

Structural and Optoelectronic Characterization of $(\text{Ag}_x\text{Cu}_{1-x})_2\text{ZnSnSe}_4$ solid solution

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Abstract — As the open-circuit voltage in CZTSSe devices is believed to be limited by absorber band tailing caused by the exceptionally high density of Cu/Zn disorder, replacing of Cu with Ag this density is predicted to drop. In this study, neutron diffraction and diffuse reflectance were applied to evaluate the crystal structure and optoelectronic properties of the $(\text{Ag}_{1-x}\text{Cu}_x)_2\text{ZnSnSe}_4$ solid solution (ACZTSe). The results allow us to suggest that in spite of both end members of the solid solution being reported to crystallize in kesterite type structure, at least $(\text{Ag}_{1-x}\text{Cu}_x)_2\text{ZnSnSe}_4$ with $x=0.17$ and 0.46 crystallize in the stannite type structure and thus block Cu/Zn disorder.

Index Terms — structural properties, stannite, powders, bandgap.

I. INTRODUCTION

$\text{Cu}_2\text{ZnSnSe}_4$ solar cells, containing abundant elements, with Ag alloying recently reached efficiency of 10.2% [1]. The open-circuit voltage in CZTSSe devices is believed to be limited, in between other factors, by strong band tailing caused by the exceptionally high density of Cu/Zn antisites. By replacing Cu in CZTSe with Ag, whose covalent radius is 15% larger than that of Cu and Zn, the density of I–II antisite defects (e.g Cu/Zn disorder) is predicted to drop [2].

$\text{Ag}_2\text{ZnSnSe}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ are quaternary semiconductors belonging to the adamantine compound family. The differentiation between the isoelectronic cations Cu^+ and Zn^{2+} , which is the key information for the investigation of on Cu/Zn disorder in kesterite type semiconductors, is not possible using X-ray diffraction due to their similar scattering factors. Neutrons diffraction can solve this problem; the coherent scattering lengths are sufficiently different for these cations [4]. It was shown by neutron diffraction that CZTSe crystallizes in the kesterite type structure (space group $I\bar{4}$) [3]. In case of $\text{Ag}_2\text{ZnSnSe}_4$ according to the theoretical calculations density functional theory simulations show that when Ag is substituted for Cu to form kesterite $\text{Ag}_2\text{ZnSnSe}_4$ (AZTSe) [2]. Experimentally only X-ray diffraction was used until now to determine the crystal structure of AZTSe, and the kesterite structure was obtained [4]. But in case of $(\text{Ag}_{1-x}\text{Cu}_x)_2\text{ZnSnSe}_4$ a combination of neutron and X-ray diffraction is necessary in order to determine the cation distribution in these compounds, even though Cu^+ and Ag^+ are not isoelectronic, and Ag^+ could be located in the crystal structure by using X-ray diffraction only, the problem of Cu^+ and Zn^{2+} being isoelectronic is still present.

This work presents for the first time a neutron diffraction based investigation of the crystal structure of $(\text{Ag}_{1-x}\text{Cu}_x)_2\text{ZnSnSe}_4$ mixed crystals. The aim of this study is to clarify the crystal structure of the solid solution series as well as to deduce possible cationic point defects, paying a special attention to the presence of Cu/Zn disorder in these compounds.

II. EXPERIMENTAL

Three powder samples were synthesized via solid state reaction starting with the pure elements Ag (6N), Cu (6N), Zn (6N), Sn (6N) and Se (5N) in evacuated silica tubes, similar to the CZTSe, CZGSe and CZTS compounds [2, 5, 8-10]. Due to the comparably low decomposition temperature of the $\text{Ag}_2\text{ZnSnSe}_4$ end member of the ACZTSe solid solution

[4], the maximum synthesis temperature had to be adjusted significantly, and in order to compensate for the decreased synthesis temperatures, the holding times had to be increased. As the result the samples were synthesized using the temperature regime as follows: 10K/h to 200C hold for 24h, 10K/h to 400C hold 24h, 10K/h to 550C hold for 20 days followed by natural cooling. The homogenization procedure – grinding in the agate mortar, pressing in a pellet and annealing at 550C for 20 more days had to be repeated twice.

To determine the chemical composition of the obtained samples, wavelength dispersive X-ray spectroscopy (WDX) has been performed using an electron microprobe analysis system. In order to obtain reliable results from the WDX measurements, the system was calibrated using elemental standards. High accuracy of the compositional parameters was achieved by averaging over 20 local measurement points within one grain and averaging over more than 30 grains of the ACZTSe phase to deduce its chemical composition. The averaging over all grains of the main phase is possible due to the fact that the deviations of the values for each of the measurements within each grain as well as among all of the grains did not exceed the 1%, originated by the instrumental error.

For structural characterization of these samples both neutron and X-ray diffraction (XRD) were used. XRD was performed at the PANalytical X'Pert PRO MRD diffractometer with Bragg-Brentano geometry with a focusing beam and Cu-K $\alpha_{(1+2)}$ radiation. As instrumental setup a sample spinner, 1/4 divergence slit, and a 5mm mask were chosen. The measurements were performed over a 2θ range from 10° to 130° with steps of 0.013° and a step time of 100s, in this way insuring the quality of the pattern being enough for Rietveld refinement. The collected XRD pattern were further processed by a Rietveld refinement using the FullProf Suite software package [11, 12]. The Thompson-Cox-Hastings pseudo-Voigt function was applied to describe the XRD peak shape profile [13]. Unfortunately X-ray diffraction cannot be used alone in this case. Even though Cu⁺ and Ag⁺ are not isoelectronic, and Ag⁺ could be located by using this method, the problem of Cu⁺ and Zn²⁺ being isoelectronic is still present. In order to distinguish between Cu⁺ and Zn²⁺ neutron diffraction experiments were performed at the Berlin Research Reactor BER II at the Helmholtz-Zentrum Berlin für Materialien und Energie using the fine resolution powder diffractometer FIREPOD (E9) ($\lambda = 1.7982 \text{ \AA}$; ambient temperature) [14]. In the following the data treatment was performed by a full pattern Rietveld refinement [12] using the FullProf Suite software package [11]. But unfortunately for this case only neutron diffraction is not enough as well, due to the very similar neutron scattering length of Ag and Zn ($b_{\text{Zn}}=5.680 \text{ fm}$ and $b_{\text{Ag}}=5.922 \text{ fm}$ [15]). In order to obtain reliable site occupancies for all 4 crystallographic sites, and locate all four cations within the structure, a simultaneous Rietveld refinement of neutron and X-ray diffraction data was performed. As the starting crystal structure model for the ACZTSe main phase the kesterite type structure (space group $I\bar{4}$) [3, 4] was selected. Both secondary phases deduced from chemical analysis (WDX) have been included in the refinement. The refinements have been performed without any chemical constrains.

Diffuse reflectance measurements have been performed with a hyperspectral imaging setup with a CCD camera (allied vision pike f-145) coupled with a liquid crystal tunable filter. A halogen lamp was used to illuminate the powders. The hyperspectral stack obtained from the powders is divided over the one obtained from measuring a spectralon srm-99 standard to calculate the diffuse reflectance spectra.

III. RESULTS

As the result of the WDX analysis it turned out, the obtained samples are not single phase. Besides the quaternary ACZTSe main phase, the presence of small amounts of two secondary phases was detected – ZnSe and Ag₈SnSe₆. In case of one of the ACZTSe powders (further referred as Ag- 26) as well a few grains of another quaternary phase with slightly different Ag/(Ag+Cu) ratio was detected, which made is unsuitable for detailed structural characterization via neutron diffraction. In case of the other two ACZTSe powders (further referred as Ag-17 and Ag-46), their main quaternary phase was homogeneous, but with slightly off-stoichiometric composition. Both of the samples were slightly

Zn rich and Sn poor, but while Ag-46 was also very slightly Ag/Cu poor, Ag-17 was very close to stoichiometry, concerning the Ag/Cu content.

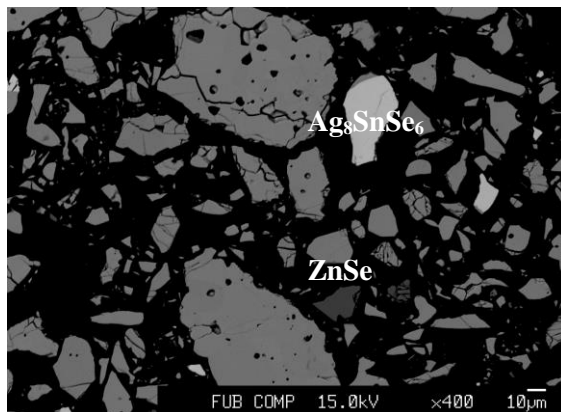


Fig. 1. BSE micrograph of the $\text{Ag}_{0.91}\text{Cu}_{1.08}\text{Zn}_{1.03}\text{Sn}_{0.99}\text{Se}_4$ (Ag-46) sample, ZnSe and Ag_3SnSe_6 secondary phases are indicated.

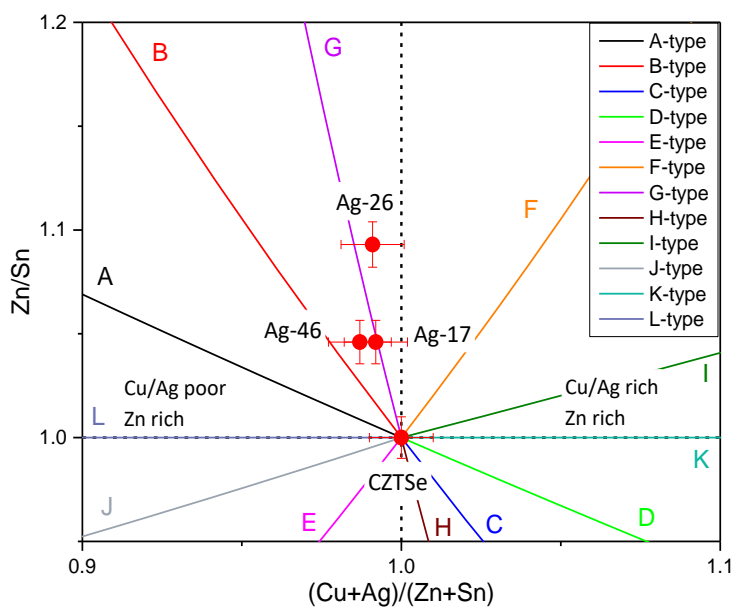


Fig. 2. Cation ratio plot $(\text{Ag}+\text{Cu})/(\text{Zn}+\text{Sn})$ vs. Zn/Sn showing the different off-stoichiometry types A to L [5 - 8]. The positions of the synthesized ACZTSe samples are indicated; (inset) BSE micrograph of the $\text{Ag}_{0.91}\text{Cu}_{1.08}\text{Zn}_{1.03}\text{Sn}_{0.99}\text{Se}_4$ (Ag-46)

Table I Overview of synthesized samples: cation ratios (Ag+Cu)/(Zn+Sn), Ag/(Ag+Cu) and Zn/Sn obtained from the WDX analysis, chemical formula, off-stoichiometry type and presence of secondary phases.

Name	(Ag+Cu)/(Zn+Sn)	Zn/Sn	Ag/(Ag+Cu)	Ag ₈ SnSe ₆	ZnSe	Final formula	Type
Ag-46	0.987	1.046	0.456	+	+	Ag _{0.91} Cu _{1.08} Zn _{1.03} Sn _{0.99} Se ₄	B-G
Ag-26	0.991	1.093	0.263	+	+	Ag _{0.52} Cu _{1.48} Zn _{1.03} Sn _{0.99} Se ₄	G-F
Ag-17	0.992	1.046	0.173	+	+	Ag _{0.35} Cu _{1.66} Zn _{1.06} Sn _{0.97} Se ₄	G

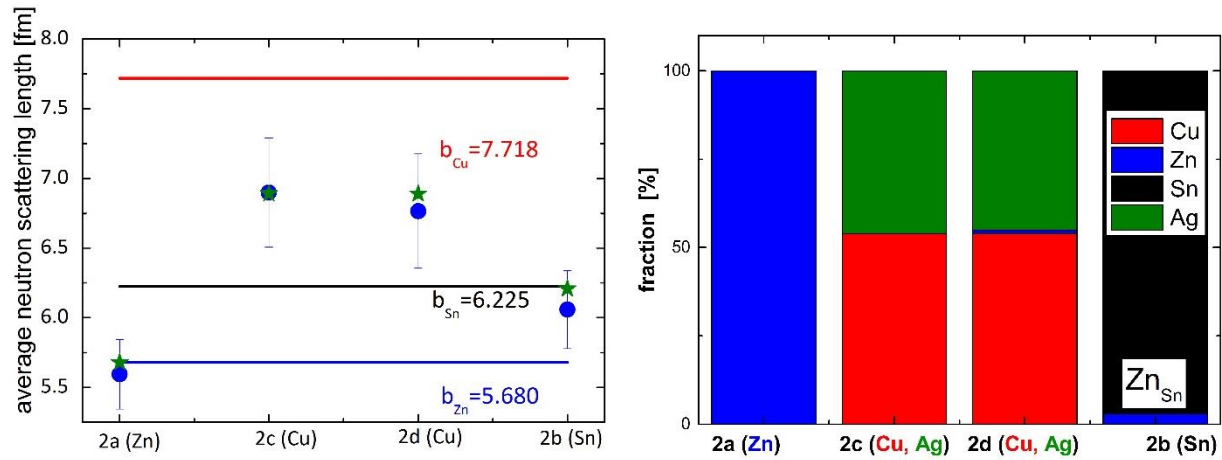


Fig. 3. (top) Average neutron scattering length \bar{b} of the cation sites $2a$, $2c$, $2d$ and $2b$, assuming kesterite type structure (full symbols – experimental values; star – calculated values according to a cation distribution model); (bottom) Resulting cation distribution and point defects in Ag_{0.91}Cu_{1.08}Zn_{1.03}Sn_{0.99}Se₄ (Ag-46).

The method of the average neutron scattering length analysis [16] was applied to determine the distribution of the cations Cu⁺, Ag⁺, Zn²⁺ and Sn⁴⁺ on the four structural cation sites of the kesterite type structure. The experimental average neutron scattering lengths of the four cation sites $2a$, $2b$, $2c$ and $2d$ were calculated as described earlier [8, 10, 16]. As the result of the comparison of the experimentally obtained values with the neutron scattering lengths of copper, silver, zinc and tin, it is obvious that the average neutron scattering length of the copper site $2a$ is extremely decreased in comparison to the copper neutron scattering length, and is equal to the neutron scattering length of zinc which means that $2a$ position is completely occupied by Zn²⁺. The $2c$ and $2d$ positions, where Cu/Zn disorder is usually present in CZTS and CZTSe kesterite type compounds, are occupied by Ag⁺ and Cu⁺ in proportions suggested by the chemical compositions (Figure 3) instead. Only Sn⁴⁺ is located on $2b$ position as expected. All of above mentioned are very strong indications of stannite type structure ($I\bar{4}2m$). An additional refinement of the neutron diffraction pattern using the stannite type structure as starting model in the Rietveld analysis was performed. A lower value for both R_{bragg} and χ^2 were obtained. A slight presence of type related defects was detected as well, namely Zn_{Sn} and Zn_{Cu} as well as Zn_i corresponding to B, G and F type off-stoichiometry [5].

The bandgap values calculated from the diffuse reflectance measurements for the Ag-17, Ag-26 and Ag-46 are 0.92 eV, 0.98 eV and 1.08 eV respectively. These bandgap values are in a reasonably good agreement with the ones reported for ACZTSe thin films with similar Ag/Cu ratio [4].

IV. CONCLUSIONS

To conclude we investigated powder samples from two $(\text{Ag}_{1-x}\text{Cu}_x)_2\text{ZnSnSe}_4$ solid solutions, grown by solid state reaction, by means of neutron and X-ray diffraction. The results allow us to suggest that in spite of both end members of the $(\text{Ag}_{1-x}\text{Cu}_x)_2\text{ZnSnSe}_4$ solid solution being reported to crystallize in kesterite type structure, at least the $(\text{Ag}_{1-x}\text{Cu}_x)_2\text{ZnSnSe}_4$ mixed crystals with ($x=0.17$ and 0.46) crystallize in the stannite type structure. Here the site 2a is completely occupied by the divalent cation (Zn), whereas the 4d site is occupied by Cu and Ag randomly. The latter corresponds to the sites 2c and 2d in the kesterite type structure, in which the Cu/Zn disorder in kesterite type CZTSe occurs. In this way the possibility for the formation of Cu/Zn disorder is completely blocked in $(\text{Ag}_{1-x}\text{Cu}_x)_2\text{ZnSnSe}_4$. The bandgap values obtained from the diffuse reflectance measurements are in a reasonably good agreement with the ones reported for ACZTSe thin films with similar Ag/Cu ratios. The possible reasons for such a structural anomaly as well as the influence on the physical properties of these compounds have to be further investigated.

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