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 solar cells. 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 length, 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 to distinguish from that of oxygen.

Figure 1: Left, CZTS unit cell structure. Top Right, CZTS nanoparticle (NP) with organic (Oleylamine) signal capping. Bottom right, average composition (from EDX) and size distribution of CZTS NP.

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 standards to fit the CTS edge position: 40% Cu₂S + 60% CuS.

Figure 3: Cu-edge EXAFS analysis of sample #1 at 100 K and 300 K. The isolated signals in k-space (2.5–5 Å⁻¹) was Fourier transformed (FT) to indicate trends in radial distance (R-space). A splitting and sharpening of k for the 1.shell feature is observed when cooling down to 100 K. Bottom left, ratio of envelope (R = 4 Å) in k-space, simulates the most important features in R-space. These ranges is implemented in a FEFF-fitting routine.

Figure 4: Cu-edge EXAFS analysis for CZTS at 100 K. Top, dual peak 1.shell feature. Middle, FEFF-fitting including both CZTS and CuS structure. The FEFF-software calculates the effective amplitudes (f_eff), total scattering phase shift and other parameters of the individual scattering paths. Bottom, Scattering contributions to the FEFF-fits from the individual scattering atoms.

Figure 5: Cu-edge EXAFS analysis for CZTS at 100 K. Top, dual peak 1.shell feature. Middle, FEFF-fitting including both CZTS and CuS structure. The FEFF-software calculates the effective amplitudes (f_eff), total scattering phase shift and other parameters of the individual scattering paths. Bottom, Scattering contributions to the FEFF-fits from the individual scattering atoms.

Figure 6: FEFF-models for Zn- and Sn-edge (bottom) EXAFS data. 20% Cu₂S was included in the model for Zn-edge EXAFS and 20% CuO, of Sn-edge EXAFS, but data quality for Sn is in some way low, which makes the fitted oxide fraction less relevant than for Cu- and Zn-edge EXAFS data.