Sulfur-Specific Electronic Structure of Kesterite Solar Cell Absorbers: An X-ray Emission Spectroscopy Study

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Motivation

The global demand for renewable energy highlights the urgent need for sustainable and cost-effective technologies. Kesterites, including pure sulfides, pure selenides, and mixed $Cu_2ZnSn(S,Se)_4$ (CZTSSe) chalcogenides, have emerged as promising next-generation thin-film solar cell absorbers due to their earth-abundant and non-toxic composition. While they offer lower material consumption and manufacturing costs compared to traditional silicon cells, their current record power conversion efficiency (PCE) of 14.6% remains far below the theoretical limit of >32%. This significant performance gap is primarily driven by challenges such as secondary phase formation, defect regulation, non-ideal band gap grading and alignment, as well as severe recombination losses. To help address these fundamental issues, this project aims to:

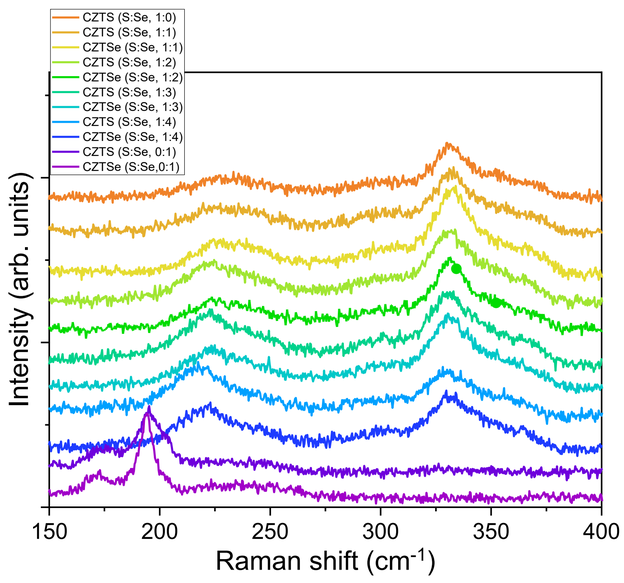
- Model the electronic structure of kesterite materials using Density Functional Theory (DFT) calculations.
- Compare the theoretical X-ray spectra with experimental measurements.

Sample preparation

Magnetron sputtering deposition [2]

Substrate: Glass and Film Thickness: ~1 µm

A set of 12 samples was annealed at 550°C for 30 minutes in a graphite box under atmospheres with varying S:Se ratios. An additional 12 samples were prepared using a different set of parameters. Along with these, two standard samples (ZnS and SnS_2) were included. All samples were characterized by Raman, Energy-Dispersive X-ray Spectroscopy, and XRD.

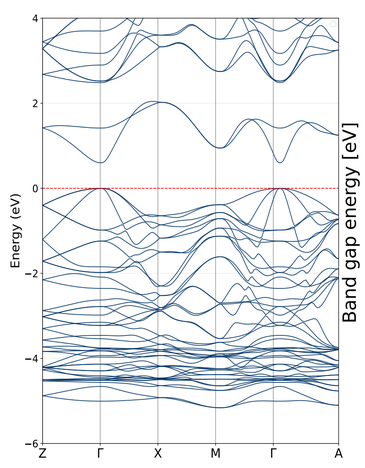


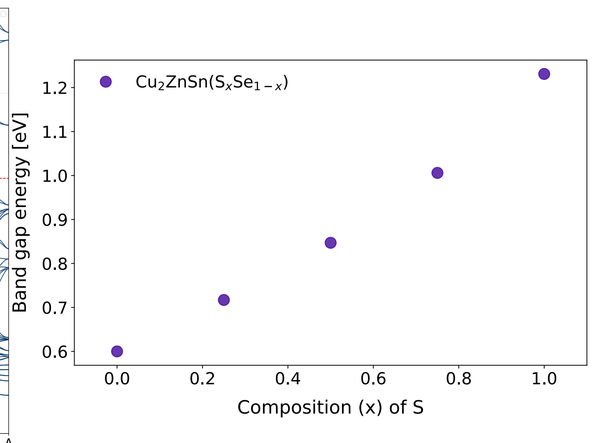
Annealing ratio	CZTSe	CZTS
(S:Se, 1:0)	$Cu_{2.02}Zn_{0.95}Sn_{1.09}S_{3.46}Se_{0.48}$	$Cu_{1.91}Zn_{1.03}Sn_{0.97}S_{3.35}Se_{0.74}$
(S:Se, 1:1)	$Cu_{2.02}Zn_{0.93}Sn_{1.02}S_{3.35}Se_{0.68}$	$Cu_{1.84}Zn_{1.05}Sn_{0.97}S_{3.40}Se_{0.74}$
(S:Se, 1:2)	$Cu_{2.08}Zn_{0.99}Sn_{1.02}S_{3.10}Se_{0.81}$	$Cu_{1.79}Zn_{1.03}Sn_{1.10}S_{2.99}Se_{1.09}$

Theoretical Methods

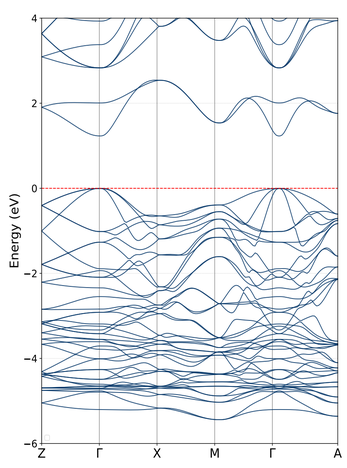
Density-functional-theory (DFT) calculations using the PBE functional with a Hubbard U correction (DFT+U) were employed to model and interpret the measured valence-to-core (VtC) X-ray emission spectra. VtC spectra were computed using two different software packages, FDMNES and CP2K/Quickstep, while CP2K was used for electronic-structure and band-gap calculations.

$Cu_2ZnSnSe_4$





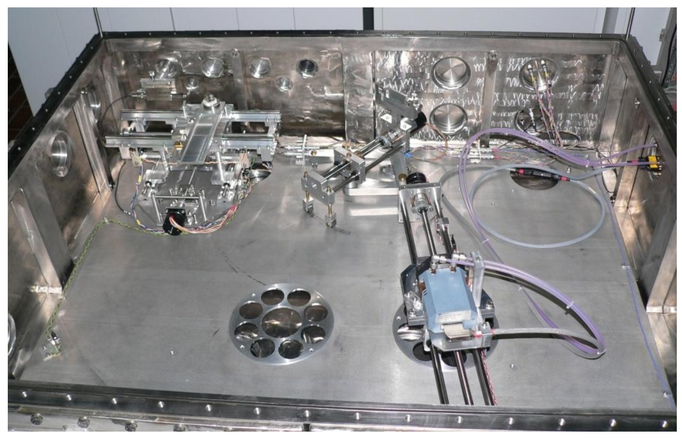
Cu_2ZnSnS_4



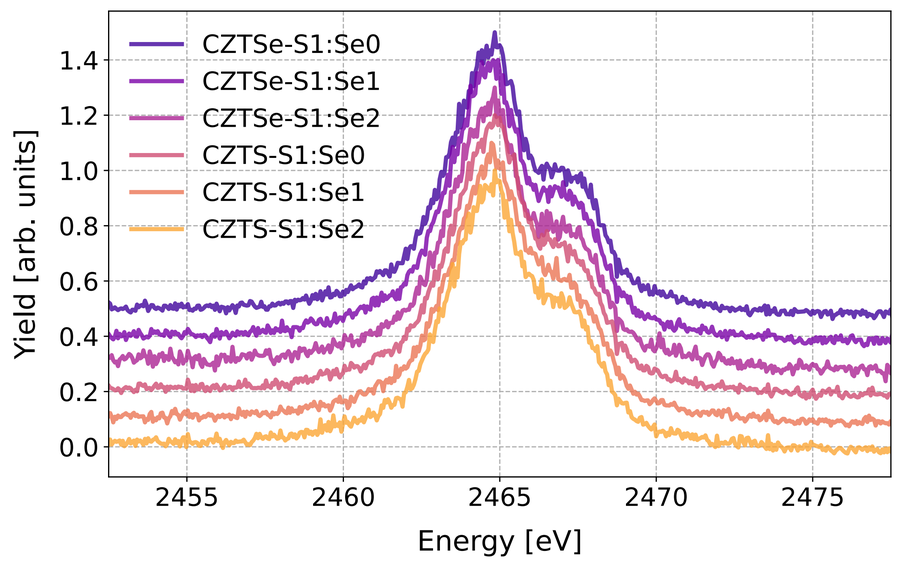
Sulfur Kβ XES Spectra Measurements

The measurements were performed at the Jožef Stefan Institute using a wavelength-dispersive X-ray emission spectrometer in Johansson geometry[1]. Targets were irradiated by 3 MeV protons with proton current in the range 100 - 150 nA. Thermoelectrically cooled CCD camera (770x1152 pixels and with size 22.5x22.5 µm2) was used for position sensitive detection of X-rays.

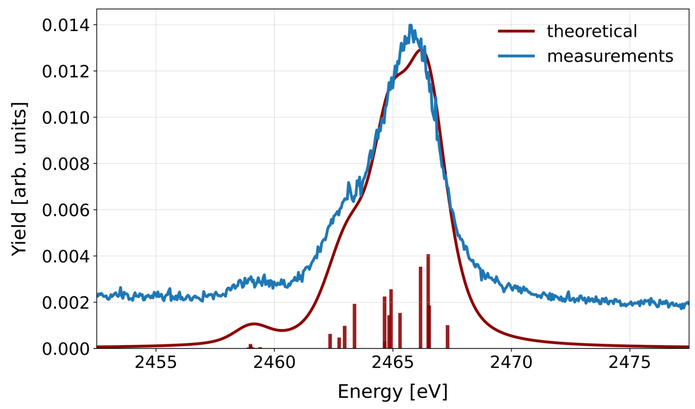
The spectrometer resolving power E/ΔE ≈ 7000!

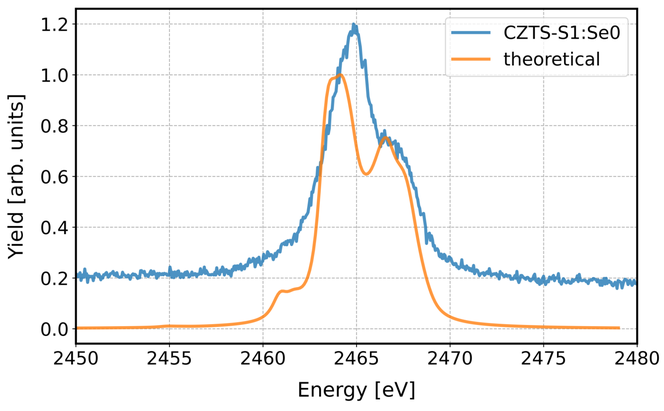


Results



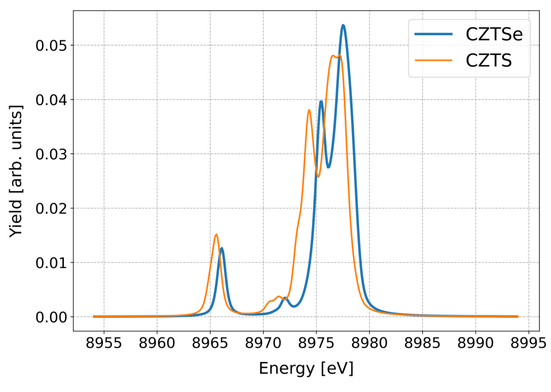
Comparison between theoretical and experimental Sulfur Kβ spectra of ZnS





Comparison between theoretical and experimental Sulfur Kβ spectra of Cu_2ZnSnS_4

Theoretical Prediction of Copper Valence-to-Core X-ray Emission Spectra as a Probe of Electronic Structure



References

[1] M. Kavčič, M. Budnar, A. Mühleisen, F Gasser, M. Žitnik, K Bučar, R Bohinc, Rev. Sci. Instrum. 83: 033113, 2012

[2] Zaki, M. Y., Sava, F., Simandan, I. D., Mihai, C., & Velea, A. (2024). Structural and Compositional Analysis of CZTSSe Thin Films by Varying S/(S+Se) Ratio. Energies, 17(15), 3684

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