



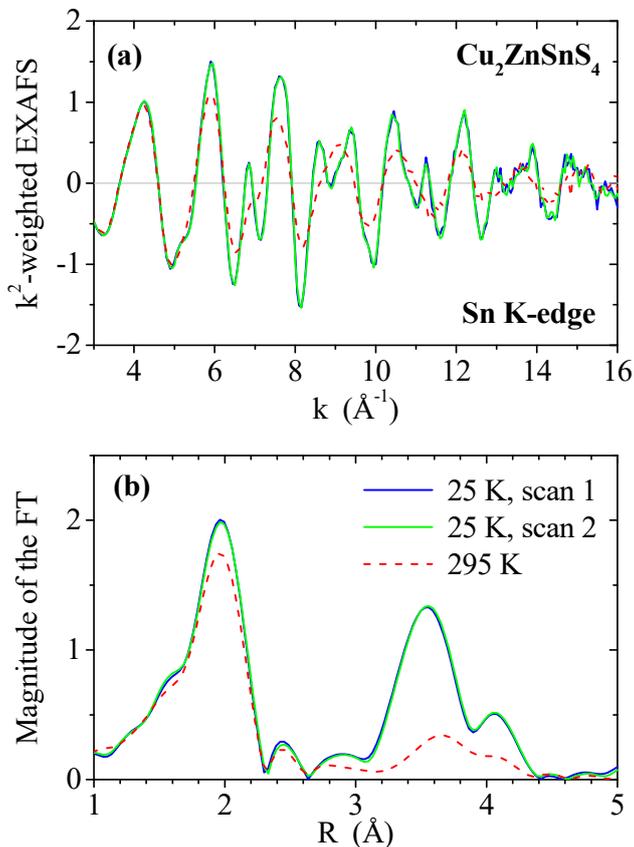
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|   | <b>Experiment title:</b><br>Atomic-scale structure of stoichiometric and non-stoichiometric $\text{Cu}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnS}_4$ kesterites | <b>Experiment number:</b><br>HC-2412 |
| <b>Beamline:</b><br>BM08  | <b>Date of experiment:</b><br>from: 03/06/16 to: 07/06/16   | <b>Date of report:</b><br>15/08/2016 |
| <b>Shifts:</b><br>12  | <b>Local contact(s):</b><br>Dr. Alessandro Puri   | <i>Received at ESRF:</i>             |
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## Report:

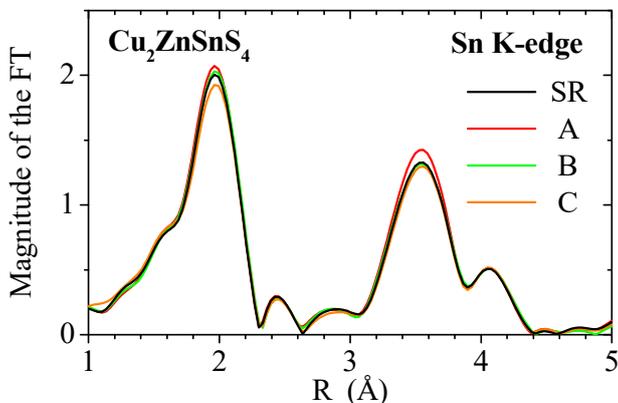
It is the aim of this project to study the atomic-scale structure of stoichiometric and non-stoichiometric  $\text{Cu}_2\text{ZnSnSe}_4$  and  $\text{Cu}_2\text{ZnSnS}_4$  kesterite compounds using extended X-ray absorption fine structure spectroscopy (EXAFS). The results will provide original insight into the correlation between material composition and structural parameters and will help to exploit the full potential of these compounds as absorber material in thin film solar cells.

$\text{Cu}_2\text{ZnSnSe}_4$  and  $\text{Cu}_2\text{ZnSnS}_4$  powders with varying  $\text{Cu}/(\text{Zn}+\text{Sn})$  and  $\text{Zn}/\text{Sn}$  ratios were synthesized by solid state reaction from the pure elements [1]. The actual chemical composition was determined by wavelength dispersive X-ray analysis with an electron microprobe system while the phase content of the material was investigated using X-ray diffraction. Four and nine single-phase non-stoichiometric  $\text{Cu}_2\text{ZnSnSe}_4$  and  $\text{Cu}_2\text{ZnSnS}_4$  samples, respectively, were chosen for the EXAFS study together with the corresponding stoichiometric references. The  $\text{Cu}/(\text{Zn}+\text{Sn})$  and  $\text{Zn}/\text{Sn}$  ratios for these samples varied from 0.91 to 1.01 and from 1.00 to 1.15, respectively. Additionally, five  $\text{Cu}_2\text{ZnSn}(\text{Se,S})_4$  samples with  $0.48 \leq \text{Se}/(\text{Se}+\text{S}) \leq 0.90$  were investigated.

EXAFS spectra were recorded in transmission mode at the Cu (8.979 keV), Zn (9.659 keV), and Sn (29.200 keV) K-edges. To that end, the powders were mixed with graphite, ball-milled and then pressed into pellets of 8 mm diameter. For each sample, two pellets were prepared with the amount of material optimized for measurement at either the Cu and Zn or the Sn K-edge. The measurements were performed at a sample temperature of approximately 25 K to minimize thermally induced disorder and to resolve subtle structural differences of the various samples. Spectra were recorded up to a photoelectron wavenumber  $k$  of approximately  $17 \text{ \AA}^{-1}$  for the Zn and Sn K-edge and  $14 \text{ \AA}^{-1}$  for the Cu K-edge.



**Figure 1:** (a)  $k^2$ -weighted EXAFS spectra and (b) magnitude of the Fourier transformation (FT) measured at the Sn K-edge of stoichiometric  $\text{Cu}_2\text{ZnSnS}_4$  at 25 and 295 K.



**Figure 2:** Magnitude of the Fourier transformation (FT) for  $k^2$ -weighted EXAFS spectra of  $\text{Cu}_2\text{ZnSnS}_4$  with different stoichiometry taken at the Sn K-edge at 25 K.

As an example, Figure 1 (a) shows the  $k^2$ -weighted EXAFS spectra recorded at the Sn K-edge for the stoichiometric  $\text{Cu}_2\text{ZnSnS}_4$  reference at both 25 K (green and blue solid lines) and room temperature (red dashed line). The corresponding Fourier transformations are plotted in Figure 1 (b). It is readily apparent that the signal intensity is strongly enhanced for the low temperature measurement compared to the room temperature measurement allowing a more precise determination of the local structural parameters. Furthermore, a comparison of the two different spectra recorded at 25 K demonstrates excellent reproducibility of these measurements.

Figure 2 plots the Fourier transformation of the  $k^2$ -weighted EXAFS spectra for three different non-stoichiometric  $\text{Cu}_2\text{ZnSnS}_4$  samples (A, B, C) and the stoichiometric  $\text{Cu}_2\text{ZnSnS}_4$  reference (SR) measured at the Sn K-edge at 25 K. Clearly, the four spectra are very similar as expected from the fact that all materials exhibit the kesterite type crystal structure. Nevertheless, subtle differences can be observed for the first nearest neighbor S peak at  $R \sim 2 \text{\AA}$  and the scattering signal of higher coordination shells at  $R \sim 3.2 - 4.4 \text{\AA}$  indicating slight variations of the local atomic arrangements in these four different samples.

A detailed analysis of all spectra measured at the Cu, Zn, and Sn K-edge is currently under way using the IFEFFIT/LARCH software package [2] and the computer code FEFF9 [3]. It yields local structural parameters such as the element-specific average bond lengths and bond length variations as a function of sample composition. Correlating these results with other important properties including type and concentration of point defects or the band gap energy will help to better

understand these complex semiconductor material systems. Additionally, the atomic-scale structural parameters serve as starting point for advanced first-principles calculations of the electronic band structure in stoichiometric and non-stoichiometric  $\text{Cu}_2\text{ZnSnSe}_4$  and  $\text{Cu}_2\text{ZnSnS}_4$  kesterites.

- [1] L. E. Valle Rios, K. Neldner, G. Gurieva, S. Schorr, *J. Alloys Comp.* 657, 408 (2016).
- [2] B. Ravel and M. Newville, *J. Synchrotron Radiat.* 12, 537 (2005).
- [3] J. J. Rehr *et al.*, *Phys. Chem. Chem. Phys.* 12, 5503 (2010).