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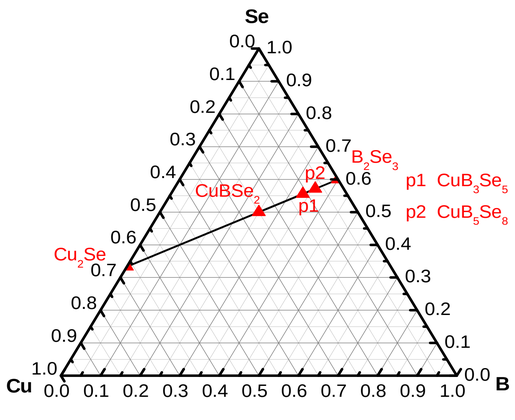
The role of gallium addition on the defect characteristics in off stoichiometric $CuInSe_2$

The role of stoichiometry in chalcopyrite type absorbers

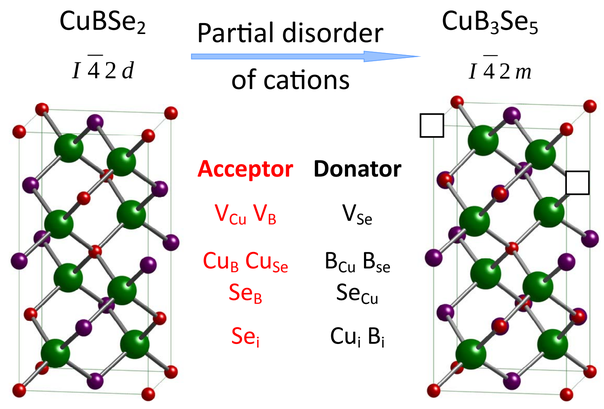
Motivation

- high efficient thin film solar cells exhibit in general an off stoichiometric composition
- deviation from stoichiometry always causes structural inhomogeneities and charge mismatches, which influence the properties of a material
- electronic, optical and theoretical defect characterisation has to be supplemented by structural studies

Fundamental and systematic structural studies are necessary to understand the off stoichiometry phenomena in chalcopyrites!

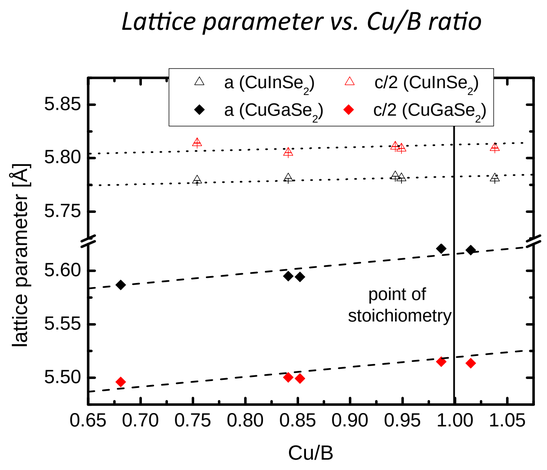


- chalcopyrite type crystal structure accepts strong deviation from stoichiometric composition
- broader homogeneity region of ch-phase for $CuGaSe_2$ than for $CuInSe_2$[1]



- V_{Cu} causes p-type conductivity
- neutralization of B_{Cu} anti-site defects by the formation of neutral defect complexes ($B_{Cu}+2V_{Cu}$)[2]

Lattice parameter vs. Cu/B ratio



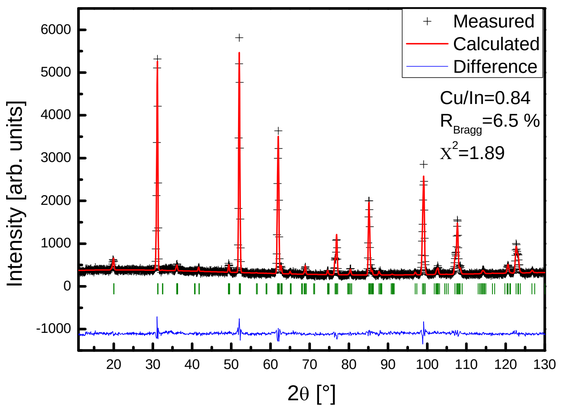
Decrease of ***a*** and ***c*** for $CuGaSe_2$ and almost no decrease for $CuInSe_2$, with increasing Cu-deficit!

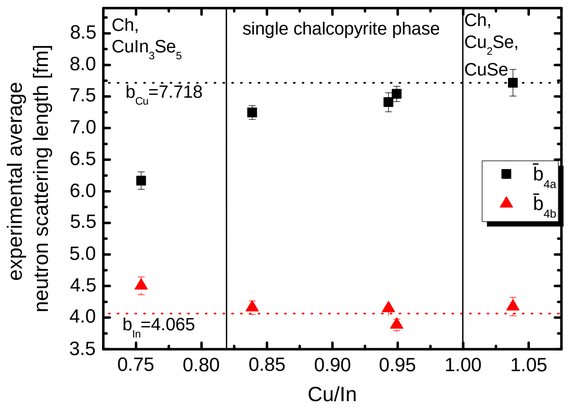
→ Hint for the presence of different point defects!

Strategy

- synthesis of powder samples with defined composition by solid state reaction of the pure elements in sealed and evacuated silcia tubes (T = 850°C)
- pre-characterisation by XRD and electron microprobe analysis, including wavelength dispersive X-ray (WDX) analysis on polished samples

Neutron Powder Diffraction





Rietveld refinement → average neutron scattering length[3]

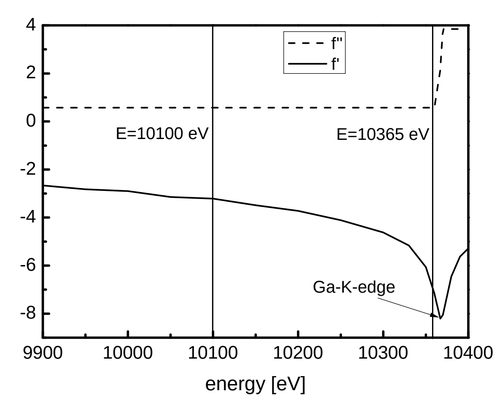
$\bar{b}^{exp}$ vs. $\bar{b}^{calc}$

- cation distribution
- anion position

$$\bar{b}_j^{calc} = SOF\,(Cu)_j \cdot b_{Cu} + SOF\,(In)_j \cdot b_{In} + SOF\,(V)_j \cdot b_V$$

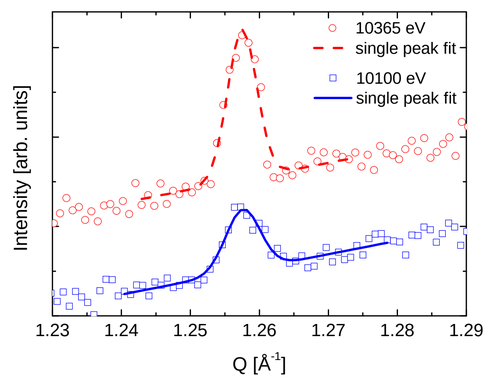
Anomalous X-ray diffraction

$$f_i(\omega) = f_{i0} + f_i'(\omega) + i \cdot f_i''(\omega)$$



E [eV]	Ga^{3+} *f'*	Ga^{3+} *f''*	Cu^{+} *f'*	Cu^{+} *f''*	Se^{2-} *f'*	Se^{2-} f''
10365	**-8.29**	0.491	**-0.91**	3.00	-1.40	0.73
10100	**-3.22**	0.515	**-1.17**	3.20	-1.34	0.76

- energy dependent and element specific
- experiment close to and far-off Ga-K absorption edge [E = 10367 eV]

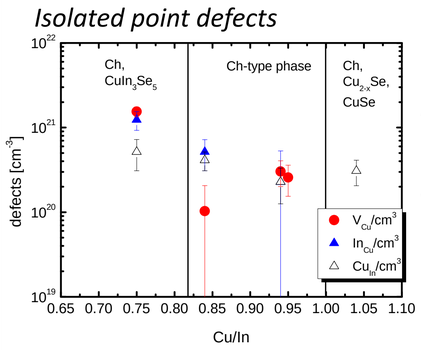


101 Bragg peak of $Cu_{0.897}Ga_{1.103}Se_{2.103}$ (Cu/Ga = 0.81) at two different photon energies

Cationic point defects in off stoichiometric $Cu(In, Ga)Se_2$

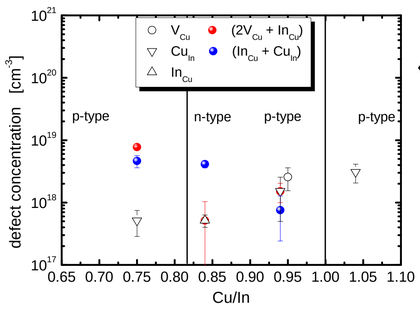
$CuInSe_2$

Isolated point defects



- large concentration of V_{Cu}, In_{Cu}, Cu_{In}
- point defect concentration increases with increasing Cu-deficit

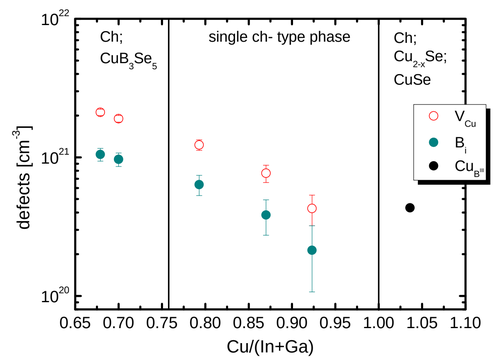
Assuming defect complexes



- clustering of point defects to electrical neutral defect complexes reduces concentration of isolated defects by an order of magnitude[4]

$Cu(In_xGa_{1-x})Se_2$

Isolated point defects

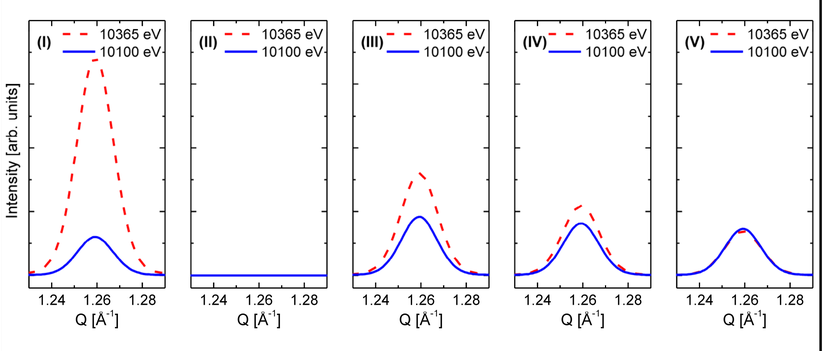


- study of defects by neutron powder diffraction
- modelling of present point defects by the method of average neutron scattering length
- large concentration of V_{Cu} and B_i
- point defect concentration increases with increasing Cu-deficit

The repression of B_{Cu} defect may supress the formation of the CuB_3Se_5 vacancy phase and explains the broader homogeneity region for Ga-substituted $CuInSe_2$!

$CuGaSe_2$

ordered	disordered	ordered	partially disordered
no V_{Cu} / no Ga_i	no V_{Cu} / no Ga_i	10% V_{Cu} / 10% Ga_i	10% V_{Cu} / 10% Ga_i



Modelling of cation distribution / present isolated point defects according to WDX analysis and neutron diffraction.

- ordered structure with V_{Cu} and Ga_i
- maximum amount of 4% site fraction Ga_{Cu}/Cu_{Ga} (10^{20} /cm^3)
- clustering of point defects to neutral defect complexes cannot be assumed

Summary

Compound	Defects
$CuInSe_2$	V_{Cu} In_{Cu} Cu_{In}
$CuGaSe_2$	V_{Cu} Ga_i
$Cu(In_xGa_{1-x})Se_2$	V_{Cu} B_i

- sucessful determination of cationic point defect concentration in off stoichiometric $CuInSe_2$, $CuGaSe_2$ and $Cu(In_xGa_{1-x})Se_2$
- repression of B_{Cu} defect in Cu-poor $CuGaSe_2$ and $Cu(In_xGa_{1-x})Se_2$ may supress the formation of the $CuGa_3Se_5$ vacancy phase and thus supports the chemical homogeneity of a $Cu(In_{1-x}Ga_x)Se_2$ absorber layer

References:
[1] C. Stephan, S. Schorr, H.W. Schock, New Structural Investigations in the Cu2Se(S)-In2Se(S)(3)/ Cu2Se(S)-Ga2Se(S)(3) Phase Diagram, Thin-Film Compound Semiconductor Voltaics-2009, 1165 (2010) 411-417.
[2] S.B. Zhang, S.H. Wei, A. Zunger, H. Katayama-Yoshida, Defect physics of the CuInSe2 chalcopyrite semiconductor, Phys Rev B, 57 (1998) 9642-9656.
[3] S. Schorr, C. Stephan, R. Mainz, T. Thörndahl, Advanced Characterization Techniques for Thin Film Solar Cells, in: D. Abou-Ras, U. Rau, T. Kirchhartz (Eds.), Wiley-VCH GmbH & Co. KGaA, 2011.
[4] C. Stephan, S. Schorr, M. Tovar, H.W. Schock, Comprehensive insights into point defect and defect cluster formation in CuInSe(2), Appl Phys Lett, 98 (2011).
[5] C. Stephan, S.Schorr, T. Scherb, C.A. Kaufmann, H.W. Schock, A structural perception of cationic point defects in CuGaSe2, Appl Phys Lett, submitted (2012).

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