Supplemental Information:

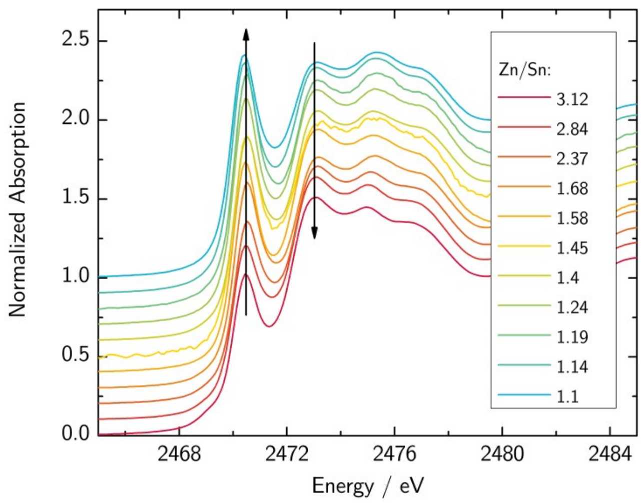

Fig. S1: Edge step normalized XANES spectra at the K-edge of sulfur of CZTS thin film samples with varying Zn/Sn ratio, as well as varying Cu/Sn-ratio.

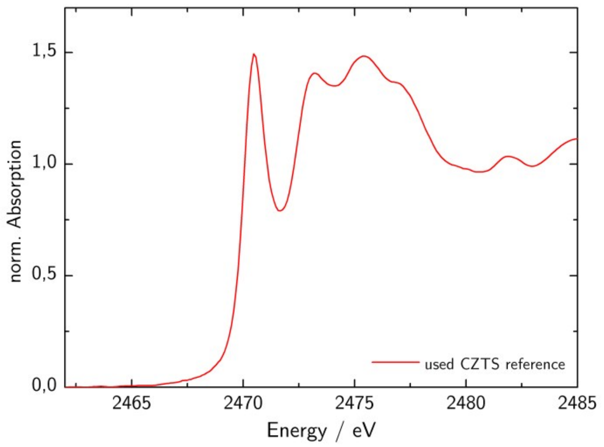

Fig. S2 Edge step normalized XANES spectrum at the K-Edge of sulfur of a CZTS reference powder used for the linear combination analysis in the present study.

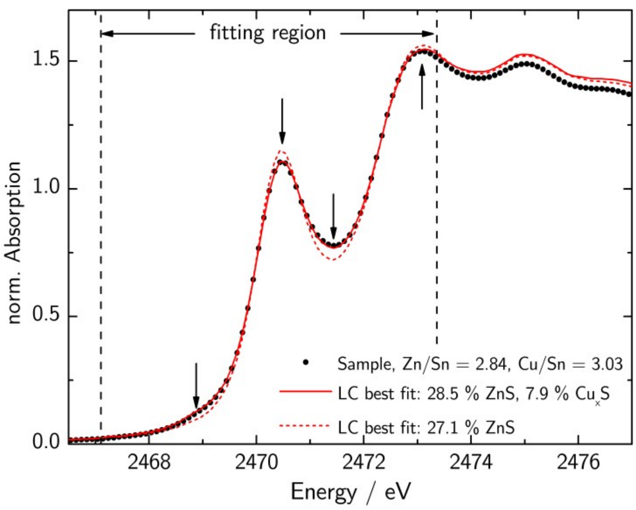

Fig. S3: Edge step normalized XANES spectrum at the K-edge of sulfur of one particular CZTS thin film sample together with fits obtained by a linear combination of CZTS and zinc sulfide only and a linear combination of all three phases: CZTS, zinc sulfide and copper sulfide. This demonstrates the sensitivity of the linear combination analysis in three phase samples.

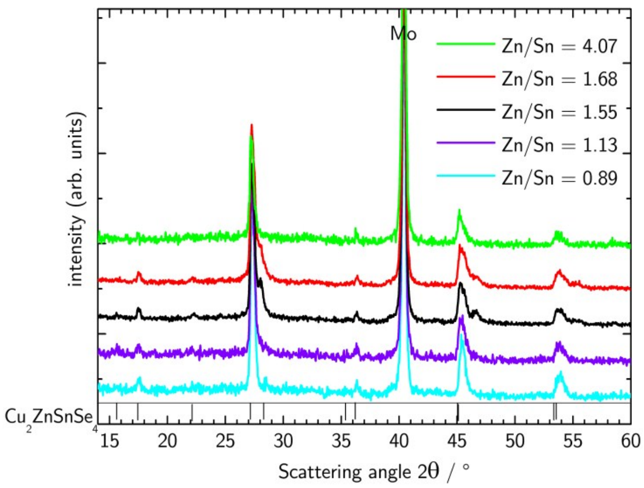

Fig. S4: Measured X-ray diffraction pattern of several Cu-Zn-Sn-Se thin films with various Zn/Sn total atomic ratios. Diffraction reflexes of ZnSe overlap completely with those of CZTSe, while no other secondary phase is observable.

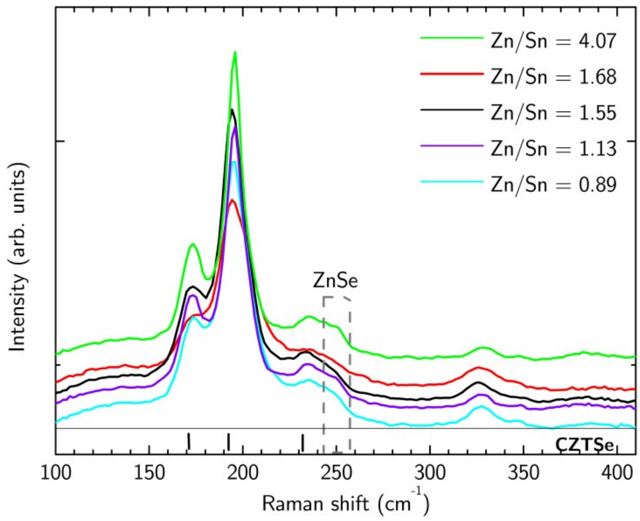

Fig. S5: Measured Raman scattering spectra of several Cu-Zn-Sn-Se thin films with various Zn/Sn total atomic ratios, excited at 633 nm.

Derivation of equations 5 and 7:

The amount of zinc in phase $X(Zn_X)$ can be described by:

$$Zn_{CZTS} = Zn_{total} - Zn_{ZnS} = Zn_{total} - p_{ZnS} \cdot S_{total} \qquad \text{(Eq. 4)}$$

this assumes a stoichiometric ZnS phase, as well as that Zn is present in ZnS and CZTS only. No other phase contains Zn.

$$\Leftrightarrow p_{ZnS} = \frac{Zn_{total} - Zn_{CZTS}}{S_{total}}$$

$$\Leftrightarrow p_{ZnS} = \frac{\frac{Zn_{total}}{Sn_{total}} - \frac{Zn_{CZTS}}{Sn_{total}}}{\frac{S_{total}}{Sn_{total}}}$$

We assume no tin containing secondary phase, therefore $Sn_{CZTS} = Sn_{total}$. Assuming a certain threshold value for $\frac{Zn}{Sn} = Z$ above all excess Zn segregates into ZnS, the Zn/Sn-ratio of the CZTS phase equals Z: $\frac{Zn_{CZTS}}{Sn_{total}} = \frac{Zn_{CZTS}}{Sn_{CZTS}} = Z$. This leads to Eq. 4a:

$$p_{ZnS} = \frac{2\left(\frac{Zn_{total}}{Sn_{total}} - Z\right)}{2\frac{S_{total}}{Sn_{total}}} \Leftrightarrow$$

We now assume only ZnS to form as secondary phase. For samples, where Cu_xS and ZnS is formed we can subtract Cu in the copper sulfide from the sample composition and assume the Cu/Sn-value C to be limited to 2 for Cu-rich samples (as shown in the manuscript). Considering the octet-rule (Eq. 2) we get:

$$\frac{S_{total}}{Sn_{total}} = \frac{1Cu_{total}}{2Sn_{total}} + \frac{Zn_{total}}{Sn_{total}} + 2$$

inserting this expression into Eq. 4a yields Eq. 5:

$$p_{ZnS} = \frac{2\left(\frac{Zn_{total}}{Sn_{total}} - Z\right)}{C + 2\frac{Zn_{total}}{Sn_{total}} + 4}$$

Eq. 7 of the manuscript is derived in complete analogy. The assumption made here for c to be limited to 2 is shown to be correct, fitting the data of the quantification of the copper sulfide.