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# Crystal structure and point defect characteristics of quaternary compound semiconductors by neutron diffraction.

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Quaternary semiconductors Cu2BIICIVX4(BII–Zn,Cd,Hg;CIV–Si,Ge,Sn;X–S,Se,Te) are considered as interesting material for applications in optoelectrics and non-linear optics. Cu2ZnSn(S1-xSex)4 mixed crystals (CZTSSe) are promising semiconductor materials for absorber layer in thin film solar cells due to a direct band gap in the range 1-1.5 eV and a high absorption coefficient (>104cm-1). A record efficiency of 12.6% was reported for a CZTSSe based thin film solar cell, here the polycrystalline absorber layer exhibit an off-stoichiometric composition. The non-stoichiometry can be attributed to the presence of various point defects (such as vacancies, interstitials, antisites, etc.). These defects influence the generation, separation, and recombination of electron-hole pairs and overall, the efficiency of the photovoltaic device.

All of the compounds from the CZTSSe solid solution contain the isoelectronic cations Cu+ and Zn2+, which makes the accurate structure determination using X-ray diffraction not possible, due to their similar scattering factors. Neutrons diffraction can solve this problem; the coherent scattering lengths are sufficiently different for these cations. Using neutron diffraction it was shown that both of the stoichiometric end members of this solid solution, crystallize in the kesterite type structure (space group $I\bar{4}$). Moreover we have demonstrated that kesterite type materials can self-adapt to Cu-poor and Cu-rich compositions without any structural change except the cation distribution.
A detailed structural analysis of stoichiometric CZTSSe as well as off-stoichiometric CZTS and CZTSe powder samples, grown by solid state reaction, was performed by neutron diffraction, the data were collected at the Berlin Research Reactor BER II at the Helmholtz-Zentrum Berlin für Materialien und Energie using the fine resolution powder diffractometer FIREPOD (E9) (λ = 1.7982 Å;RT). Rietveld refinement of neutron diffraction data using the FullProf suite software lead to accurate values of lattice constants and site occupancy factors. Applying the average neutron scattering length analysis method, the cation distribution was evaluated. Taking into account the necessity to keep the charge balance, point defect types and their concentrations have been elaborated from the cation distribution. We have shown that the evaluated off-stoichiometry and the concentration of intrinsic point defects correlate with the variation in chemical composition in CZTS/Se from Cu-poor to Cu-rich related stoichiometry deviations. Thus we have revealed the possibility to deduce occurring point defects from the chemical composition of the kesterite phase.
The correlated information about changes in lattice parameters and cation site occupancies in dependence on the off-stoichiometry in CZTS and CZTSe and on the Se content in stoichiometric CZTSSe and details on the existing intrinsic point defects and their concentrations will be discussed.

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