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Existence of off-stoichiometric single phase kesterite

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In this work the flexibility of the kesterite structure is discussed. It is shown that kesterite type CZTS and CZTSe can deviate from stoichiometric composition by the formation of intrinsic point defects leading to different off-stoichiometric kesterite types. For this study off-stoichiometric CZTS and CZTSe powder samples have been synthesized by solid state reaction from pure elements. Their chemical composition was determined by WDX spectroscopy and the structural characterization was conducted by X-ray diffraction. Amongst the studied 49 samples, a number of them have been identified to contain only an off-stoichiometric kesterite type phase which exhibit Cu-poor/Zn-rich composition. On the other hand, Cu-rich/Zn-poor kesterite type CZTS and CZTSe always coexists with secondary phases. Thus it has been demonstrated, that the kesterite type structure can self-adapt to Cu-poor and Cu-rich compositions in CZTS and CZTSe without any structural change except the cation distribution.

1. Introduction

In the last years quaternary chalcogenides have gained a lot of attention; especially the kesterite type semiconductor compounds $Cu_2ZnSn(S,Se)_4$ which consist mostly of earth abundant and non-toxic elements. These compounds are a promising low cost alternative absorber material for thin film solar cells due to its suitable criteria for photovoltaic applications: *p*-type semiconductor behavior, direct band-gap between 1.0 and 1.5 eV and absorption coefficient $>10^4$ cm^{-1} [4,5].

The best performance of kesterite-based thin film solar cells with conversion efficiency of 12.6% [6] were obtained with a material quite different from the stoichiometric compound (stoichiometric CZTS/Se), especially with a Cu-poor/Zn-rich composition. Because the electronic properties of a semiconductor are highly related to its crystal structure, it is of strong interest to study the nature of stoichiometry deviations and to connect issues such as phase existence limits.

Kesterite belongs to the $A^{I}_{2}B^{II}C^{IV}X^{IV}_{4}$ compound family and crystallizes in a tetragonal structure type. As was described in literature [1], the kesterite type structure (Fig. 1) is characterized by alternating layers of Cu–Sn, Cu–Zn, Cu–Sn and Cu–Zn at z = 0, ¼, ½ and ¾ respectively. Thus one copper occupies the 2a (0, 0, 0) position with zinc and the remaining copper orders at 2c (0, ½, ¼) and 2d (0, ½, ¾) resulting in the space group $I\bar{4}$.

One reason for the success of chalcopyrite (CIGSe)-based thin film solar cells is related to the high flexibility of its chalcopyrite type crystal structure. This flexibility is an essential key point for multinary compounds, because the growth process of thin films is a non-equilibrium process that goes along with slight local inhomogeneities in composition to be balanced by the structure type.

A study on the flexibility of the kesterite structure and its ability to deviate from stoichiometry was introduced by A. Lafond [2,7]. Taking into account the charge balance, four cation substitution reactions and related intrinsic point defect complex formations were proposed. This led to four off-stoichiometry types: A-type Cu-poor/Zn-rich where copper is substituted forming a copper vacancy (V_{Cu}) and zinc on copper antisite (Zn_{Cu}), B-type Cu-poor/Zn-rich where copper and tin are substituted by zinc forming zinc on copper (Zn_{Cu}) and zinc on tin (Zn_{Sn}), C-type Cu-rich/Zn-poor which zinc substitutions form copper on zinc (Cu_{Zn}) and tin on zinc (Sn_{Zn}) defects and D-type Cu-rich/Zn-poor where copper substitute zinc forming copper on zinc antisite (Cu_{Zn}) and additional copper interstitial (Cu_i). All those cation substitutions are illustrated in Fig. 2 and summarized in Table 1.

This work focusses on the flexibility [2,7–10] of the kesterite type structure aiming in synthesizing off-stoichiometric CZTS/Se according to the off-stoichiometry types. Furthermore the

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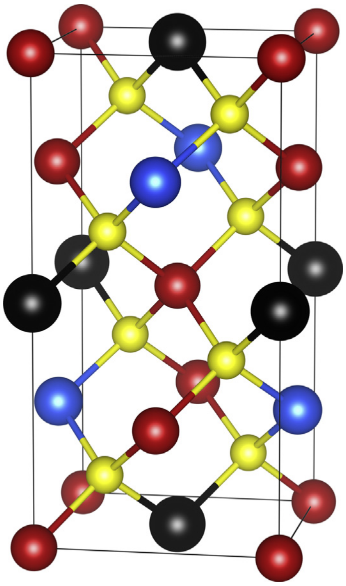

Fig. 1. Kesterite type structure (space group $I\bar{4}$) [1] with copper in red, zinc in blue, tin in black and the yellow spheres represent the anions S/Se. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

possibility of obtaining single phase off-stoichiometric kesterite type CZTS/Se should be proven.

2. Experimental

This work focusses on the investigation of kesterites according to the A-, B-, C- and D-type. Off-stoichiometric CZTS and CZTSe powder samples were synthesized by solid state reaction. The intended chemical composition was calculated using the formulae corresponding to different cation substitutions (see Table 1). The synthesis starts from the pure elements Cu, Zn, S and Se (99.999%) and Sn (99.9999%) which were placed in pyrolytic graphite boats. For the CZTS samples a 10% excess of sulfur and, for CZTSe samples 2% excess selenium was added to the calculated amount in order to assure the reaction of all cations. The boats were loaded into silica tubes which were subsequently evacuated to 10^{-5} mbar vacuum and sealed with H_2/O_2 flame. Afterwards the sealed tubes were placed in a one-zone furnace and annealed according to an optimized temperature program (see Table 2).

The first reaction step was crucial for a successful synthesis. To avoid explosion of the tubes, several intermediate temperature steps were introduced. In the second reaction step the samples were heated up to the final temperature of 750 °C. During the synthesis of Cu-poor/Zn-rich CZTS samples lots of sulfur was found at the ampoules glass after the sample was cooled down. In contrast to the Cu-poor/Zn-rich CZTS samples, almost no sulfur was observed at the ampoules glass of the Cu-rich/Zn-poor samples. This means all excess sulfur reacted with the synthesized material. Furthermore some loss of Sn was observed by WDX spectroscopy for some Cu-poor/Zn-rich CZTS samples during the synthesis. The CZTSe samples were cooled down to room temperature by switching off the furnace. The furnace cooling profile displayed a decreased of temperature from 750 °C to 400 °C in 4 h. After this point the cooling rate decreased slower and the samples reached room temperature after approximately 24 h. In between the reaction steps the synthesized material was ground in an agate mortar and pressed into pellets, which were placed into an evacuated silica tube for the next annealing step.

In total 20 CZTS and 29 CZTSe samples have been successfully synthesized.

To determine the phase content and chemical composition of the synthesized polycrystalline powder samples, an electron microprobe system (JEOL-JXA 8200) equipped with a wavelength dispersive X-ray spectroscopy unit (WDX) was used. In order to calibrate the measurement, elemental standards for Cu, Zn, Sn, Se and the mineral chalcopyrite as standard for S have been used. In Fig. 3, backscattered electron micrographs of 4 samples, for all sample 30–60 grains were measured, and on each grain 10–15 measurement points were averaged, to obtain reliable values. Grains which were identified to belong to the same phase (same

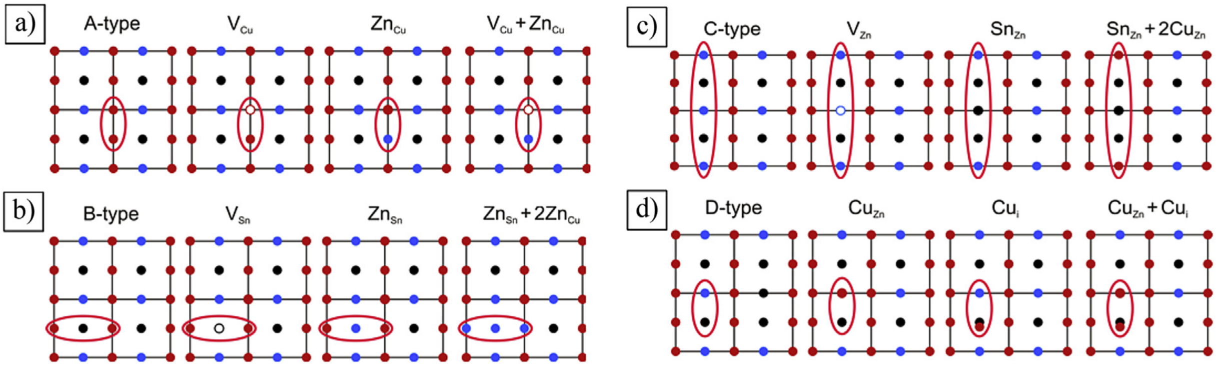

Fig. 2. Cation substitution process resulting in A-, B-, C- and D-type [2] off-stoichiometric CZTS/Se. The circles represent: copper in red, zinc in blue and tin in black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Overview of cation substitution reactions and off-stoichiometry types with related intrinsic point defects and the corresponding chemical formulae.

Type	Composition	Cation substitution reaction	Intrinsic point defects	Formulae
A	Cu-poor/Zn-rich/Sn-const.	$2Cu^{+} \rightarrow Zn^{2+}$	$V_{Cu} + Zn^{2+}{}_{Cu}$	$Cu_{2-2x}Zn_{1+x}SnS/Se_4$
B	Cu-poor/Zn-rich/Sn-poor	$2Cu^{+} + Sn^{4+} \rightarrow 3Zn^{2+}$	$2Zn^{2+}{}_{Cu} + Zn^{2+}{}_{Sn}$	$Cu_{2-2y}Zn_{1+3y}Sn_{1-y}S/Se_4$
C	Cu-rich/Zn-poor/Sn-rich	$3Zn^{2+} \rightarrow 2\ Cu^{+} + Sn^{4+}$	$2Cu^{+}{}_{Zn} + Sn^{4+}{}_{Zn}$	$Cu_{2+2z}Zn_{1-3z}Sn_{1+z}S/Se_4$
D	Cu-rich/Zn-poor/Sn-const.	$Zn^{2+} \rightarrow 2Cu^{+}$	$Cu^{+}{}_{Zn} + Cu^{+}{}_{i}$	$Cu_{2+2m}Zn_{1-m}SnS/Se_4$