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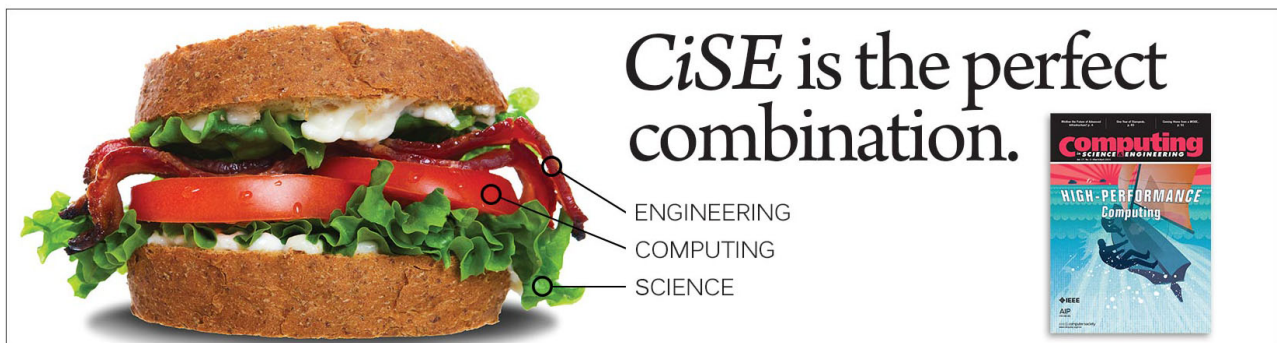Cationic point defects in CuGaSe2 from a structural perspective
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Comprehensive insights into point defect and defect cluster formation in CuInSe$_2$

Christiane Stephan,[1,a)] Susan Schorr,[2] Michael Tovar,[1] and Hans-Werner Schock[1]

[1]*Helmholtz-Zentrum Berlin fuer Materialien und Energie, Hahn-Meitner Platz 1, 14109 Berlin, Germany*
[2]*Faculty of Earth Science, Free University Berlin, Malteserstraße 74-100, 12249 Berlin, Germany*

The concentration of native point defects in CuInSe$_2$ powder material as a function of stoichiometry has been experimentally determined by neutron powder diffraction. A correlation between the Cu/In ratio and the density of V_{Cu} as well as In$_{Cu}$ has been established and their concentrations are quantified. It is demonstrated, that assuming the spontaneous formation of defect pairs, the density of native point defects is reduced significantly by an order of magnitude. The functionality of a solar device, assuming same conditions like in the analyzed material, may be explained by a neutralization due to the formation of electrically inactive defect complexes. © *2011 American Institute of Physics*. [doi:10.1063/1.3559621]

The electronic properties of a polycrystalline heterojunction thin film solar cell are strongly influenced by the presence of electrical active defects. Especially the native defects in the most important component of the device, the compound semiconductor CuInSe$_2$ (CISe) acting as absorber, are crucial. These defects, such as vacancies, interstitials and antisites, are resulting from deviations from the stoichiometric composition. To achieve a p-type CISe absorber an overall slightly copper-poor composition is necessary,[1] whereas the region close to the buffer/absorber interface should be of n-type character by exhibiting a very copper-poor composition.[2–4] High efficient devices are actually fabricated by a complex vacuum based multistage process using three separate elemental sources of Cu, In, and Se.[5,6] The carrier type and concentration is implemented by carefully controlling the Cu/In and Se/M (M=Cu+In) ratio adjusting the stoichiometry with respect to Cu. Native point defects and the carrier type in CISe are still under discussion. It is generally believed that Cu vacancies (V_{Cu}) cause p-type conductivity, whereas copper on interstitial positions (Cu$_i$) or In$_{Cu}$ antisites act as donors and promote a n-type character.[4] Numerous investigations of CISe thin films[7,8] and a few studies concerning the electronic defect levels in CISe single crystals[9,10] could not solve the problem of the structural origin of defects, producing these levels. To date, no quantitative study has been made on the variation of native point defects as a function of stoichiometry. Besides the need of a high carrier concentration a crucial prerequisite for a high conversion efficiency is the chalcopyrite type structure (space group $I\bar{4}2d$) of the absorber. With deviations from stoichiometry the chalcopyrite type structure still consists over a relatively wide compositional range in CISe.[11] However, structural parameters like the tetragonal distortion Δ ($\Delta = |1 - c/2a|$, a and c are the lattice constants) and the displacement of the anion from the ideal tetrahedral position, expressed by the parameter u with $u = |0.25 - x|$ (x is the anion position coordinate), are changing. An investigation of the lattice parameter in nonstoichiometric CuInSe$_2$ bulk

samples grown by the Bridgman method has been reported by Merino *et al.*[12] They assumed without experimental evidence the existence of copper on interstitial positions and the generation of copper vacancies with increasing copper deficiency.

In this letter, we report on experimental correlations between the stoichiometry of CISe polycrystalline bulk material and the concentration of native point defects, such as copper and indium vacancies, interstitials, and antisites.

Powder samples of Cu$_{1-y}$In$_y$Se$_{0.5+y}$ with various composition ($0.49 < y < 0.60$) have been prepared by solid state reaction of the pure elements. Details of the growth procedure are described by Stephan *et al.*[11] During the synthesis the selenium partial pressure was not controlled, therefore all detailed results presented here are valid just for the synthesis method used. Compositional investigations were carried out by electron microprobe analysis [wavelength dispersive x-ray (WDX) measurements using a JEOL-JXA 8200 system]. In order to obtain reliable results from the WDX measurements, the system was calibrated using elemental standards of Cu, In, and Se. By means of the decided fabrication and characterization of the polycrystalline bulk material a series of CISe powder reference samples with various well determined chemical compositions was produced. The composition and phase content of this sample series is summarized in Table I. Thus a systematic study of structural trends in CISe bulk material in dependence on the stoichiometry could be performed over a wide compositional range.

In order to determine the cation distribution in the crystal structure of the chalcopyrite type phase, which is the basis for the calculation of the point defect concentrations, the

TABLE I. Composition and phase content for the powder samples studied by neutron powder diffraction (Cu$_{1-y}$In$_y$Se$_{0.5+y}$, Ch-chalcopyrite type phase).

Sample	y	Cu/In	Phases
A	0.49(1)	1.04(1)	Ch, Cu-selenides
B	0.51(1)	0.95(1)	Ch
C	0.52(1)	0.94(1)	Ch
D	0.54(1)	0.84(1)	Ch
E	0.57(1)	0.75(1)	Ch, CuIn$_3$Se$_5$

a)Author to whom correspondence should be addressed. Electronic mail: christiane.stephan@helmholtz-berlin.de.
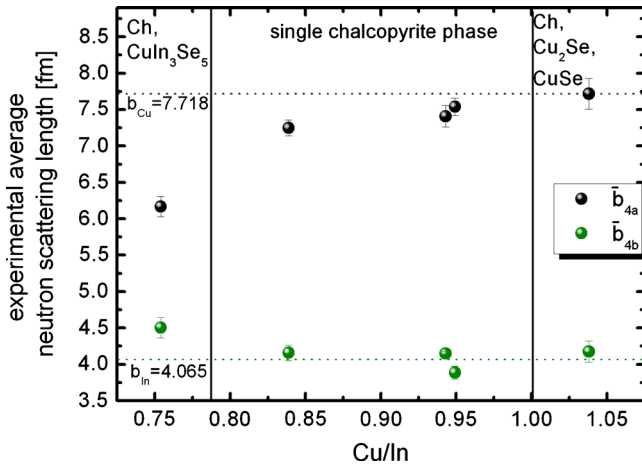
FIG. 1. (Color online) Experimentally observed average neutron scattering length of the cation sites 4a and 4b of the chalcopyrite type structure as a function of stoichiometry. The horizontal dotted lines show the neutron scattering length for Cu(b_{Cu}) and In(b_{In}) for comparison.

method of the average neutron scattering length has been adopted.[13] A detailed introduction to this method applied to $CuB^{III}X_2^{VI}$ absorber materials is explained elsewhere.[14] In the present study this powerful approach, which is based on neutron powder diffraction, is used to determine defect concentrations with structural origin in nonstoichiometric CISe. The approach is based on the fact, that vacancies (V_{Cu} and V_{In}) as well as antisite defects (In_{Cu} and Cu_{In}) will change the neutron scattering length of the cation sites 4a (copper site) and 4b (indium site) in the chalcopyrite type structure significantly, because the neutron scattering lengths of copper and indium are different [$b_{Cu}=7.718(4) fm$, $b_{In}=4.065(2) fm$ (Ref. 15)]. Thus the distribution of copper and indium on the both cation sites of the chalcopyrite type structure can be revealed on the basis of the cation site occupancy values determined by Rietveld analysis of the neutron diffraction data. Neutron powder diffraction data were collected at the Berlin Research Reactor BERII using the fine resolution powder diffractometer E9 ($\lambda=1.79\,776$ Å). The data treatment was performed by full pattern Rietveld refinement[16] using the FULLPROF suite software package.[17] Free parameters of the structural refinement of the chalcopyrite type phase have been lattice constants (a and c), the anion x-coordinate, site occupation numbers for the copper (occ_{4a}) and indium (occ_{4b}) position as well as anisotropic atomic displacement parameters for all three structural sites. The R_{Bragg} values of the refinements are between 5 and 6. The cation site occupation numbers were used to determine the experimental average neutron scattering lengths $\bar{b}_j^{exp}$ (with $j=4a,4b$) of the cation sites 4a and 4b according to

$$\bar{b}_{4a}^{exp} = occ_{4a} \cdot b_{Cu} \quad \bar{b}_{4b}^{exp} = occ_{4b} \cdot b_{In}. \quad (1)$$

The experimental average neutron scattering length as a function of stoichiometry (see Fig. 1) shows a decrease of $\bar{b}_{4a}^{exp}$ and an increase of $\bar{b}_{4b}^{exp}$ with decreasing Cu/In ratio. The latter can only be caused by the formation of Cu_{In} antisite defects (because $b_{Cu} > b_{In}$). To realize a decrease of the $\bar{b}_{4a}^{exp}$ values, the structural site 4a has to be occupied by copper, indium (In_{Cu}) and/or copper vacancies (V_{Cu}). Only the copper-rich sample (A) with Cu/In>1 shows no indication for an In_{Cu} antisite defect, because there is no decrease of the

$\bar{b}_{4a}^{exp}$ value. Thus the structural site 4a seems to be fully occupied by copper. On the other hand a slight increase in the $\bar{b}_{4b}^{exp}$ value can be observed.

For the quantitative evaluation of the cation distribution from $\bar{b}_j^{exp}$ of the cation sites 4a and 4b, the following procedure was developed. Assuming copper and indium as well as vacancies would occupy the same structural site j, the average neutron scattering length of the site ($\bar{b}_j$) is given by Eq. (2)

$$\bar{b}_j = N_{Cu_j} \cdot b_{Cu} + N_{In_j} \cdot b_{In} + V_j. \quad (2)$$

Here N_{Cu_j} and N_{In_j} are the fractional amounts of copper and indium on the corresponding site, b_{Cu} and b_{In} are the neutron scattering lengths of copper and indium and V_j is the fraction of vacancies on the site.

The fractional amounts of copper and indium on the both cation sites 4a and 4b have to be in agreement with the chemical composition of the chalcopyrite phase. On the basis of Eq. (2) and the additional requirement $N_{Cu_j}+N_{In_j}+V_j=1$, as well as assuming a certain cation distribution, a theoretical average neutron scattering length ($\bar{b}_j^{calc}$) can be calculated. In the beginning a simple distribution model without cation vacancies was applied, just assuming In_{Cu} antisite defects for copper-poor samples (B-E). The comparison between experimental and theoretical average neutron scattering lengths showed discrepancies like $\bar{b}_{4a}^{exp}<\bar{b}_{4a}^{calc}$ and $\bar{b}_{4b}^{exp}>\bar{b}_{4b}^{calc}$. In the next step the cation distribution model was modified by introducing copper vacancies and Cu_{In} antisite defects to achieve the $\bar{b}_{4a}^{exp}$ and $\bar{b}_{4b}^{exp}$ values, respectively. Thereby the total amount of copper in the chalcopyrite phase, was distributed on the two cation sites 4a and 4b, thus the occupation of interstitial positions by copper (Cu_i) could be excluded. For the copper-rich sample A it can be concluded, that a Cu_{In} antisite defect, which would act as a donor, with a maximal site fraction of $(3\pm2)\%$ on the 4b site has to be the reason for the increase in the $\bar{b}_{4b}^{exp}$ value. This means the chalcopyrite type crystal structure tolerates an additional copper incorporation for copper-rich CISe of up to 3% into the cation substructure.

Finally the defect concentrations per cubic centimeter can be calculated using the extracted fractional amounts of V_{Cu}, Cu_{In}, and In_{Cu} antisite defects. The unit cell volume was determined by the obtained lattice constants. The concentration of intrinsic point defects as a function of stoichiometry in polycrystalline CISe bulk samples is summarized in Fig. 2, where the development of the different kinds of intrinsic point defects in dependence on the Cu/In ratio is shown. The observed trend of an increasing amount of copper vacancies with increasing copper deficiency corresponds to the defect formation energies calculated by Zhang *et al.*[18] Due to the negative defect formation energy (-1.9 eV) of V_{Cu} in copper-poor CISe it is traceable to observe high concentrations of copper vacancies in copper-poor samples. Cu_{In} and In_{Cu} antisite defects are present for Cu/In<0.95 and increase with decreasing Cu/In ratio but with a different slope. The increment of native defects in CISe with decreasing Cu/In ratio gives rise to the formation of the ordered vacancy compound (OVC) $CuIn_3Se_5$. The latter appears as secondary phase besides the chalcopyrite type phase in the very copper-poor sample E. The growth of the OVC phase can be re-
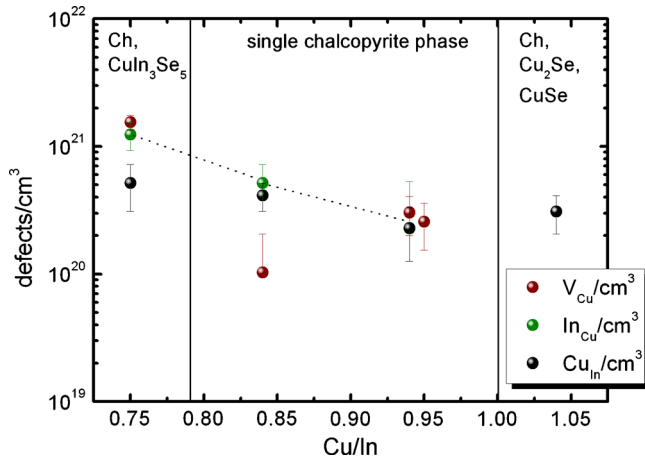
FIG. 2. (Color online) Concentration of different kinds of intrinsic point defects as a function of nonstoichiometry. The values always refer to the chalcopyrite phase in the samples. The dotted line indexes the increase of the In_{Cu} antisite defect and is just a guide to the eye. The solid lines mark the region where different phases occur.

TABLE II. Estimated defect pair density and residual concentration of native point defects in the chalcopyrite type phase (normalized to the total defect concentration).

Cu/In	0.75	0.84	0.94	0.95	1.05
Defect pairs	96%	90%	60%	0	0
Native defects	4 % Cu_{In}	10% In_{Cu}	40% Cu_{In}	100 % V_{Cu}	100% Cu_{In}
Type	p-type	n-type	p-type	p-type	p-type

terial can be experimentally determined by neutron powder diffraction. Assuming the formation of defect pairs, it is possible to deduce a change in the carrier type character from p-type to n-type if the material is very copper-poor, whereas the chalcopyrite type phase, coexisting with the OVC, is p-type again. Assuming a similar scenario for CISe thin films, it is possible to realize that non-stoichiometric CISe is well performing as absorber material in thin film solar cells despite a high concentration of native defects.

garded as an accumulation of copper vacancies, leading to the generation of very small $CuIn_3Se_5$ exsolutions like domains within the chalcopyrite type phase, resulting in more complex electronic properties.

The depicted experimental correlation between stoichiometry of CISe polycrystalline bulk material and the concentration of native point defects can be used to get an impression of the situation in nonstoichiometric CISe thin films. The calculated defect concentrations are relatively high and increase with increasing copper deficiency. On the other hand, high efficient devices exhibit a copper-poor composition of the CISe absorber layer, especially the very copper deficient CISe surface.[3] The formation of defect arrays as proposed by Zhang *et al.*[18,19] can be considered to explain the functionality of CISe absorbers with Cu/In < 1. They showed by *ab initio* calculations, that the defect pairs $(2V_{Cu}^- + In_{Cu}^{2+})$ and $(Cu_{In}^{2-} + In_{Cu}^{2+})$ in CISe have very low formation energies, moreover these defect pairs are predicted to be electrically inactive. Therefore the calculated defect concentrations were used to estimate the defect pair density and the resulting carrier type (Table II). It can be shown, that assuming the spontaneous formation of defect pairs, the density of native defects is reduced significantly by an order of magnitude. Thus the surprising electrical tolerance of CISe to its huge concentrations of native defects could be explained.

In conclusion, we have shown that the concentration of native cation point defects in polycrystalline CISe bulk ma-

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