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A mechanochemical route to single phase Cu_2ZnSnS_4 powder

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ABSTRACT

With respect to absorber materials in solar cells, Cu_2ZnSnS_4 (CZTS) has been a focus of interest in recent years. In this work, a new route leading to single phase CZTS powders is presented. For structural characterization X-ray and neutron powder diffraction measurements were performed. Further structural and compositional analysis of the CZTS powder was carried out by means of X-ray absorption near edge spectroscopy (XANES) and wavelength-dispersive X-ray spectroscopy (WDS). The obtained CZTS powder with an actual composition of $Cu_{2.00(4)}Zn_{1.02(2)}Sn_{0.99(2)}S_{4.00(8)}$ adopts the kesterite-type structure. A detailed cation distribution analysis using the average neutron scattering length method revealed a partial disorder of copper and zinc on the (2c) and (2d) sites.

1. Introduction

The quaternary chalcogenide Cu_2ZnSnS_4 recently gained attraction as a prospective absorber material for thin film photovoltaic applications. As it consists merely of earth-abundant, non-toxic and low-cost elements, it would be a suitable alternative to other chalcogenide-based absorber materials such as CdTe or CIGS ($CuIn_xGa_{(1-x)}Se_2$) that are currently used in thin films. It is a direct band gap p-type semiconductor with an optical band gap energy value of 1.5 eV and has a large absorption coefficient in the order of 10^{-4} cm^{-1} [1–3]. Up to now record efficiencies of CZTS-based thin films reached values up to 8.4 % [4]. Yet, compared to the currently used chalcopyrite materials, efficiencies are significantly lower.

In order to enhance the quality and the efficiency of CZTS thin film photovoltaics it is necessary to gain a deeper insight into the absorber material. Systematic analysis of the semiconductor compound and its structural, chemical, and physical properties has been in the focus of interest in the last few years [5–10]. Due to the formation of secondary phases it is challenging to prepare phase-pure CZTS powder, which is important for detailed experiments concerning the correlations between structural and electronic properties. Consequently, the main motivation of the here-presented research is the development of a new chemical route for the synthesis of phase-pure stoichiometric kesterite powder and its structural characterization.

CZTS is a quaternary semiconductor belonging to the I_2-II-IV-VI_4 compound family. It adopts a tetragonal structure that can be derived from the zinc blende type by doubling the c-axis of the cubic sphalerite unit cell and by substituting the cations. A substitution scheme from binary ZnS to ternary Cu_2ZnSnS_4 is shown in Fig. 1.

The correct crystal structure of CZTS has been a controversial issue. Two main structure types are described for quaternary $A^I_2B^{II}C^{IV}X^{VI}_4$ compounds, stannite (see Fig. 2a) and kesterite (see Fig. 2b) [11]. In these types the sulfur atoms form a ccp array where half of the tetrahedral voids are occupied by the cation species. The structures are closely connected but differ in the distribution of Cu^+, Zn^{2+}, and Sn^{4+}.

First reports on the crystal structure of natural specimen suggested the kesterite-type structure, space group $I\bar{4}$ (No. 82) [11], with a complete ordering of Cu^+ and Zn^{2+}. Cu fully occupies the Wyckoff position 2a (0, 0, 0) whereas remaining Cu and Zn occupy the positions 2c (0, 1/2, 1/4) and 2d (0, 1/2, 3/4), respectively. Thus,

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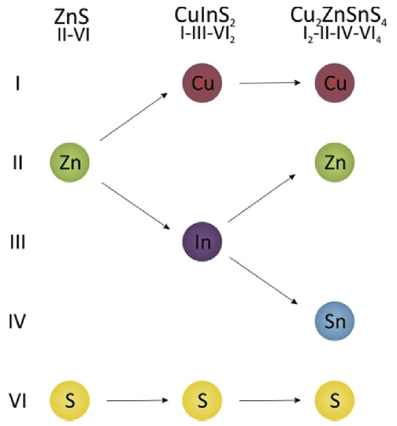

Fig. 1. Cross-substitution steps from binary II-VI compound (ZnS) via ternary I-II-VI_2 ($CuInS_2$) to quaternary I_2-II-IV-VI_4 (Cu_2ZnSnS_4).

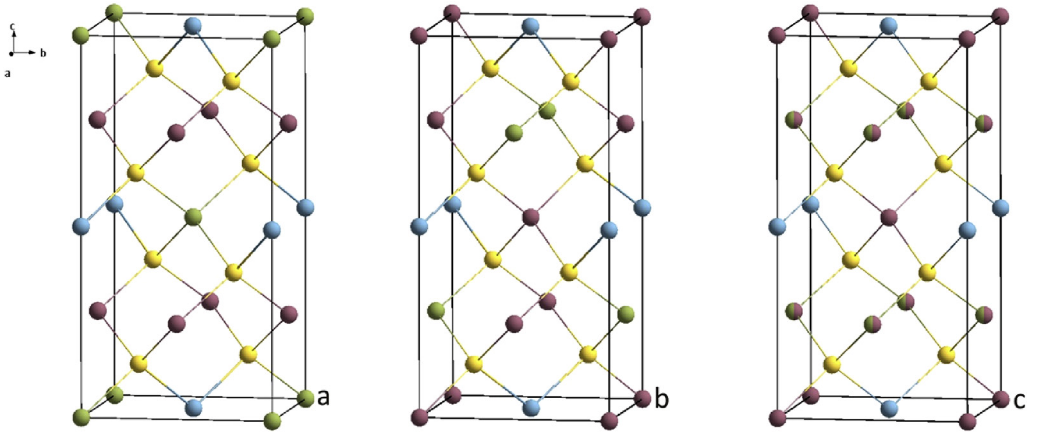

Fig. 2. Unit cells of the (a) stannite, (b) kesterite, and (c) disordered kesterite structure; Cu(red) Zn(green) Sn(blue) S(yellow) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

the structure can be described by stacking cation layers Cu/Sn Cu/Zn Sn/Cu Cu/Zn Cu/Sn along the c-axis. Recently several groups could confirm that Cu_2ZnSnS_4 adopts the kesterite-type structure [5,12,13].

Using conventional X-ray diffraction methods, Cu^+ and Zn^{2+} are not distinguishable due to their isoelectronic characteristic. As there is a significant difference in the neutron scattering length ($b_{Cu} = 7.718(4)$ fm, $b_{Zn} = 5.680(5)$ fm), neutron diffraction is the method of choice. Neutron diffraction studies of Cu_2ZnSnS_4 powder samples confirm the kesterite-type structure, yet report a partial [14] or complete disorder [5] of Cu and Zn on the 2c and 2d positions. Kesterite-type phases exhibiting a statistical distribution of Cu/Zn can be described in space group $I\bar{4}2m$ (No. 121) with Zn and Cu occupying the 4d Wyckoff position (1/2, 0, 1/4) which is called disordered kesterite [15] (see Fig. 2c).

It was also suggested by *ab initio* calculations [16,17] that point defects Cu_{Zn} and Zn_{Cu} have very low formation energies, which underlines the possibility for Cu/Zn disorder. Recent studies on CZTS thin films determined the critical temperature for the transition from ordered to disordered kesterite to be at 260 ± 10 °C [18], which is also visible by a kink in the temperature dependent lattice parameter variation [6].

As four elements are present in the material, the formation of secondary phases such as CuS, Cu_2S, ZnS, SnS, SnS_2 and Cu_2SnS_3 seems probable. According to theoretical and experimental work [1,19] the homogeneity region of the CZTS phase in the ternary phase diagram is rather small. Due to its small enthalpy of formation ZnS is likely to form and has been found to have a detrimental influence on solar cell performance [7,8,20]. Identification and quantification of the secondary phases ZnS and Cu_2SnS_3 by X-ray and neutron diffraction is difficult because of diffraction pattern overlap. As reported in Ref. [7] it is possible to identify the most important secondary phases with X-ray absorption spectroscopy (XAS).

In this study we investigate chemical composition and structural properties of a stoichiometric CZTS powder synthesized by a newly developed mechanochemical process. Phase purity and composition was determined by WDS and XANES. X-ray and neutron diffraction measurements were used to identify the crystal structure with a closer look to the cation distribution of the powder sample. Two refinement strategies will be discussed.

2. Experimental

2.1. Synthesis

The quaternary sulfide with the general formula Cu_2ZnSnS_4 was prepared by mechanical milling in a Fritsch Planetary Mono Mill PULVERISETTE 6 starting from the corresponding binary sulfides CuS, ZnS, and SnS followed by an annealing step.

Starting chemicals were prepared either by precipitation (CuS), sulfidation of the oxide (ZnS) or solid state reaction of the elements (SnS). Copper monosulfide (CuS) was precipitated from a 0.1 M $Cu(NO_3)_2$-solution (Merck, 99.5 %) with H_2S (Air Liquide, 99.5 %) and annealed at 230 °C in H_2S atmosphere for 2 h in a tube furnace. For the preparation of zinc sulfide (ZnS) reaction of the oxide ZnO (Merck, 99.5 %) in a tube furnace with H_2S-gas at 650 °C for 3 h was performed. Tin monosulfide (SnS) was synthesized by a solid state reaction of the elements Sn (Merck, 99.9 %) and S (Fluka, 99.99 %) in an evacuated and sealed silica ampoule in a muffle furnace. Stoichiometric amounts of tin and sulfur were loaded in a silica ampoule. Due to the significant vapor pressure of sulfur the sealed and evacuated tube was first heated to 300 °C to avoid explosion. The temperature was increased to 800 °C with a rate of 15 °C/h and the sample was annealed for 30 h. According to [21] the compound was sublimed three times in the ampoule (750 °C → 550 °C) to ensure complete reaction. Identification of the binary compounds