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

Rein, Christian; Ramos, Tiago; Andreasen, Jens Wenzel

Publication date:
2019

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
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DTU Energy, Technical University of Denmark, Risø, Denmark. *chrir@dtu.dk

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 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 to distinguish from that of oxygen.