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Off-stoichiometric CZTS: Neutron scattering investigations on mechanochemically synthesized powders

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ABSTRACT

In this work a series of B- and C-type off-stoichiometric CZTS samples was prepared by a mechanochemical synthesis route. For structural characterization X-ray diffraction measurements were performed. Furthermore, compositional analyses of the powder samples were carried out by means of wavelength-dispersive X-ray spectroscopy (WDS). For detailed cation distribution analyses of two off-stoichiometric single-phase samples neutron diffraction methods were used. The method of the average neutron scattering length was applied revealing the occurrence of Zn_{Cu}, Cu_{Zn}, and Zn_{Sn} point defects in the Cu-poor/Zn-rich sample (B-type, $Cu_{1.95}Zn_{1.09}Sn_{0.96}S_{4.00}$), whereas for the Cu-rich/Zn-poor sample (C-type, $Cu_{2.04}Zn_{0.95}Sn_{1.01}S_{4.00}$) Zn_{Cu}, Cu_{Zn}, and Sn_{Zn} defects are suggested.

1. Introduction

The quaternary p-type semiconductor compound Cu_2ZnSnS_4 has been examined intensively as an alternative absorber material for thin film solar cells in recent years. It is considered as a suitable candidate for photovoltaic applications due to its high absorption coefficient ($>10^{-4}$ cm^{-1}), a desirable direct optical bandgap (1.5 eV) as well as the sufficient abundance and the non-toxicity of the raw materials [1–3].

The crystal structure of Cu_2ZnSnS_4 has long been a controversial topic. Different studies proved that the quaternary sulfide adopts the kesterite structure type (space group $I\bar{4}$) [4,5]. In this sphalerite-derived crystal structure four cation positons are available. Sn is located on Wyckoff position 2b (0, 0, 1/2) and Cu on position 2a (0, 0, 0), occupying the lattice planes at z = 0 and 1/2, respectively. The lattice planes at z = 1/4 and 3/4 are filled with Zn (site 2d (0, 1/2, 3/4)) and the remaining Cu (site 2c (0, 1/2, 1/4)). Additionally, partial or complete disorder of Cu and Zn on Wyckoff positions 2c and 2d are reported [6–8]. As shown by theoretical calculations [9,10], the defect cluster [Zn_{Cu} + Cu_{Zn}] has the lowest formation energy compared to other defect complexes in the CZTS system, which underlines the possibility of copper/zinc disorder in the sample.

Until now, record efficiencies of thin film solar cells based on CZTS have reached 8.4% [11] and for devices with additional selenium even 12.6% were achieved [12]. In both cases, these photovoltaic performances were not obtained using stoichiometric compounds; the applied materials rather exhibit Cu-poor/Zn-rich compositions. Consequently, it is of strong interest to study and elucidate the relation between composition, crystal structural, and electronic properties of the material.

In recent studies it was shown that also compositions beside the ideal Cu_2ZnSnS_4 stoichiometry can exhibit the kesterite-type structure. This structural flexibility was first investigated by Lafond et al. [13,14], who introduced 4 off-stoichiometry types of kesterite, which can be characterized by different cation substitution reactions and the formation of related point defect clusters in order to maintain the charge balance in the structure. In CZTS literature the substitution types are mainly related to the cation ratios Cu/(Zn + Sn) and Zn/Sn resulting in a cation ratio plot as depicted in Fig. 1 (right). It can be seen that the plot is divided into four regions: Cu-poor/Zn-rich, Cu-poor/Zn-poor, Cu-rich/Zn-rich, Cu-rich/Zn-poor. These regions can be associated with the

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different off-stoichiometric types. In the so-called A-type (Cu-poor, Zn-rich region) defect complexes with zinc on copper antisites and copper vacancies ($[Zn_{Cu} + V_{Cu}]$) are present. Another Cu-poor/Zn-rich type can be attained by the substitution of copper and tin forming copper (Zn_{Cu}) and tin (Zn_{Sn}) point defects (B-type). The C-type point defects can be seen as the opposite of the B-type ones, forming copper on zinc antisites by substitution with copper (Cu_{Zn}) and tin (Sn_{Zn}). The reverse of the A-type is the D-type (Cu-rich/Zn-poor region) where zinc is replaced by copper forming copper on zinc antisites (Cu_{Zn}) and copper interstitials (Cu_i). While A-, B- and C-type off-stoichiometric CZTS samples were also observed experimentally by Lafond et al. [13], D-type was introduced only according to charge balance considerations. To our knowledge, no single phase D-type sample could be prepared yet. Valle-Rios et al. [15] prepared C-D- and D-F-type mixtures with kesterite as major phase but with additional secondary phases.

Recently, investigations on the ability of CZTS(Se) to deviate from the stoichiometry were performed on kesterite powder samples by Valle-Rios et al. [15] introducing a new off-stoichiometry type, the so-called F-type. To form this special type of off-stoichiometric kesterite, tin is replaced in the structure forming a Cu-rich/Zn-rich composition. Two defect complexes are possible, the formation of zinc on tin positions with additional copper interstitials ($[Zn_{Sn} + 2Cu_i]$) or copper on tin sites and two interstitials ($[Cu_{Sn} + Cu_i + Zn_i]$).

The opposite of this type of cation substitution would be the E-type which first appeared in Ref. [16]. In this Cu-poor/Zn-poor type copper and zinc are substituted forming either tin on zinc antisites (Sn_{Zn}) and copper vacancies (V_{Cu}) or tin on copper antisites (Sn_{Cu}) as well as copper and zinc vacancies ($V_{Cu} + V_{Zn}$). According to our research, no information about single phase E- or F-type CZTS can be found in literature, except B-F-type mixture samples [15] up to 76% F-type fraction. Due to the high formation energies of interstitial Zn and Cu compared to other point defects in the CZTS system [9,10], it seems to be rather unlikely that single phase F-type samples are formed.

The formation energies of the defect complexes [2 $Cu_{Zn} + Sn_{Zn}$] and $[Zn_{Cu} + V_{Cu}]$ have rather low values, with 0.2–0.6 and 0.4 eV, respectively [9,10]. This may be an indication that single-phase A- and C-type samples are generally more easily formed. In Table 1 all off-stoichiometry types are summarized.

CZTS powder has been usually synthesized via a solid state reaction process at 750 °C in evacuated silica ampoules [8,15]. Using this procedure it is not so easy to control the final composition of the sample. For example: in Ref. [15] only a few sample compositions can be correlated to solely one off-stoichiometry type, most of the synthesized samples show a mixture of two different types. However, for a comprehensive clarification of the cation order in each off-stoichiometry type the synthesis of single-type powders is important. As it is seen in our recent studies, it is nicely possible to control the composition of the synthesized CZTS powder with the developed mechanochemical process [7,17]. In this contribution the new process was used to synthesize off-stoichiometric CZTS samples (B- and C-type). The limits of single-phase samples for the B- and C-type were investigated. Furthermore, a detailed study on the cation ordering in selected off-stoichiometric samples was performed. As Cu and Zn are not distinguishable with X-rays, neutron powder diffraction measurements were performed.

2. Experimental

14 CZTS powder samples of the B- and C-type were prepared according to our recently developed two-step mechanochemical process [17]. The synthesis starts from the corresponding binary sulfides (CuS, ZnS, SnS) which were filled in an 80 ml agate jar (including 5 grinding balls, Ø 20 mm) and milled in a Fritsch Planetary Mono Mill PULVERISETTE 6 for 5 h with a rotational speed of 350 rpm. In a second step each sample was annealed in a conventional tube furnace (SiO_2-tube, Ø 70 mm) under flowing H_2S-gas for 3 h at 500 °C. After this heat treatment the samples were cooled down with a cooling rate of 60 K/h. At this annealing step powder samples with good crystallinity are achieved.

For the determination of the exact chemical composition and phase contents (possible secondary phases) of the synthesized CZTS samples, the powders were analyzed by wavelength dispersive X-ray spectroscopy (WDS) using an electron microprobe analyzer (JEOL-JXA 8200 System). For calibration of the system elemental standards of Cu, Zn, and Sn as well as the mineral chalcopyrite for S was used. In order to obtain accurate and reliable values for the chemical composition of each sample 20 grains averaging over 15 point measurements within each grain were measured.

Structural characterization and quantitative phase analysis were done by X-ray powder diffraction using a Panalytical X'Pert PRO diffractometer (Bragg-Brentano geometry, Cu-Kα radiation). Additionally, neutron powder diffraction measurements of one

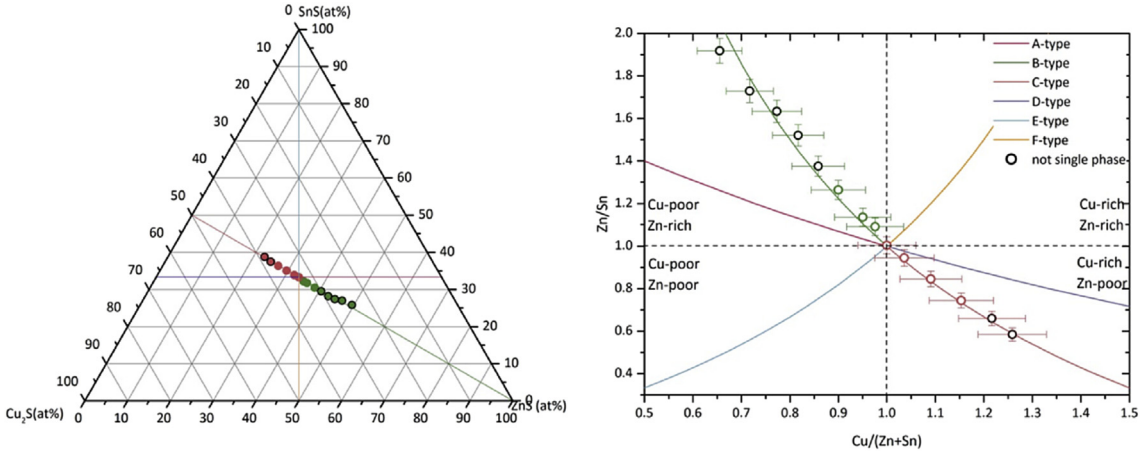

Fig. 1. Prepared B-type (green) and C-type (red) CZTS powder samples. **Left**: Ternary phase diagram. **Right**: Cation ratio plot of the synthesized off-stoichiometric sampels. Each line corresponds to one off-stoichiometric CZTS type (calculated according the formulas described in Table 1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)