Cryo X-ray Absorption Spectroscopy of Copper Zinc Tin Sulfide Nanoparticles

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X-ray absorption spectroscopy (XAS) is used to probe the atomic environment in quaternary compounds, like the earth abundant and non-toxic Cu₂ZnSnS₄ (CZTS) absorber material (Fig. 1) used in 3rd generation generation solar cells¹. Cooling the structure down to 100 K decreases thermal fluctuations and improves XAS data quality for an improved FEFF-based fitting (Fig. 2 & 3).

Cryo-EXAFS analysis indicates two different neighbors to Cu-atoms (Fig. 4, top). The shortest radial distance can be simulated by a 16% bond shortening of the Cu-S bond (2.33 Å → 1.95 Å). But cooling have previously been observed to change only <1% in bond length², which indicate other factors must be causing the deviation.

An oxidized CZTS shell:
Only by replacing a fraction of the Cu-S bonds in the model of CZTS with the shorter Cu-O bonds (CuO: 1.963 Å) can a reasonable (R-factor = 0.01) fit to the EXAFS signal be obtained (Fig. 4, middle and bottom). In the fit, scattering amplitudes related to the oxide are set to proportionally reduce the scattering amplitudes of those related to CZTS, which allow us to assess the degree of oxidation (Fig. 5). Similarly for Zn- and Sn-edge EXAFS, dual peak 1.shell features are observed, which can be partly fitted with oxides products (Fig. 6). XPS analysis of similar CZTS compound have also revealed a 15.2% oxidation of CZTS. A 20% oxidation of the CZTS NP would be equivalent with the formation of a 3.6 Å oxide shell around the 10 nm diameter CZTS NP. Nitrogen bonds from the ligand capping could also contribute to the deviations, but their effect is difficult from that of oxygen.

Figure 1: CZTS single cell structure. Top Right, CZTS nanoparticles (NP) with organic (Oleylamine) ligand capping. Bottom Right, average composition (from EDX) and size distribution of CZTS NPs.

Figure 2: XAS data analysis can be divided into XANES and EXAFS analysis. XANES analysis can indicate oxidation level of the probed element (here Cu) by using Linear Combination Fitting (LCF) of known standard sample data. An oxidation level of Cu is 1.5 for standard sample data. An oxidation level of Cu is 1.95 Å before 3.842 K. Cooling of the compounds still reveals a 13.5% oxidation state. An oxidation level of Cu is 1.0189 Å. Copper standards 

Figure 3: Cu-edge EXAFS analysis of sample #1 at 100 K and 300 K. The isolated peaks are in space (2.33 Å to 1.95 Å) and an additional peak (E = 1.6 eV) was found for the K-edge EXAFS data. The oxidation level of Cu is 1.6 is smaller for the K-edge EXAFS data. The oxidation state of Cu is 1.0604 Å. Copper standards 

Figure 4: Cu-edge EXAFS analysis of sample #1 at 100 K and 300 K. The isolated peaks are in space (2.33 Å to 1.95 Å) and an additional peak (E = 1.6 eV) was found for the K-edge EXAFS data. The oxidation level of Cu is 1.6 is smaller for the K-edge EXAFS data. The oxidation state of Cu is 1.0604 Å. Copper standards

Figure 5: FEFF-fitted parameters for the Cu-edge EXAFS data at 100 K. Linear values of bond distances (Å) can be grouped into “shells” that have similar R-space features. The amplitude from the scattering data is reduced by a factor 10 and an additional amplitude factor is applied depending on whether the structure is a CZTS (top group) or CuO (bottom group).

Figure 6: FEFF-fitted parameters for the Cu-edge EXAFS data at 100 K. Linear values of bond distances (Å) can be grouped into “shells” that have similar R-space features. The amplitude from the scattering data is reduced by a factor 10 and an additional amplitude factor is applied depending on whether the structure is a CZTS (top group) or CuO (bottom group).

Reference: