zn/Sn ratio. It should be noted that all samples constitute a Cu-poor, Zn-rich state relative to the stoichiometric CZTS ratios, which matches well with reported high photocurrent samples.^{8,11,22}

Minor changes in the Zn/Sn ratio appear to correlate inversely to the amount of sulfur found in each sample. A higher ratio (Sample 4) can be seen to have less sulfur presence than samples of lower Zn/Sn ratio (Sample 5). Conversely, changes in the Cu/(Zn+Sn) ratio correlate directly with the sulfur content of the sample, though to a lesser degree. The higher Cu sample (Sample 2) shows a slight increase in sulfur relative to that of the lower Cu ratio of Sample 1. The importance of such will be explored further in the EXAFS section.

XANES. Each metal K-edge was examined to identify changes in the local environment resulting from the changes in chemical composition. Given that large deviations would be expected to have significant impact on the photoresponse, it is expected that only minor deviations will be present at all edges. Figure 2 shows the Cu K-edge for both ranges, slightly offset vertically for improved visualization.

Fig. 2: Cu K-edge XANES spectra showing changes in the Cu/(Zn+Sn) ratio (red < green < purple), and changes in the Zn/Sn ratio (blue < green < blue). Vertical lines (maroon and grey) are shown at peak locations of 8982.6 eV and 8986.3 eV respectively. Samples are ordered by sample number, with Sample 1 (red) being at the top, and Sample 5 being at the bottom (blue). Derivative of the XANES spectra is shown in the inset (top left).

Analysis of all spectra shows highly similar absorption edges, with very similar features. The Cu pre-edge region, below 8,980 eV, is completely devoid of features. This region arises from dipole-forbidden, quadrupole-allowed $1s \rightarrow 3d$ excitations.^{13,17} These transitions occur with far less frequency than dipole-allowed transitions, leading to weaker absorbance.²³ As such, they are highly sensitive to any minor disruption to the electric fields around the metal center.²⁴ This means that it will show features related to the spin state, centrosymmetry, and ligand-field effects.¹⁷ In all the spectra shown in Figure 2, there is a complete lack of a pre-edge peak, which indicates that these transitions are not available. This means that either the Cu centers have a full d-shell, or the centrosymmetry is highly conserved about the metal center. In CZTS, the Cu should be bound in a tetrahedral geometry, wherein the 4p orbitals will have t_2 symmetry, and the 3d orbitals will have t_2 and e symmetry. This should allow significant mixing of the symmetry-paired orbitals. Given the complete lack of a pre-edge, the center must therefore be in the $3d^{10}$ state. This is consistent in Figure 2, regardless of the metal ratios, and is indicative of both a Cu^+ metal center, and a highly conserved ligand field around the Cu-centers, regardless of the metal ratio.

The Cu rising-edge contains additional information arising from the dipole-allowed $1s \rightarrow 4p$ transitions. These transitions are a lot stronger, making the features in the rising-edge much stronger than the pre-edge features. Changes in geometric layout, as well as oxidation state, and orbital overlap between the metal center and surrounding atoms, will all contribute to changes in the rising-edge features. As seen in Figure 2, all samples share a common peak at 8982.6 eV, followed by a slightly shifted main absorption peak in the 8986 eV region. This gives the appearance of p-orbitals are split into a single, and double degeneracy as seen in 3-coordinate Cu^+ compounds; however, that should then lead to a double peak, or large broadening in the main peak, as expressed in the literature.²⁴⁻²⁷ Therefore, this explanation does not fit. Furthermore, the peak at 8982.6 eV is more of a shoulder, rather than a distinct absorption. According to literature, such features are common among 4-coordinate Cu^+ compounds bound to sulfur, due to higher covalent strength contributing to shake-down transitions.^{24,28-30} This

explanation fits far better than the 3-coordinate explanation, although these features could also arise from Cu^{2+} centers.²⁴ The latter option was discounted due to the lack of a pre-edge peak around 8979 eV, and lack of higher energy features around 8990 eV, that would be present in a Cu^{2+} situation.²⁷ This leaves the conclusion that the copper centers in a tetrahedral geometry, in the Cu^+ oxidation state. This would supply the consistent ligand field strength indicated by the lack of pre-edge features

The location of the main absorption peak remains within 0.3 eV with changes in the Cu and Zn ratios, as seen in the derivative of the XANES spectra (Figure 2 inset, or Figure S2 in the Supplementary Material); however, given the core-hole lifetime and photon resolution, these changes must be acknowledged as being extremely small. The use of multiple passes and multiple film locations all yielding the same shifts suggest that these changes are present, and so have been interpreted as such. The $1s \rightarrow 4p$ transition noted at 8982.6 eV is identical in all samples, it can be easily interpreted that these shifts signify minor changes in the ligand field strength around the center. These peaks are also in the $1s \rightarrow 4p$ region, which signifies an unequal distribution of the p-orbitals.^{17,27,30} The known metal ratio deviations, coupled with the clear differentiation in the zero crossing of the derivative spectra, provide compelling evidence of the subtle nature of the changes to the overall structure in the film. This would ultimately appear to contradict the previously discussed features, and so was discounted as an option. Instead, these small changes must be considered the result of changes in ligand arrangement, and in metal-ligand overlap.^{17,27,30} As seen in the second grey marker in Fig. 2, this peak occurs at 8986.2 eV in Sample 1 (red), 8986.4 eV in Sample 2 (purple), and 8986.2 eV in Sample 3 (green). This is a very small shift, and therefore likely associated with very small changes structurally. Fundamentally, the effects of changes in the ligand arrangement, or metal-ligand overlap, would manifest as a shift in the peak position relative to the edge onset, as the molecular orbital energy levels change slightly due to both electron and orbital redistribution.^{13,17,31} These come about from small structural changes in the ligands surrounding the absorber atom, and constitute changes in the charge transfer from ligand to metal center.^{13,17} In the case of CZTS, the ligands would equate to the sulfur atoms bound to other metals. The primary bond between the Cu absorber, and sulfur, would not change; however, the other metals to which that S atom is bound do not remain static. Small deviations in these secondary bounds are enough to explain the observed changes in electronic structure. As such, the noted deviations must arise from

substitutions in the crystal lattice that lead to changes in the metals bound to the sulfur atom, which is bound to the absorbing Cu center. Therefore, the above noted changes must be caused by changes in shallow $Zn_{Cu}^{\bullet}$ antisites (Zn replacing Cu in the crystal lattice, as shown in the red circle of Fig. 1B).^{5,9,32-33} These create slight charge mis-matches throughout the film, as the Zn^{2+} center holds an additional charge relative to the Cu^+ . This creates an advantageous shallow donor level just below the conduction band that promotes high photoresponse. The formation of this antisite is known to favor the formation of a Cu'_{Zn} antisite that pairs to the $Zn_{Cu}^{\bullet}$, creating a $[Cu'_{Zn} + Zn_{Cu}^{\bullet}]^0$ antisite pair. In the presence of excess Zn relative to Cu, while some pairing does occur, there will be additional $Zn_{Cu}^{\bullet}$ antisites relative to Cu'_{Zn} .^{7,22,33} This would then alter the charge distribution on the sulfur atoms, which in turn is leading to the small changes seen in the Cu XANES. Sample 2 (Fig. 2) shows the largest peak value, and has the smallest peak area in the derivative spectra and therefore greatest charge transfer to Cu (Table S1 in Supplementary Material), because it is very close to stoichiometric, and thus lacks the $Zn_{Cu}^{\bullet}$ antisite. Sample 3 has the lowest energy value in the main absorption peak, suggesting it has more of these antisites than the other samples. Sample 1 was expected to have an even lower peak position and more antisites, but instead the peak energy is identical to that of Sample 3, and has a slightly larger peak area under the derivative spectra indicating decreased charge transfer from S to Cu (Table S1 in Supplementary Material). This leads to the conclusion that the increase in Zn content relative to Cu initially forms antisite $Zn_{Cu}^{\bullet}$, but eventually produces more V'_{Cu} . There is therefore a threshold at which a vacancy at the Cu site forms predominantly.^{5,33} This would manifest as a pocket of excess negative charge, which would alter the local field strength around those sulfurs, and thus around the remaining Cu centers. Sample 1 has crossed that threshold.

This trend remains when holding Cu ratios constant, and instead increasing the Sn content relative to the Zn (as seen in Fig. 2). In that case, the principle absorption peak, as seen in the derivative spectra, occurs at 8986.3 eV in Sample 4 (black), and 8986.4 eV in Sample 5 (blue). In both cases, the Cu ratios are held constant with respect to Zn relative to Sample 3, so the change in peak position is not related to any Cu-related antisite structure. Instead, the immediate area surrounding the Cu-absorber must be altered vis-à-vis changes in the ligand strength. To instigate this in Sample 4, it is likely that an area of excess Zn-S bonds are forming in close proximity due to excess $Zn_{Cu}^{\bullet}$ pairing with V'_{Cu} . This causes $[V'_{Cu} + Zn_{Cu}^{\bullet}]^0$ antisite-vacancy pairs to form.³³ This pairing would act to isolate the effects of the antisites and greatly

reduce their effects on the charge transfer. This would then result in the slightly decreased area under the peak in Sample 4 relative to Sample 3, but in a larger area relative to Sample 2. This is exactly what is observed (full peak analysis can be found in the supplementary material, Table S1). Conversely, in Sample 5 (Fig. 2), the shift to higher energy could be associated with deep-donor level $Sn_{Zn}^{\bullet\bullet}$ antisites due to the high Sn presence, or simply reduced $Zn_{Cu}^{\bullet}$ relative to the other samples.^{5,22,34} Again, reduced Zn antisites would reduce the peak area relative to Sample 3, and Sn antisites would further decrease it. Instead, the actual peak area is almost identical to that of Sample 3, suggesting Cu vacancies must also be present.

In much the same way, the Zn XANES can give information regarding the local environment for that metal center. Zn spectra are presented below in Fig. 3 slightly offset to provide improved visualization.

Fig. 3: Zn K-edge XANES spectra showing changes in the Cu/(Zn+Sn) ratio (red < green < purple), and changes in the Zn/Sn ratio (blue < green < blue). A vertical line (grey) is shown to denote the main peak at 9665.1 eV. Samples are ordered by sample number, with Sample 1 (red) being at the top, and Sample 5 being at the bottom (blue). Derivative of the XANES spectra is shown in the inset (top left).

The Zn XANES contain far less features relative to the Cu XANES, but just as much information. The lack of any pre-edge features prior to the edge-onset at 9,659 eV confirms the lack of any quadrupole-allowed $1s \rightarrow 3d$ mixing. This lack of pre-edge features in all spectra suggests a well conserved symmetry around the Zn, with a d^{10} structure and no ligand-metal orbital mixing. Furthermore, the Zn XANES lacks any rising edge features prior to the principle absorption peak, which occurs at exactly 9665.1 eV in every measured sample. This is especially clear when viewing the derivative spectra (Fig. 3 inset, or Fig. S3 in the Supplementary Material), with all 5 samples intersecting at the zero crossing. The peak area is a bit higher for both Sample 2 (highest), and Sample 1 (Table S1 in Supplementary Material), both of which have reduced $Zn_{Cu}^{\bullet}$ antisites, and thus less charge transfer to the Zn sites. Samples 3, 4, and 5 all show the same peak areas. While at first glance, this seems counterintuitive, the consistency shows that there are equivalent $Zn_{Cu}^{\bullet}$ antisites throughout these films. We can thus conclude the high similarity is due to the shared antisite formation in all 5 films.

The lack of a rising edge feature in any of the spectra shown in Fig. 3 means that the ligands are not contributing to the spectra through shake-down transitions. While not indicative of anything particular to the Zn spectra, this lack of shake-down transitions is vital when comparing the Zn and Cu spectra (Figs. 3 and 2 respectively). The Cu spectra were subject to the subtle changes in the ligand environment, whereas the Zn centers are not. As such, the Zn spectra are far more consistent, and show next to no deviations from each other. The Zn metal center must remain highly unchanged, regardless of the position within the crystal lattice.³⁵ A corollary of this, the aforementioned $Zn_{Cu}^{\bullet}$ must distort the lattice to create even Zn sites across the film. The Zn site must also be highly conserved, with no geometric or charge deviations, to yield a single absorption peak for all samples.³⁶ The full d-shell ensures the absorption is directly related to the geometry, and the single absorption peak seen in all spectra of Fig. 3 highlights the singular nature of the Zn site in all samples.³⁵

The Sn XANES (Fig. 4) are very similar to the Zn spectra (Fig. 3) in that there are limited features to observe.

Fig 4: Sn K-edge XANES spectra showing changes in the Cu/(Zn+Sn) ratio (red < green < purple), and changes in the Zn/Sn ratio (blue < green < blue). A vertical line (grey) is shown to denote the main peak at 29212.0 eV. Samples are ordered by sample number, with Sample 1 (red) being at the top, and Sample 5 being at the bottom (blue). Derivative of the XANES spectra is shown in the inset (top left).

Sn spectra will naturally show less features due to the increased broadening in the absorption peak. This arises due to the core-hole lifetime, which are much shorter in heavier elements.³⁷⁻³⁸ Shorter core-hole lifetimes result in spectral broadening that can blur out small features in the XANES spectra.³⁷ As such, only major changes in geometry or charge will be accurately detected in the XANES spectra.

As with the other two metal centers, Sn shows no pre-edge feature in any of the spectra seen in Fig. 4, indicating the metal center once again shares similar symmetry across all samples, with a d^{10} structure and no ligand-metal orbital mixing. The principle peak, however, shows small deviations around 29212 eV, the expected peak associated with Sn(IV) centers.³⁹ These deviations are most visible in the derivative of the XANES (Figure 4 inset, or Figure S4 in the supporting information). The deviations follow the same general pattern as with the Cu centers,

with the Sample 1 (red) peak occurring at 29212.3 eV, Sample 2 (purple) occurring at 29212.7 eV, and Sample 3 (green) at 29212.3 eV. Again, these are smaller deviations than the core-hole lifetime, but are strongly suspected to result from changes in the metals bound to the sulfur centers around Sn, for the same reasons as previously indicated in the Cu XANES discussions. Furthermore, the peak area ratios are generally opposite to those of Cu, with Samples that have a higher Cu peak area tending to have a lower Sn peak area (Table S1 in Supplementary Material). The close to stoichiometric Sample 2 shows the highest peak value, and the greatest peak area. Increases in the antisite $Zn_{Cu}^{\bullet}$ occurrence throughout the film will lead to increased electron withdrawing on the sulfur centers, which is manifesting in the decreased absorbance peak, and thus decreased peak area. Again, Samples 3 and 1 have the same peak maximum, and similar peak area, corroborating the previously discussed presence of Cu vacancies. Any Sn related antisite formation in these samples remains highly unlikely, due to both the lack of change in the photoresponse – any $Sn_{Zn}^{\bullet\bullet}$ antisites would result in deep-level charge carrier traps and reduce the photoresponse – and lack of deviation in the Sn content. Sample 4 (black) with less Sn, and Sample 5 (blue) with more Sn, have the potential for these defects. Both samples show peaks at 29212.5 eV, which is more than the corresponding sample with equivalent Cu ratios (Sample 3), and higher peak area ratios. In the case of additional Zn, the explanation of higher $Zn_{Cu}^{\bullet}$ antisites remains convincing; however, in an environment of excess Sn, as in Sample 5, the presence of some $Sn_{Zn}^{\bullet\bullet}$ antisites is more likely, as this is the one instance where the Sn peak area ratio differs from the trend observed in the Cu spectra (Table S1 in Supplementary Material). In both cases, the higher charge on the replacement atom in the antisite would have similar effects, with $Sn_{Zn}^{\bullet\bullet}$ antisites having two times as much of a charge change as $Zn_{Cu}^{\bullet}$. It is possible that the number of $Sn_{Zn}^{\bullet\bullet}$ is small enough to not detract from the photoresponse, but will require additional EXAFS analysis to corroborate it.

Taken as a whole, the XANES spectra (Figs. 2, 3, and 4) provide a clear breakdown of the electronic properties of each metal center in the nanocrystals. Each metal center has a distinct tetrahedral geometry, and is tetrahedrally bound to 4 sulfur atoms. At near stoichiometric values of the Cu/(Zn+Sn) ratio, there are very limited $Zn_{Cu}^{\bullet}$ antisites present, but these increase as the Cu content decreases. These substitutions appear to effect the site significantly, as there are no apparent changes to the Zn structure despite this change. As such, the substitution site appears to adapt an identical feature as the typical Zn site, with no major

changes to the Sn sites. Further decreases to the Cu/(Zn+Sn) ratio to 0.89 appear to introduce some Cu vacancies in addition to the antisites, again without affecting the Sn. Changes in the Zn/Sn ratio have less of an effect on the metal sites. The relatively small peak shifts in the Cu and Sn XANES, along with the unchanged Zn XANES, suggest that the underlying changes in composition are both subtle, and highly delocalized. To further explore these trends, full EXAFS analysis and fitting were required.

EXAFS. The structural information contained in the EXAFS region is even more useful. The EXAFS region is often plotted as a wave vector, known as k-space. In these spectra, the energy is converted to a photoelectron wavenumber, k , where $k = \frac{\sqrt{(2m_e)(E-E_0)}}{\hbar}$.⁴⁰ As such, k is a function of the absorption oscillations relative to the threshold energy, E_0 . This serves to create a sinusoidal wave with a distinct frequency for each absorber-scatterer relationship.^{13,41-42} This ensures that any minor change in the local structure will manifest as a change in the k-space spectra.⁴⁰ Through a Fourier transform, the k-space is converted to the pseudo radial (R-space) spectrum. Each peak of the R-space spectrum corresponds with a single scattering path length.^{13,32,40} Through fitting the peaks to a model compound, the exact path lengths can be established.^{37,40,43} Fitting parameters for all three metal centers are presented in Table. 2.

Table 2: EXAFS fitting parameters for each Sample and metal center. Each bond length has an error of ± 0.02 Å and are fairly close across all samples, as expected. Energy shifts (e_0) were held constant for all scattering paths, and were less than 3.5 eV in all cases.

Edge	Neighbor	Sample 1			Sample 2			Sample 3		
		N	σ^2 (Å ²)	r (Å)	N	σ^2 (Å ²)	r (Å)	N	σ^2 (Å ²)	r (Å)
Cu	S	4.0	0.00724	2.294	4.0	0.00775	2.291	4.0	0.00802	2.296
	Cu/Zn	4.0	0.00709	3.776	4.0	0.00995	3.786	4.0	0.00914	3.838
	Sn	4.0	0.00792	3.772	4.0	0.0108	3.783	4.0	0.00735	3.817
	S2	12	0.0143	4.450	12	0.0197	4.488	12	0.0186	4.465
Zn	S	4.0	0.00676	2.322	4.0	0.00885	2.331	4.0	0.00660	2.329
	Cu/Zn	4.0	0.00417	3.819	4.0	0.00846	3.917	4.0	0.00596	3.889
	Sn	4.0	0.0166	3.828	4.0	0.0103	3.802	4.0	0.00787	3.863
	S2	12	0.0104	4.521	12	0.0120	4.512	12	0.0143	4.635
Sn	S	4.0	0.00640	2.387	4.0	0.00619	2.412	4.0	0.00649	2.385
	Cu/Zn	4.0	0.00982	3.797	4.0	0.00867	3.987	4.0	0.00878	3.741
	Sn	4.0	0.0150	3.992	4.0	0.00892	3.968	4.0	0.00962	4.061
	S2	12	0.0149	4.642	12	0.0114	4.531	12	0.0138	4.607
		Sample 4			Sample 5					
		N	σ^2 (Å ²)	r (Å)	N	σ^2 (Å ²)	r (Å)			
Cu	S	4.0	0.00699	2.293	4.0	0.00834	2.293			
	Cu/Zn	4.0	0.00826	3.758	4.0	0.00943	3.691			
	Sn	4.0	0.00717	3.756	4.1	0.00910	3.702			
	S2	12	0.0195	4.425	12	0.0191	4.384			
Zn	S	4.0	0.00909	2.345	4.0	0.00602	2.321			

	Cu/Zn	4.1	0.00871	3.748	4.0	0.00631	3.831
	Sn	4.0	0.00785	3.764	4.1	0.00669	3.814
	S2	12	0.0107	4.590	12	0.0169	4.499
	S	4.0	0.00729	2.379	4.0	0.00713	2.386
Sn	Cu/Zn	4.1	0.00891	3.867	4.0	0.00932	4.001
	Sn	3.9	0.00906	3.981	4.0	0.00963	3.972
	S2	12	0.0147	4.662	12	0.00931	4.600

Based on the fitting parameters presented in Table 2, it becomes very quickly apparent that the coordination changes are very small. The results of these fits, and their corresponding spectra are discussed by metal center below, with respect to the underlying structural differences identified in the XANES spectra. The full Cu EXAFS can be seen in both k-space and R-space in Figure 5.

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Fig. 5: Cu EXAFS for each sample in k-space A), and R-space B). The k-space spectra are divided by periodic grey lines every $1.7 \text{ \AA}^{-1}$ beginning at $2.7 \text{ \AA}^{-1}$ for ease of comparison. Each R-space spectrum has been overlain with its corresponding fit (dashed line) using the Artemis software package. Samples are ordered by sample number, with Sample 1 (red) being at the top, and Sample 5 being at the bottom (blue), with fitting mismatch factors of 0.020, 0.021, 0.019, 0.023, and 0.021 respectively. The rest of the fitting parameters are presented in Table 2.

On changing the Cu/(Zn+Sn) ratio, the Cu k-space spectra (Fig. 5A) are comparable in the early k-space oscillations ($2-6 \text{ \AA}^{-1}$), indicating that the local Cu-S bonding structure is well conserved.^{15,40} Only Sample 1 (red) shows some minor deviations in the peak at $7.8 \text{ \AA}^{-1}$, though it is hard to determine if this is simply due to the noise in the region, or due to disorder. This is consistent with the structural properties identified in the XANES (Fig. 2). The late k-space oscillations ($7-12 \text{ \AA}^{-1}$) of Fig. 5A are not as comparable in intensity, though maintain the periodicity, as indicated by the highly congruent peak mid-points occurring at each grey divider. Beyond $12 \text{ \AA}^{-1}$, interference from the nearby Zn K-edge prevents any meaningful data. This means that the data is only complete up to the interactions of $3.5 \text{ \AA}$ (the approximate square root of the total length of the k-space spectra). This means the data for the second shell fit, which contains the metals, is an approximation only. As such, the overall structure does not change – thus no observable changes in the periodicity – but features several small, random deviations throughout the structure that mute the signal in the late k-space spectrum of Sample 2. This is observed in the intensity of the peak at $7.8 \text{ \AA}^{-1}$, which is reduced in Sample 2 (purple) compared to the samples containing less Cu: Sample 1 (red) and Sample 3 (green). This indicates a less rigid ordering in the higher Cu samples.^{37,43} Given the expected lack of extensive $\text{Zn}_{\text{Cu}}^{\bullet}$ antisites present throughout this sample, it is likely that the $[\text{Cu}'_{\text{Zn}} + \text{Zn}_{\text{Cu}}^{\bullet}]^0$ antisite pairs and V'_{Cu} occur randomly throughout the sample.^{5,33} Conversely, Sample 1 (red) has plenty of excess Zn, but due to the comparable oscillations with Sample 3 (green), the total $\text{Zn}_{\text{Cu}}^{\bullet}$ antisite appear to be relatively the same between these two samples. This further confirms the presence of V'_{Cu} in Sample 1, to go along with the known $\text{Zn}_{\text{Cu}}^{\bullet}$ antisite present in each of the Samples. These additional antisites in Sample 1 and 2 relative to Sample 3 are likely contributing to the signal breakdown observed around the $11.2 \text{ \AA}^{-1}$ period.

A similar event occurs on alteration of the Zn/Sn ratio. Sample 4 (black) is highly comparable to Sample 3 (green) until very late in the k-space spectra (Fig. 5A) at $11.2 \text{ \AA}^{-1}$, whereas Sample 5 (blue) shows decreased intensity at the $7.8 \text{ \AA}^{-1}$ peak. The lower Zn content of Sample 5 exhibits the same features as those observed in Sample 1 (red). With similar Zn and Cu, Sample 5 contains regions of $\text{Zn}_{\text{Cu}}^{\bullet}$ substitutions similar to Sample 1, and excess Sn. This would lead to non-uniform distribution of the more limited Cu and Zn, likely creating small, albeit significant, regions of excess Sn-S structure.⁴⁴ This can be contrasted with Sample 4,

which exhibits comparable structure to Sample 3. Here, while the excess Zn can be associated with increased pairing between Cu and Zn antisites, it has already been established above that these contribute little disorder at the given Cu/(Zn+Sn) ratio. This leaves deep-donor level $Sn_{Zn}^{\bullet\bullet}$ antisite as the primary source of these discrepancies in Sample 5, while Sample 4 appears to be a good balance of the metals. Overall, the data points to less rigid ordering being a function of higher Cu, Zn, and Sn contents.

The R-space spectra (Fig. 5B) are overlain with a multishell fit incorporating Cu-S, Cu-Cu, Cu-Zn, and Cu-Sn bonds from a theoretically unblemished kesterite CZTS crystal. As such, site-specific bond lengths were determined for each of the different scatterers. The principle interaction in the first shell, the Cu-S bond, shows a high degree of consistency, regardless of the Cu/(Zn+Sn) ratio, with each bond appearing at 2.29 Å (Fig. 5B). This agrees with the XANES data (Fig. 2) and the k-space spectra (Fig. 5A), as any deviation here would manifest in the principle absorption, and in the early k-space oscillations. There are, however, some deviations observed in the surrounding metals that make up the second shell. Samples 1 (red) and 2 (purple) show Cu-Cu/Zn distances of 3.77 Å, and of 3.79 Å. Their corresponding Cu-Sn bond is 3.77 Å for Sample 1, and 3.78 Å for Sample 2. Each is well within margins of error for these to be considered equivalent bonds, and given truncated nature of the usable k-space, must be taken as such. Sample 3 (green) shows slightly elongated lengths of 3.84 Å Cu-Cu/Zn, and 3.82 Å Cu-Sn, but these must be evaluated alongside the values determined via the Zn and Sn spectra to eliminate the greater error associated with the weaker Cu data. In each case, the slightly longer distances between atoms in Sample 3 suggests a more loosely-bound structure, which is more in line with the bond lengths of the pure CZTS kesterite structure.^{10,45} This is likely the reason for the comparable photoresponses, despite the reported changes. While the increase in ideal substitutions would contribute favourably to the photoresponse, the above-noted changes in the bond lengths would create unfavourable size constraints, allowing less vibrational freedom in the crystal structure, and additional disorder in crystal alignment due to the smaller size. Both would contribute adversely to the photoresponse of both Sample 1 and 2.

Similar results can be seen in the R-space as a result of changes in the Zn/Sn ratio (Fig. 5B). The initial Cu-S bond remains at 2.29 Å in both Samples 4 and 5, as expected. At high Zn content, Sample 4 (black) has 3.76 Å Cu-Cu/Zn distance, and 3.76 Å for Cu-Sn distances. This is an equivalent crystal to the high Cu-content samples. The increase in $Zn_{Cu}^{\bullet}$ antisite alone does

not contribute to shorter bonds within the structure. At increased Sn content (Sample 5), the Cu-Cu/Zn distance is further reduced to 3.70 Å, and the Cu-Sn bonds reduced to 3.70 Å. This is now the source of the reduced crystal structure. Given the expanded charge associated with increased Sn(IV) content, this also makes sense. It is therefore consistent with $Sn_{Zn}^{\bullet\bullet}$ antisite formation, which would place the heavier, larger Sn atoms throughout, contributing to increased lattice distortions.^{8,33}

The close correlation between the Cu and Zn centers previously noted would then manifest in the Zn EXAFS. These signals are in both k-space, and R-space spectra are displayed in Figure 6.

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Fig. 6: Zn EXAFS for each sample in k-space A), and R-space B). The k-space spectra are divided by periodic grey lines every 1.6 $\text{\AA}^{-1}$ beginning at 2.7 $\text{\AA}^{-1}$ for ease of comparison. Each R-space spectrum has been overlain with its corresponding fit (dashed line) using the Artemis software package. Samples are ordered by sample number, with Sample 1 (red) being at the top, and Sample 5 being at the bottom (blue), with fitting mismatch factors of 0.015, 0.010, 0.019, 0.005, and 0.021 respectively. The rest of the fitting parameters are presented in Table 2.

As in the Cu (Fig. 5A), the Zn k-space spectra (Fig. 6A) show conserved periodicity throughout all samples further confirms the lack of distinct secondary phases, though Sample 1 does show some late deviations.^{40,46} That these deviations occur more pronounced in the Zn spectrum than those seen in the Cu spectrum indicate that this is a disorder, rather than an artifact. This further confirms the presence of both $Zn_{Cu}^{\bullet}$ antisites, and V_{Cu}' , located randomly throughout the film. Disorder in crystal alignment can also create such patterns, though to a lesser extent.¹³ Decreases in the Cu/(Zn+Sn) ratio appear to remove this issue in periodicity, yet Sample 2 (purple) shows decreased intensity at the 10.7 Å⁻¹ and 12.3 Å⁻¹ peaks, similar to the observations made in the Cu k-space (Fig 5A). The same appears to be true for deviations in the Zn/Sn ratio. Sample 4 (black) and Sample 5 (blue) show decreased intensity in the late regions, at 10.7 Å⁻¹ and 12.3 Å⁻¹, again consistent with the Cu data, indicating increased disorder among the antisites. This corresponds with the previously reported Zn-S abundance due to excess $Zn_{Cu}^{\bullet}$ antisites, and shows higher disorder in samples of low Zn/Sn.

The R-space spectra (Fig. 6B) visually appear to have variation about the Zn centers; however, the first shell, Zn-S bond, appears at 2.32 Å in Samples 1 and 5, 2.34 Å for Sample 4, and 2.33 Å in Samples 2 and 3. All of these are within margins of error, and thus not significantly changed.^{8,13} Second shell metal-to-metal bond lengths for Zn-Cu/Zn were 3.82 Å for Sample 1, and 3.89 Å for Sample 3. This bond length extends to 3.92 Å in Sample 2. Given that the Cu was shown to be less rigidly ordered in Sample 2, it is expected that Zn sites would also show this trend. Changes to the Zn/Sn ratio were also found to contribute to the bond lengths. The high Zn content Sample 4 showed Zn-Cu/Zn bonds of 3.74 Å. The low Zn content Sample 5 showed 3.83 Å. In both cases, deviations from the 1:1 ratio of Zn:Sn contribute to bond shortening, and a contraction of the observed crystal lattice. This leaves Sample 3 with the least vibrational rigidity, but the most consistent kesterite crystal lattice.^{5,8-10}

Unlike the Cu and Zn centers, Sn has been consistent throughout all of the samples, and throughout all of the analyses discussed herein. As such, the Sn EXAFS spectra should maintain a high degree of similarity, with the only expected changes to be the metal-metal bond lengths, and confirmation or repudiation of deep-donor level $Sn_{Zn}^{\bullet}$ antisites in Sample 5.

The Sn k-space and R-space spectra are shown in Figure 7.

Fig. 7: Sn EXAFS for each sample in k-space A), and R-space B). The k-space spectra are divided by periodic grey lines every $1.6 \text{ \AA}^{-1}$ beginning at $2.8 \text{ \AA}^{-1}$ for ease of comparison. Each R-space spectrum has been overlain with its corresponding fit (dashed line) using the Artemis software package. Samples are ordered by sample number, with Sample 1 (red) being at the top,

and Sample 5 being at the bottom (blue), with fitting mismatch factors of 0.054, 0.035, 0.040, 0.079, and 0.056 respectively. The rest of the fitting parameters are presented in Table 2.

As expected, the k-space spectra (Fig. 7A) show only small deviation among the samples. All of the spectra show high periodicity, with no unexpected changes, even at high wavenumber. Even the peaks at $9.2 \text{ \AA}^{-1}$, $10.8 \text{ \AA}^{-1}$, and $12.4 \text{ \AA}^{-1}$ of Sample 5 show consistent oscillations with the other samples. This is easily observable despite the increased noise in the region. This strongly refutes the notion of any $\text{Sn}_{\text{Zn}}^{\bullet\bullet}$ antisites presence in Sample 5. Presence of $\text{Sn}_{\text{Zn}}^{\bullet\bullet}$ would contribute adversely to photoresponse, so a lack of these substitutions is more in-line with the consistent photoresponse among all five samples.

The R-space spectra (Fig. 7B) shows the expected well conserved first shell, with each sample showing a Sn-S bond distance of around 2.38 to 3.41 Å. The metal-metal bonds differentiate, however, with changes in the Cu/(Zn+Sn) ratio. Samples 1 and 2 show Sn-Cu/Zn bonds of 3.80 and 3.99 Å, and Sn-Sn bonds of 3.99 and 3.97 Å respectively. These bonds are slightly deviated in Sample 3, with the Sn-Cu/Zn bond being shorter at 3.74 Å, while the Sn-Sn bonds show higher at 4.06 Å. This deviation would arise due to the size difference in the crystal lattice predicted previously. Coupled with the k-space spectra (Fig. 7A), the Sn is evenly distributed across each lattice, despite the size differences. Changes in the Zn/Sn ratio have more of an effect on this. At high Zn/Sn ratios (Sample 4), the Sn-Cu/Zn bond expands to 3.87 Å, and to 4.01 Å in low Zn environments (Sample 5). This is offset by changes in the Sn-Sn bonds, which are 3.98 Å and 3.97 Å in each respectively. This suggests additional crystal strain in both Samples 4 and 5 relative to the others, and would be the reason for the extended disorder noted in these samples.

Conclusions

The various antisites present in high photoresponse CZTS nanocrystal-based films of different compositions were explored through SR-XAFS measurements. It was found that samples with a Cu/(Zn+Sn) ratio of 0.95 and Zn/Sn ratio of 1.0 showed the most beneficial structure, with advantageous $\text{Zn}_{\text{Cu}}^{\bullet}$ antisites spread periodically throughout the films. Increases in either ratio introduced increased disorder among the antisites. Increasing the Zn content created too many $\text{Zn}_{\text{Cu}}^{\bullet}$ antisites, and created regions of high Zn-S like structure, while increased Cu content allowed for additional Cu'_{Zn} antisites, which in turn leads to $[\text{Cu}'_{\text{Zn}} + \text{Zn}_{\text{Cu}}^{\bullet}]^0$ antisite pairs. These contribute to increased disorder within the films, but also tighter packing of the

crystal. This appears to be the trade-off that creates the equivalent photoresponse observed in all of these samples. Similarly, decreases in Zn content contribute to additional disadvantageous Cu'_{Zn} antisites, but again result in smaller bond lengths. Decreases in Cu content lead to increased disorder in the $[Cu'_{Zn} + Zn_{Cu}^{\bullet}]^0$ antisite pairs due to the decreased Cu'_{Zn} antisites. Both cases also lead to more contracted bond lengths. From this, it appears that a trade-off occurs between the creation of these advantageous substitutions, and the increased disorder due to crystal mis-alignment across the film. This is the likely reason for the equivalent photoresponse despite the differing metal concentrations, and therefore differing amounts of advantageous antisites within the films. Initial decreases in the Cu content yield increased $Zn_{Cu}^{\bullet}$ antisites, but eventually start forming increasing Cu vacancies, which eliminate any advantageous effects of the antisites. Increased Cu content, however, also leads disadvantageous $[Cu'_{Zn} + Zn_{Cu}^{\bullet}]^0$ antisite pairs. This gives the idea that each structural abnormality has some effect on the photoresponse, and that samples constructed with similar composition will experience different ratios of these antisites, but ultimately have a relatively equal balance of advantageous and disadvantageous ones, thereby yielding equivalent photoresponse. As such, film fabrication in low-cost environments should include the above mentioned ratios to maximize the formation of advantageous antisites, without overly increasing the disorder.

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