Kai Neldner [1], Susan Schorr [1, 2], Daniel Többens[1], Pamela Whitfield[3], Galina Gurieva[1]

[1] Helmholtz-Zentrum Berlin , Hahn-Meitner-Platz 1, 14109 Berlin, Germany
[2] Freie Universität Berlin, Malteserstr. 74-100, 12247 Berlin, Germany
[3] Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

2015 MRS SPRING MEETING & EXHIBIT

Freie Universität Berlin

HZB Helmholtz Zentrum Berlin

Phase content and structural analysis of off-stoichiometric Cu_2ZnSnS_4 (CZTS)

Motivation

Thin film solar cells based on $Cu_2ZnSn(S,Se)_4$ (CZTSSe) as absorber layer have seen a rapid development leading to a world record efficiency of 12.6% [1].

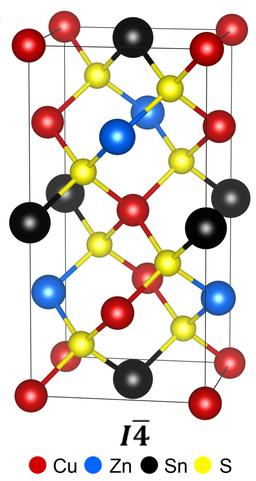
Properties of CZTS

- abundant
- optical band-gap energy of 1.5 eV
- optical absorption coefficient of 10^4 cm^{-1}

Goal ► learn more about ...

- stability of off-stoichiometric kesterite type phase and corresponding secondary phases
- structural origin of cationic point defects
- point defects and cation distribution

kesterite [3]
Cu_2ZnSnS_4



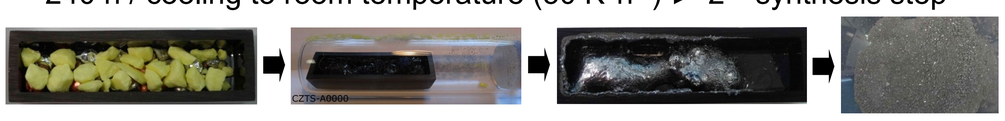
Synthesis by solid state reaction

In literature four different cation substitution processes to build defect complexes for off-stoichiometric CZTS are proposed [4].

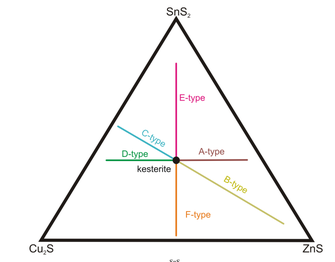
► A-, B-, C- and D-type (E- and F-type proposed by our group)
► most efficient solar cells correspond to A-type (Cu-poor, Zn-rich)
expected point defects: copper vacancies (V_{Cu}) and Cu-Zn antisites.

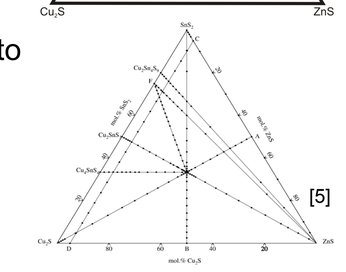
Synthesis starts with pure elements in sealed silica tubes

1) heating with 10 $K*h^{-1}$ to 250°C, 450°C, 600°C, 820°C / hold for 240 h / cooling to room temperature (50 $K*h^{-1}$) ► 1st synthesis step
2) homogenization of material (grinding, pressing pellets) annealing at 750°C for 240 h / cooling to room temperature (50 $K*h^{-1}$) ► 2nd synthesis step



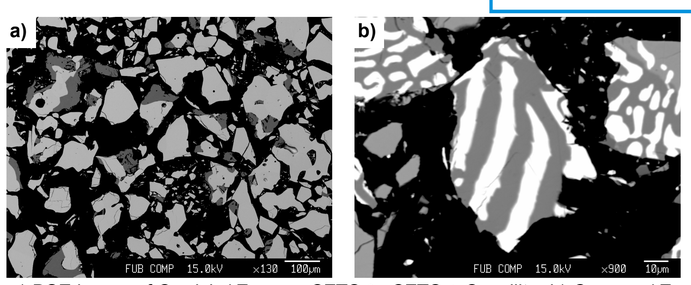
First synthesis step: elements, sealed tube with pyrolytic graphite boat, synthesized material, powder (from left to right)



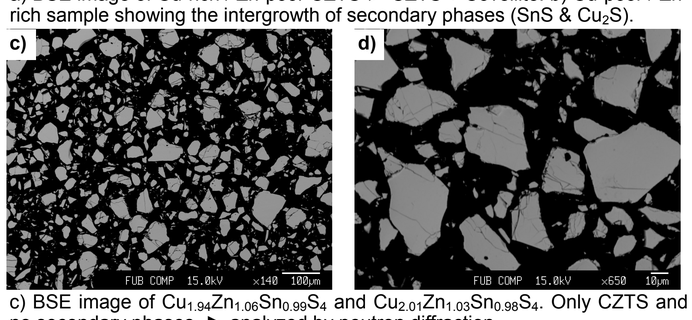

[5]

Ternary diagrams Cu_2S-ZnS-SnS_2

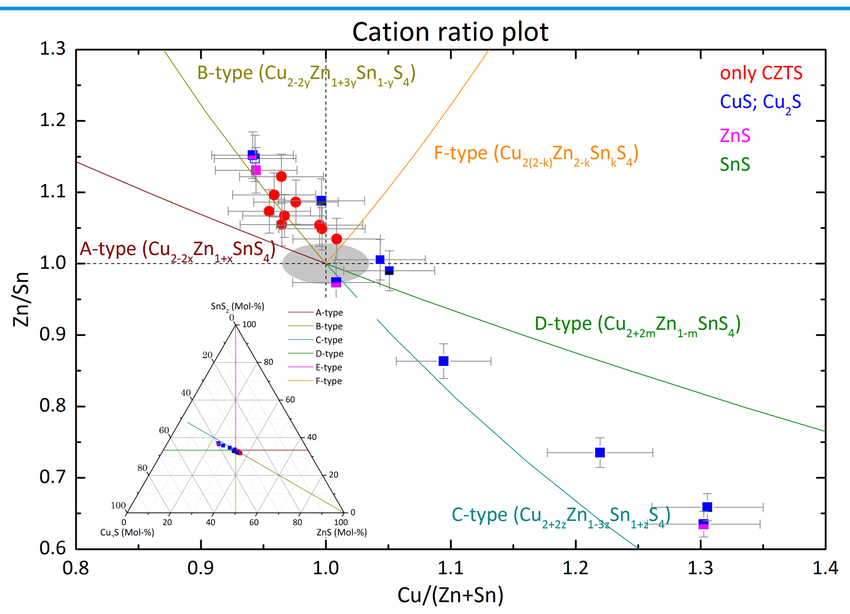
Characterization by electron microprobe (WDX) and X-Ray diffraction (XRD)

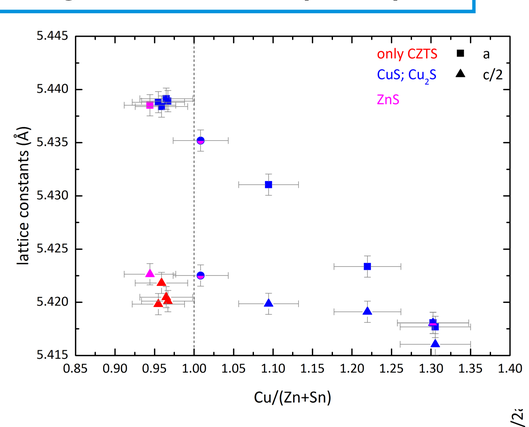


a) BSE image of Cu-rich / Zn-poor CZTS ► CZTS + Covellite. b) Cu-poor / Zn-rich sample showing the intergrowth of secondary phases (SnS & Cu_2S).



c) BSE image of $Cu_{1.94}Zn_{1.06}Sn_{0.99}S_4$ and $Cu_{2.01}Zn_{1.03}Sn_{0.98}S_4$. Only CZTS and no secondary phases ► analyzed by neutron diffraction.

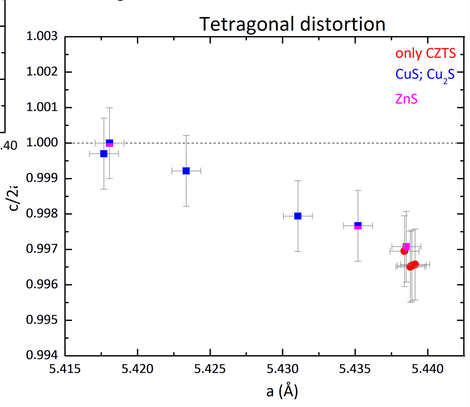




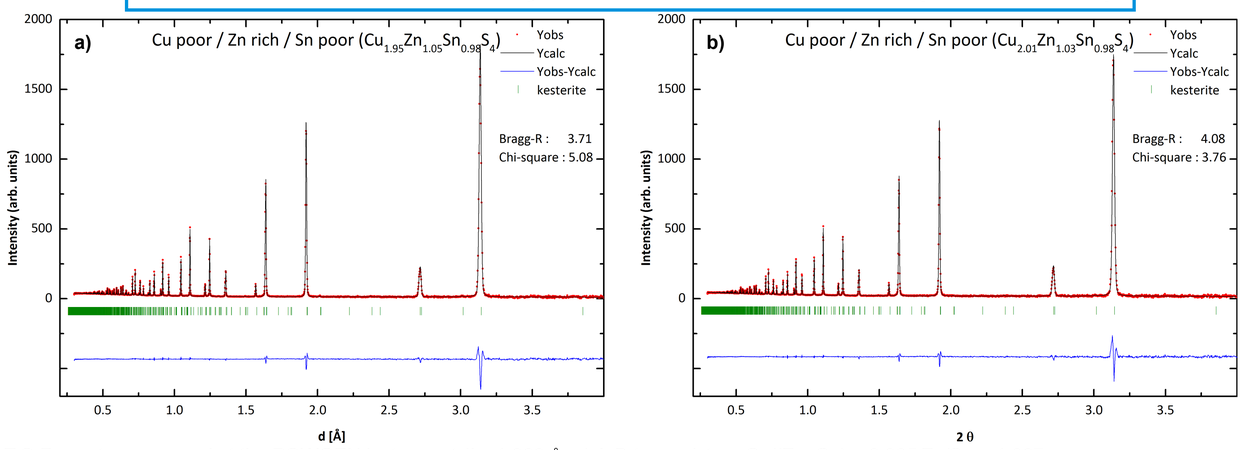
Cation ratio plot: Zn/Sn vs. Cu/(Zn+Sn) of the kesterite type phase: only CZTS = red, secondary phases: CuS / Cu2S = blue, ZnS = magenta, SnS = black and grey field = stoichiometric kesterite. Inserts: sample positions in the ternary phase diagram. Also the six different cation substitution processes are highlighted.

Lattice constants vs Cu/(Zn+Sn). Lattice constants are decreasing from A-B-type mixture to C-D-type mixture composition. Only CZTS = red, Sec. phases: CuS / Cu2S = blue, ZnS = magenta.

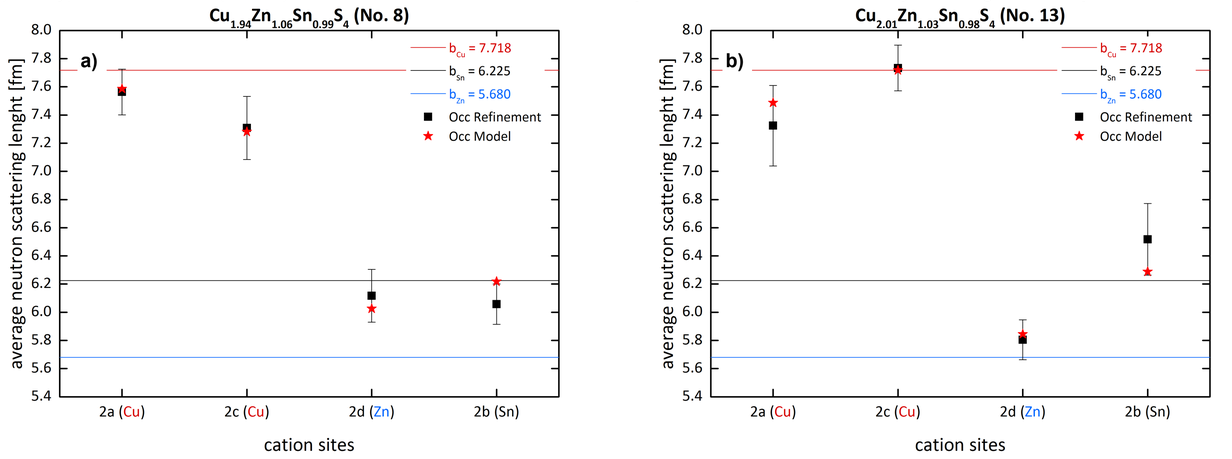
Overview of CZTS samples in c/2a vs a. When c/2a is 1 there is no tetragonal distortion. Only CZTS = red, Sec. phases: CuS / Cu2S = blue, ZnS = magenta.



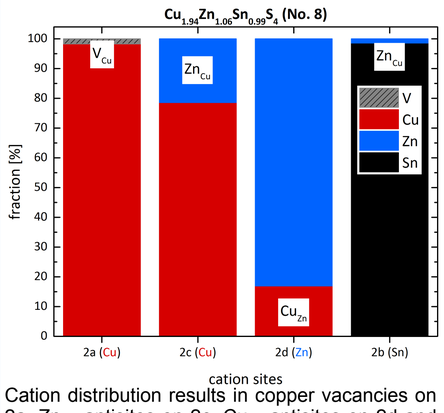
Cation distribution by neutron diffraction (POWGEN)



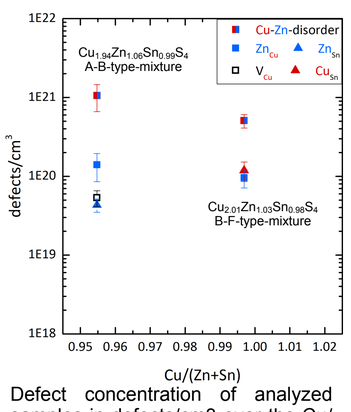
T.O.F spectra measured at the POWGEN instrument (λ =1.066 Å: a) A-B-type mixture Cu/(Zn+Sn) = 0.995 Zn/Sn = 1.067
b) B-F-type mixture ► Cu/(Zn+Sn) = 0.997, Zn/Sn = 1.049. Rietveld analysis done with FullProf Suite by J. Rodriguez-Carvajal.



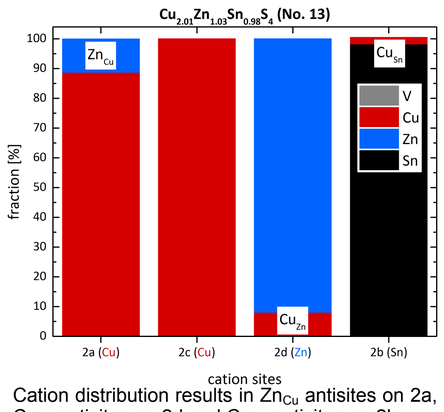
Calculation of the average neutron scattering length of the cation sites: 2a, 2c, 2d and 2b [6]. a) A-B-type mixture Cu/(Zn+Sn) = 0.995 Zn/Sn = 1.067 b) B-F-type mixture ► Cu/(Zn+Sn) = 0.997, Zn/Sn = 1.049.



Cation distribution results in copper vacancies on 2a, Zn_{Cu} antisites on 2c, Cu_{Zn} antisites on 2d and Zn_{Sn} antisites on 2b.



Defect concentration of analyzed samples in defects/cm3 over the Cu/(Zn+Sn) ratio.



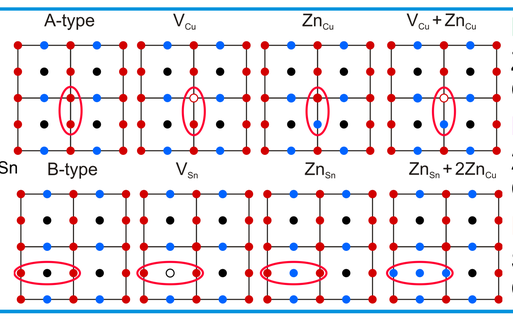
Cation distribution results in Zn_{Cu} antisites on 2a, Cu_{Zn} antisites on 2d and Cu_{Sn} antisites on 2b.

Cation substitution processes

A-type:
$2\,Cu^+ \rightarrow V_{Cu} + Zn^{2+}{}_{Cu}$
Cu poor / Zn rich / Sn constant

B-type:
$2\,Cu^+ + Sn^{4+} \rightarrow 2\,Zn^{2+}{}_{Cu} + Zn^{2+}{}_{Sn}$
Cu poor / Zn rich / Sn poor

C-type:
$3\,Zn^{2+} \rightarrow 2\,Cu^+{}_{Zn} + Sn^{4+}{}_{Zn}$
Cu rich / Zn poor / Sn rich

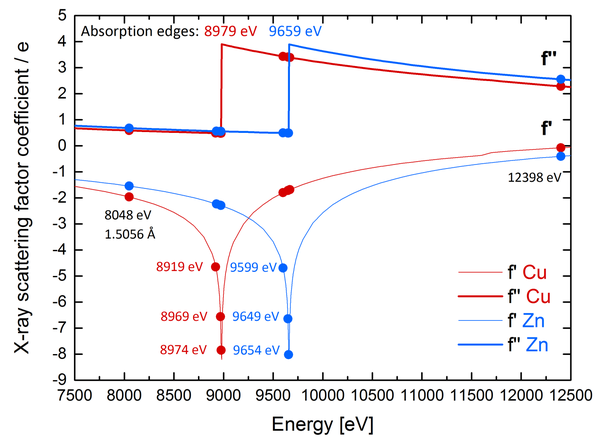


D-type:
$Zn^{2+} \rightarrow Cu^+{}_{Zn} + Cu^+{}_i$
Cu rich / Zn poor / Sn constant

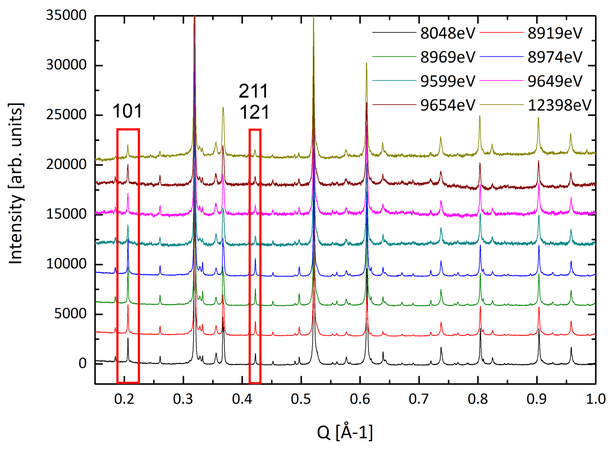
E-type:
$2\,Cu^+ + Zn^{2+} \rightarrow 2\,V_{Cu} + Sn^{4+}{}_{Zn}$
Cu poor / Zn poor / Sn rich

F-type:
$Sn^{4+} \rightarrow Cu^+{}_{Sn} + Zn^{4+}{}_{Sn} + Cu^+{}_i$
Cu rich / Zn rich / Sn poor

Structural analysis by anomalous X-ray diffraction (KMC-2)



Energies measured near the Cu- and Zn-K-edge.



Patterns measured at all eight energies with some highlighted reflexes (101 and 211/121) which change relative intensities.

Results

- synthesized samples contain off-stoichiometric kesterite as main phase

⇒ in total 20 synthesized samples ► 8 single phase ► Cu-poor, Zn-rich composition

⇒ annealing is a prerequisite for good quality powder samples (homogeneous kesterite type phase)

- anomalous X-ray diffraction suitable method to distinguish isoelectronic cations

⇒ sample preparation is really important (well-ground samples are needed)

⇒ Rietveld analysis of data has to be done with great care to get reliable cation distributions

- neutron diffraction suitable method to distinguish isoelectronic cations

⇒ Rietveld analysis of T.O.F spectra and average neutron scattering method ► cation distribution [6]

⇒ cation distribution of analyzed samples correspond to defect complexes proposed in literature [4]

[1] Wang et al., Adv. En. Mat. (2013)
[2] Raulot, et al., J. Phys. Chem. Solids 66 (2005) 2019.
[3] Hall et al., Can. Mineral. 16 (1978) 131
[4] Lafond et al., Z. Anorg. Allg. Chem., 638, 2571–2577 (2012)
[5] Oleksyuk et al., J. Alloys Comp. 368 (2004) 135
[6] Schorr, Sol. Energ. Mat. Sol. Cells, 2011. 95(6): 1482-1488.

Acknowledgment
This work was financially supported by the HZB Graduate School MatSEC (Materials for Solar Energy Conversion).

MatSEC

Kai Neldner
kai.neldner@helmholtz-berlin.de
Fon +49-30-8062-43098

www.helmholtz-berlin.de