

Influence of Cu purity and low temperature annealing on Cu/Zn disorder and efficiency of CZTSSe monograins

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Thin film solar cell technologies are mainly based on polycrystalline absorber layers, which is also the case for kesterite-based photovoltaic devices. An alternative technology, which is promising and low cost, is based on kesterite-type $\text{Cu}_2\text{ZnSn}(\text{S}, \text{Se})_4$ (CZTSSe) monograins as absorbers, which are fixed in a polymer matrix to form a flexible solar cell. The large band tailing observed in Cu-based kesterite-type semiconductors is believed to cause voltage losses, limiting the efficiency of kesterite-based devices. Cu/Zn disorder, which is always present in these compounds, is discussed in literature as a possible reason for band tailing. The experimental determination and quantification of Cu/Zn disorder is possible by in-depth analysis of neutron diffraction data. This work reveals that the purity of copper used in the synthesis of CZTSSe monograins has an influence on the degree of Cu/Zn disorder in the semiconductor and thus on optical and PV parameters. Comparing CZTSSe monograins, less Cu/Zn disorder was observed for the monograins synthesized using copper with higher purity; the respective monograin-based solar cell shows a higher power conversion efficiency. On the other hand, the band gap energy as well as the photoluminescence maximum (PL_{max}) of both monograins are the same. Applying a low-temperature annealing procedure allowed us to increase the quality of monograins synthesized using 5N copper, very close to the one grown using 6N copper. The PL_{max} slightly shifts into higher energy, which is most likely an indication of the decreased Cu/Zn disorder, either moving the defect states toward the valence band or that it reduces the formation of the tail states near the conduction band minimum.

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I. INTRODUCTION

Compound semiconductors consisting of earthabundant and nontoxic elements, such as $\text{Cu}_2\text{ZnSn}(\text{S}_{1-x}\text{Se}_x)_4$ (CZTSSe), are at the center of attention for application in photovoltaic devices [1]. Due to their nontoxicity and abundance of the constituent elements, CZTSSe is a promising low-cost alternative as an absorber layer in critical-raw material free thin film solar cells. A number of new world records were announced recently, the highest being the 15.1% in 2024 [2]. But, the low open-circuit voltage with respect to the band gap phenomenon continues to be a critical issue. The absorber band tailing caused by the exceptionally high density of Cu_{Zn} and Zn_{Cu} antisites, causing Cu/Zn disorder [3], is believed to be one of the reasons for the limited open-circuit voltage in CZTSSe-based devices [4]. However, the improvements in the efficiency of the solar cells with reduced Cu/Zn disorder have not yet been reported [5,6], and the actual mechanism limiting the performance is still to be determined.

A number of strategies were applied in order to avoid and/or decrease the level of Cu/Zn disorder in these compounds. Cationic mutations aiming on substituting Cu with Ag, substituting Zn with Cd or Fe, Mn, even Ni, as well as introducing Ge in the compound instead of Sn or additionally to it, produce improvements to the overall performance in comparison to the baseline reference cells, but did not help to avoid the Cu/Zn disorder up to now [7]. Another strategy to decrease the Cu/Zn disorder discovered not that long ago is a low temperature annealing. An order-disorder phase transition was reported for $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) at $T = 260^\circ\text{C}$ [8], in $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe), this transition occurs at $T = 200^\circ\text{C}$ [9]. In these and other studies, the distribution of the cations Cu^+ and Zn^{2+} in the kesterite-type crystal structure has been approached in various ways [10], but the decrease of Cu/Zn disorder at temperatures below the order-disorder transition temperature was mainly deducted indirectly by anomalous lattice parameter expansion [11], Raman spectroscopy and spectrophotometry [8], electoreflectance [12], and kinetics simulations [10].

There is a huge gap between all of these studies and the fundamental understanding of the Cu/Zn disorder in CZTSSe, as most of these studies are performed on thin films, by methods which can provide access to the Cu/Zn disorder only indirectly. Thin film absorber layers are usually inhomogeneous, with an off-stoichiometric absorber composition and with secondary phases being present [13]. To

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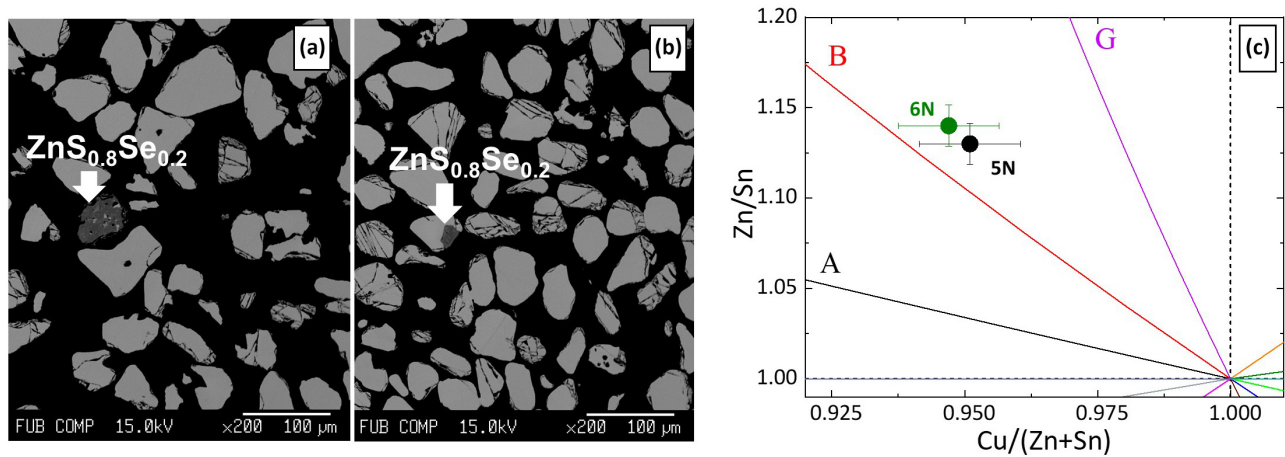


FIG. 1. (a) Back-scatter electron (BSE) micrograph of the 5N sample with highlighted $\text{ZnS}_{0.8}\text{Se}_{0.2}$ phase (darker gray); (b) back-scatter electron (BSE) micrograph of the 6N sample with highlighted $\text{ZnS}_{0.8}\text{Se}_{0.2}$ phase (darker gray); and (c) cation ratio plot showing both 5N and 6N monograins. Both CZTSSe monograins are located in the Cu-poor Zn-rich area corresponding to the B-G type off-stoichiometry [14].

separate the Cu_{Zn} and Zn_{Cu} antisite point defects which cause the Cu/Zn disorder from point defects correlated to the off-stoichiometric composition of the kesterite-type semiconductor (e.g., vacancies, interstitials, and antisites) is a very complex problem [14]. In order to have a solid knowledge and to quantify the Cu/Zn disorder, it is necessary to locate the Cu^+ and Zn^{2+} within the CZTSSe crystal structure, which is not a trivial task, as Cu^+ and Zn^{2+} are isoelectronic cations and thus have essentially the same scattering factor for x-rays. Thus, they cannot be distinguished by conventional x-ray diffraction. Only a few experimental methods allow tackling Cu/Zn disorder directly, most promising among them are anomalous x-ray and neutron diffraction. Neutron diffraction has been used to study the crystal structure, structural disorder, and point defects in stoichiometric CZTS, CZTSe, and off-stoichiometric CZTSe, as well as $\text{Cu}_2\text{ZnGeSe}_4$ (CZGSe), and a number of other compounds and solid solutions [3,14–19]. The main disadvantage related to the use of neutron diffraction is the necessity of big volumes of homogeneous material, which makes it inapplicable for the use with thin films of CZTSSe, due to their inhomogeneity, and consequently makes the correlation of the results obtained from the powder neutron diffraction and the performances of the solar cells quite complicated.

A promising low-cost alternative PV technology uses kesterite-type CZTSSe monograins (single crystals of 50 to 100 μm size), which are fixed in a polymer matrix to form a flexible solar cell. And, as neutron diffraction requires large sample volumes, kesterite monograin powders offer the unique possibility to correlate structural disorder in kesterite-type absorbers with performance parameters of a working photovoltaic device [20,21].

In the present work, we applied neutron diffraction to obtain the distribution of Cu^+ and Zn^{2+} in the crystal structure of CZTSSe in order to determine the concentration of Cu_{Zn} and Zn_{Cu} antisite defects in a unique set of CZTSSe monograins synthesized from two different precursors. The order parameter Q [9], representing the Cu/Zn disorder, as well as the occurring intrinsic point defects, have been determined. The influence of the purity of the starting material (copper),

small changes in the monograin chemical composition on the Cu/Zn disorder, resulting in different efficiency of the respective devices, was studied. Additionally, the effect of the “disordering” procedure and the long, low temperature “ordering” annealing on the Cu/Zn disorder and optoelectronic properties of the CZTSSe monograins were studied.

II. EXPERIMENTAL

The two CZTSSe monograin samples used in this work were grown following the standard monograin technology used at Crystalsol ÖU and described previously [20,21] in detail. These particular CZTSSe samples were grown using 5N Copper (99.999 Copper, the standard for production of the monograins for Crystalsol modules)—further called 5N sample, and 6N Copper (the higher purity, 99.9999 Copper)—further called the 6N sample.

To determine the chemical composition and phase content of the samples, wavelength-dispersive x-ray spectroscopy (WDX) has been performed using an electron microprobe analysis system (JEOL-JXA 8200) equipped with a wavelength-dispersive x-ray spectroscopy unit. 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 10 local measurement points within one grain and averaging over more than 40 grains of the CZTSSe. Averaging over all grains of the quaternary main phase is possible due to the fact that deviations of the values for each of the measurements within each grain, as well as among all of the grains, did not exceed a 2% error, originating from the instrumental error. For the present secondary phase, $\text{ZnS}_x\text{Se}_{1-x}$ [Fig. 1(a)], additional grains containing this secondary phase were measured in the same way. The complete overview of the obtained cation ratios and deduced chemical composition of all of the CZTSSe monograins is shown in Table I.

For structural characterization of these monograins, neutron diffraction was used. Neutron diffraction experiments have been performed at the Berlin Research Reactor BER II at the Helmholtz-Zentrum Berlin für Materialien und Energie

TABLE I. Overview of the synthesized monograin samples: the cation ratios Cu/(Zn+Sn), Zn/Sn, and the anion ratio S/(S+Se) of the main CZTSSe phase obtained from the WDX analysis, chemical formula, off-stoichiometry type, and presence of secondary phases.

Name	Cu/(Zn+Sn)	Zn/Sn	$x = S/(S + Se)$	chemical formula	secondary phases	off-stoichiometry type
5N	0.95	1.13	0.59	$Cu_{1.95}Zn_{1.09}Sn_{0.97}S_{2.37}Se_{1.63}$	$ZnS_{0.8}Se_{0.2}$	B-G
6N	0.95	1.14	0.60	$Cu_{1.95}Zn_{1.10}Sn_{0.96}S_{2.38}Se_{1.62}$	$ZnS_{0.8}Se_{0.2}$	B-G
after “ordering” annealing procedure						
5NQ	0.95	1.14	0.58	$Cu_{1.96}Zn_{1.10}Sn_{0.96}S_{2.33}Se_{1.67}$	$ZnS_{0.8}Se_{0.2}$	B-G
5NS	0.95	1.15	0.58	$Cu_{1.96}Zn_{1.10}Sn_{0.96}S_{2.32}Se_{1.68}$	$ZnS_{0.8}Se_{0.2}$	B-G

using the fine resolution powder diffractometer FIREPOD (E9) ($\lambda = 1.7982 \text{ \AA}$; ambient temperature) [22]. The data treatment was performed by a full pattern Rietveld refinement [23] using the FullProf Suite software package [24]. The kesterite type structure with Cu on Wyckoff position $2a:(0,0,0)$ and $2c:(0, \frac{1}{2}, \frac{1}{4})$, Zn on $2d:(0, \frac{1}{2}, \frac{3}{4})$, Sn on $2b:(\frac{1}{2}, \frac{1}{2}, 0)$, and S and Se on $8g:(x, y, z)$ was used as structural model in the refinement [15]. The refinement of site occupancy factors (SOF) was done without any chemical constraints.

Diffuse reflectance spectroscopy (DRS) measurements were carried out in air at room temperature in a spectrophotometer equipped with an integrating sphere—Perkin Elmer UV/Vis-spectrometer Lambda 750S. The measurement range was adjusted for this set of samples: 900 to 1400 nm with a step size of 1 nm. Tauc plots were obtained by plotting $(F(R) \cdot h\nu)^2$ versus the photon energy ($h\nu$) [25]. The linear part of the curve was extrapolated to the baseline and the optical band gap was extracted from the value of intersection in the same way it was previously reported for CZTS, CZTSe, and CZGSe powder [26].

Photoluminescence (PL) measurements were carried out at room temperature using a 660 nm diode laser as an excitation source. The PL signals were dispersed with a 1/2 m grating monochromator and detected by a liquid N₂-cooled InGaAs array-type detector.

An additional “ordering” annealing procedure adapted from [9] was applied. In order to have enough material for the repeated neutron diffraction experiment, the 5N sample was divided into three parts: 2 times 2.5 grams each for annealing, and 1 g was left unchanged in order to be used as a reference for all of the following measurements on the annealed samples. The first half was heated to 300 °C in order to adjust for the presence of the Sulphur, held for 24 hours, and quenched in iced water in order to reach the state of complete disorder, or at least make the sample as disordered as possible. For the second half of the sample, the other extreme of the procedure was adapted (Fig. 6) in order to allow the sample to achieve equilibrium at each step.

All of the measurements were repeated in the same way for the two new samples, 5NQ (the quenched “disordered” one) and 5NS (the slowly annealed “ordered” one).

III. RESULTS AND DISCUSSION

A. Cu/Zn disorder vs. efficiency

The presence of a small amount of the $ZnS_{0.8}Se_{0.2}$ secondary phase was detected in both samples. Figure 1(a)

presents a back-scatter electron (BSE) micrograph showing the homogeneity of the main phase alongside the presence of the secondary phase for the 5N sample. The 6N sample looks very similar [Fig. 1(b)]. The main quaternary phases of these samples were homogeneous, but with slightly off-stoichiometric composition [see Fig. 1(c)] [14]. The presence of the $ZnS_{0.8}Se_{0.2}$ secondary phase is in good agreement with the resulting Cu-poor/Zn-rich composition of the main CZTSSe phase of both samples [27]. The Cu/(Zn+Sn), Zn/Sn, and S/(S+Se) ratios of the mixed crystals, as well as the off-stoichiometry type information and final formulas of the quaternary compounds, calculated according to the method described in [14], are presented in Table I.

An example of the neutron diffraction pattern and corresponding Rietveld analysis for the 5N sample is shown in Fig. 2; significant results for 5N and 6N samples are listed in Table II. The $ZnS_{0.8}Se_{0.2}$ secondary phase deduced from chemical analysis has been included in the refinements (see Fig. 2). The average neutron scattering length analysis method [28] was applied to determine the distribution of the cations Cu⁺, Zn²⁺ and Sn⁴⁺ on the four structural sites of the kesterite type structure ($2a$, $2b$, $2c$, and $2d$). The experimental average neutron scattering lengths were calculated according to

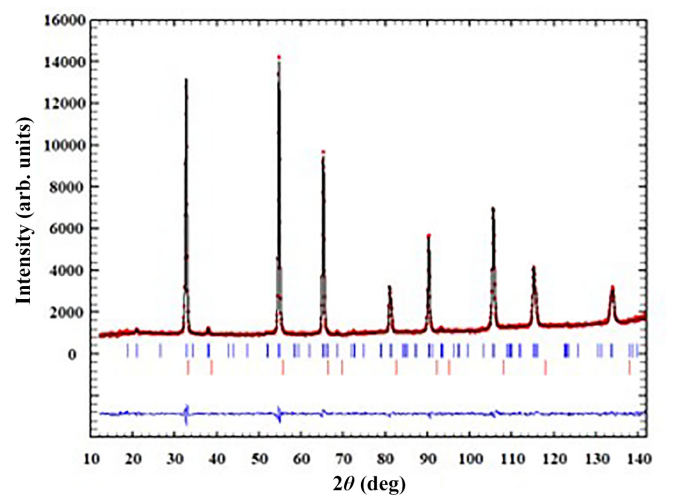


FIG. 2. Rietveld refinement of the neutron diffraction data of the 5N monograin, where the red dots are experimental data, the black line is the obtained fit, the blue ticks are the Bragg peak positions of the kesterite type structure, red ticks are the Bragg peak positions of the $ZnS_{0.8}Se_{0.2}$ phase, and the blue line is the difference between the experimental and calculated data.

TABLE II. Lattice parameters and site occupancy factors determined from neutron diffraction data.

Name	Lattice parameters		SOF				Reliability factors	
	<i>a</i> , Å	<i>c</i> , Å	Cu 2 <i>a</i>	Cu 2 <i>c</i>	Zn 2 <i>d</i>	Sn 2 <i>b</i>	R _{Bragg}	χ ²
5N	5.535(1)	11.029(2)	1.017(23)	0.958(29)	1.097(35)	0.976(26)	1.69	1.32
6N	5.533(1)	11.027(2)	1.008(27)	0.973(27)	1.067(36)	0.987(29)	1.73	1.07
after “ordering” annealing procedure								
5NQ	5.333(1)	11.040(2)	0.984(30)	0.954(42)	1.145(54)	1.000(33)	2.12	1.46
5NS	5.532(1)	11.025(2)	0.999(27)	0.988(29)	1.076(36)	0.998(28)	2.30	1.23

Eqs. (1) using the cation site occupancy values SOF_{2a} , SOF_{2c} , SOF_{2d} , and SOF_{2b} , determined by a Rietveld analysis of neutron diffraction data:

$$\begin{aligned}
 \bar{b}_{2a}(\text{exp}) &= \text{SOF}_{2a} \cdot b_{\text{Cu}}, \\
 \bar{b}_{2c}(\text{exp}) &= \text{SOF}_{2c} \cdot b_{\text{Cu}}, \\
 \bar{b}_{2d}(\text{exp}) &= \text{SOF}_{2d} \cdot b_{\text{Zn}}, \\
 \bar{b}_{2b}(\text{exp}) &= \text{SOF}_{2b} \cdot b_{\text{Sn}}.
 \end{aligned} \quad (1)$$

The details of the cation distribution model, which is introduced for each of the samples, can be found in [14], and the result can be seen in Fig. 3. It is important that the sum of a cation species on the different cation sites should be in good agreement with the chemical composition of the phase determined by WDX analysis. In the case of an excess of a cation species, e.g., the sum of a cation species distributed at the cation sites is less than the amount determined by WDX, interstitials are assumed. Taking into account the experimentally determined total amounts of each element, as obtained by WDX analysis, and assuming that all four cation sites are fully occupied, the respective cation occupancy of the sites can be derived with high reliability.

In the case of the Cu-poor/Zn-rich kesterite phase A, B, G, and L types of off-stoichiometry can be possible [14].

Based on the results of the WDX measurements, both monograins can be located between B and G off-stoichiometry types. The defect complexes expected for these samples would be B : $2\text{Zn}_{\text{Cu}}^{2+} + \text{Zn}_{\text{Sn}}^{2+}$ and G : $\text{Zn}_{\text{Sn}}^{2+} + \text{Zn}_{\text{I}}^{2+}$ (B-G-type mixtures). Summarizing both types and paying attention to the location of the monograins in the cation ratio plot closer to the B-type line, we can expect the defects belonging to the B type to be more pronounced in these samples. The slightly lower than expected value at the 2*a* site is mainly due to Zn_{Cu} (the distribution of Zn_{Cu} on both 2*c* and 2*a* sites being very typical for samples very close to the B-type line). The Zn_{Sn} is responsible for a slightly lower than expected value at the 2*b* site. The concentration of these defects is low (see Fig. 3).

It can be observed that in both cases the experimental average neutron scattering lengths of the 2*c* and 2*d* positions significantly deviate from values expected on these sites according to the kesterite type structure ($b_{\text{Cu}} = 7.718$ fm and $b_{\text{Zn}} = 5.680$ fm). The value for the 2*c* site is significantly lower, and the one for 2*d* is significantly higher than the expected neutron scattering length on this site. Such scattering length differences can be explained by the formation of intrinsic point defects. For instance, zinc on copper antisite defects (Zn_{Cu}) would decrease the average neutron scattering length of the 2*c* crystallographic site because $b_{\text{Zn}} = 5.680$ fm < $b_{\text{Cu}} = 7.718$ fm; likewise, the copper on zinc antisite defect (Cu_{Zn}) would lead to an increase of the average neutron

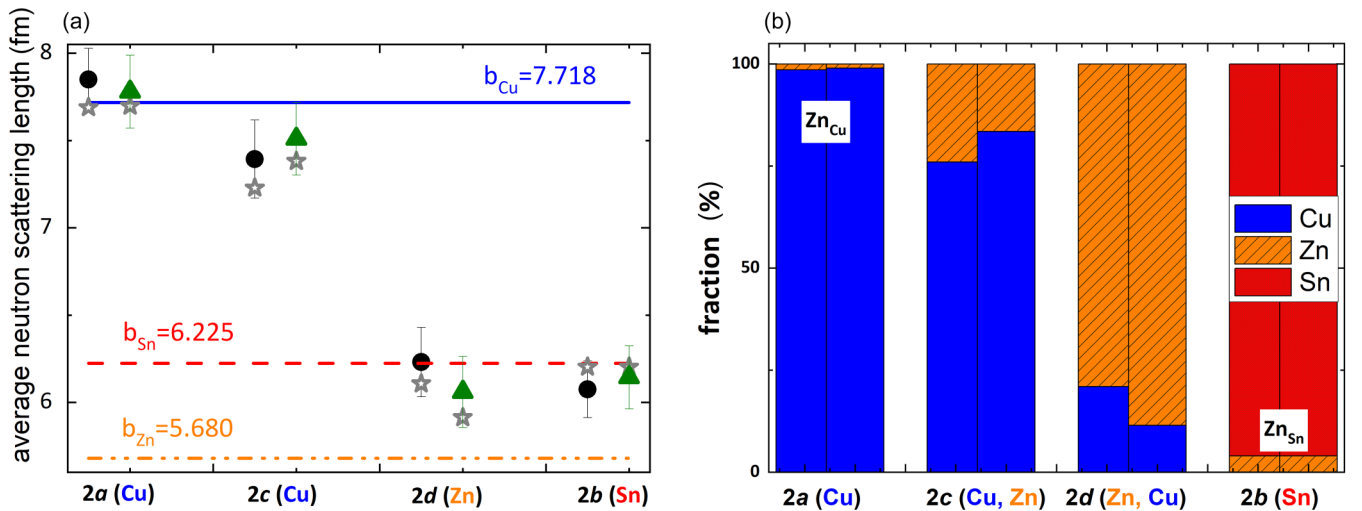


FIG. 3. (a) Average neutron scattering length $\bar{b}$ of the cation sites 2*a*, 2*c*, 2*d*, and 2*b* for 5N and 6N monograins, (full symbols—experimental values; star—calculated values from the best fitting cation distribution model; lines—pure elements). (b) The resulting cation distribution on the structural sites 2*a*, 2*b*, 2*c*, and 2*d* for 5N and 6N monograin samples, obtained from the in-depth analysis of neutron diffraction data.

TABLE III. The modeled cation distribution, intrinsic point defects (in site fractions) and Q —the quantitative measure of disorder of all investigated samples.

	$2a$		$2c$		$2d$		$2b$						
	Cu	Zn	Cu	Zn	Cu	Zn	Zn	Sn	Cu/Zn	Zn_{Cu}	Zn_{Sn}	Zn_i	Q
5N	98.6	1.4	76.0	24.0	21.0	79.9	3.4	96.7	21.0	4.4	4	1.2	0.58
6N	99.0	1.0	83.5	16.5	12.5	87.5	4.0	96.0	12.5	5	4	0.9	0.75
after “ordering” annealing procedure													
5NQ	88.5	11.5	74.0	26.0	33.0	67.0	4.0	96.0	33	4.5	4	1.5	0.34
5NS	96.4	3.6	86.5	13.5	13.5	86.5	4.0	96.0	13.5	3.6	4	2	0.73

scattering length of the $2d$ site, in this way forming the Cu/Zn disorder.

The cation distribution in both samples can be summarized with a small amount of Zn_{Cu} , Zn_{Sn} , and Zn_i in small concentrations in the presence of significant Cu/Zn disorder located on the $2c$ and $2d$ sites. The detailed cation distribution as well as each of the defect fractions of a Wyckoff site are presented in Table III. The defect concentration of Cu/Zn disorder (Fig. 4) is almost an order of magnitude higher than each of the other off-stoichiometry type-related defects. It has to be pointed out that the concentration of Zn_{Cu} and Cu_{Zn} antisites forming the Cu/Zn disorder is the only value that differs significantly for these two monograins.

Using the site occupancy factors, the order parameter Q of the Cu/Zn disorder can be calculated. This order parameter is defined in such a way that $Q = 0$ for complete disorder (Cu and Zn are distributed randomly on the Wyckoff sites $2c$ and $2d$) and $Q = 1$ for order. In literature, different approaches can be found [9,19] depending on whether the copper site $2a$ is included and how vacancies are treated. For the kesterite-type CZTSSe phases studied here, the approach discussed in [9] was used, the same way as for stoichiometric CZTSSe

powders in [19]. Thus, Eq. (2) was adapted from [9]:

$$Q = \frac{[Cu_{2c} + Zn_{2d}] - [Zn_{2c} + Cu_{2d}]}{[Cu_{2c} + Zn_{2d}] + [Zn_{2c} + Cu_{2d}]} \quad (2)$$

The order parameter Q was calculated for both monograins. $Q_{5N} = Q = 0.58(4)$ is already quite high for an as-synthesized sample, and the $Q_{6N} = 0.75(3)$ is the highest value reported for a working solar cell material, determined by a direct method.

In an attempt to correlate the obtained point defect concentrations to the optoelectronic properties of these materials, the optical band gap (E_g) was determined from the DRS measurements and the photoluminescence maximum (PL_{max}) from the room temperature photoluminescence measurements, see Table IV. The Tauc plot derived from DRS spectra is shown in Fig. 5(a). It is found that the band gap of the CZTSSe monograins is 1.22 eV for both 5N and 6N samples, implying no noticeable effect of the copper purity on the band gap energy E_g . A typical PL response of CZTSSe monograins is displayed in Fig. 5(b). Both samples show a similar type of broad PL band centered at 1.15 eV with a full width at half maximum (FWHM) of about 0.2 eV. This broad PL band can be assigned to the band-to-acceptor transition [29] involving broad acceptor states located at around 70 ± 20 meV above the valence band and estimated as a difference of the band gap and peak position of the PL band. Please note that some corrections for the acceptor states are presumably necessary because of possible contributions from the potential fluctuations [30,31]: electrostatic potential fluctuations [32], which cannot be screened by the free carrier concentration, and from the small-scale band gap fluctuations [33]. Interestingly, the band gap and PL transition energy of the CZTSSe monograins are higher than in CZTSSe polycrystalline films with $S/(S+Se) \approx 0.6$ composition [19], which is attributed to a

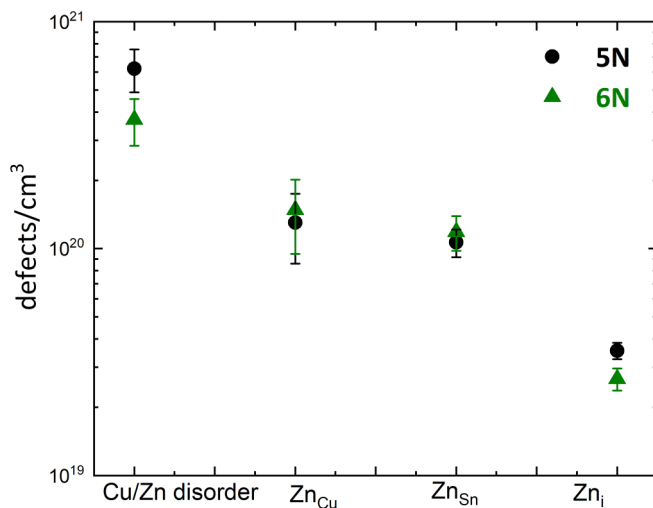


FIG. 4. Concentration of Cu_{Zn} and Zn_{Cu} antisites related to Cu/Zn disorder as well as Zn_{Cu} , Zn_{Sn} , and Zn_i point defects related to the off-stoichiometric composition (defects/cm³) obtained from the average neutron scattering length analysis of neutron diffraction data.

TABLE IV. Optoelectronic properties of the CZTSSe monograins.

Name	E_g , eV	PL_{max} , eV	Efficiency, %
5N	1.22(5)	1.15	6.84
6N	1.22(5)	1.15	9.52
after “ordering” annealing procedure			
5NQ	1.11(5)	1.04	
5NO	1.23(5)	1.18	

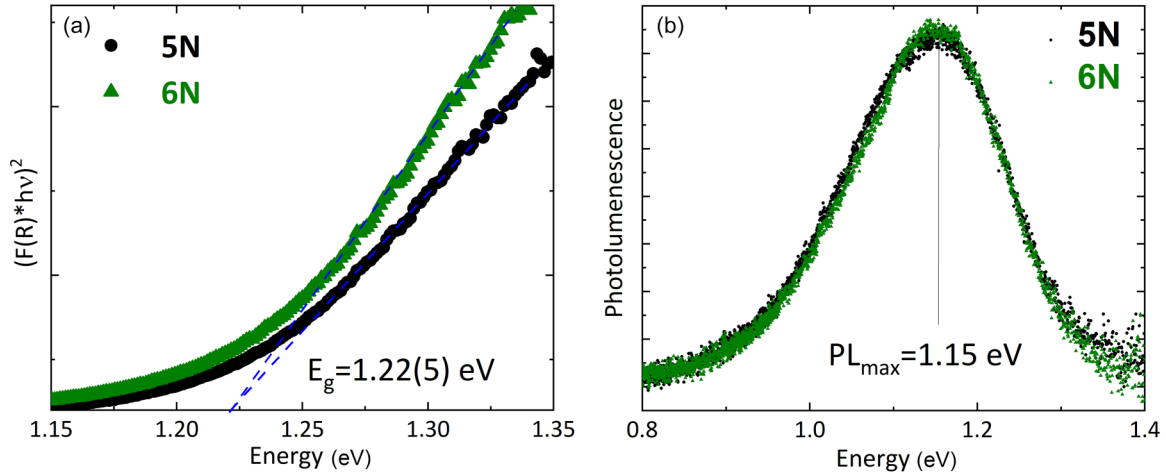


FIG. 5. (a) Tauc plot and (b) photoluminescence spectra of 5N and 6N monograins (room temperature).

higher order parameter of the grown monograins, and it will be further discussed in the next section.

In order to have a proper correlation to the performance of these monograins, working solar cells were prepared by Crystalsol, and the obtained performance parameters are presented in Table IV.

B. The “ordering” annealing procedure

The literature available at the moment suggests that long, low temperature annealing is a key to the decrease in disorder in CZTSSe [8,9,10,34]. A number of studies were devoted to developing the perfect annealing procedure, but very few conclusions were strengthened by an order parameter determination by direct methods. We decided to test such an annealing procedure on the 5N monograin sample. The choice of the 5N sample for this experiment was made based on the reasonability for the production, as the usage of 6N copper in the production of monograins would increase the price of the PV module significantly.

For the annealing procedure, the 5N sample was divided into three parts: 1 g of material was left as-grown in order to be used as a reference for all of the following measurements, and 2 times 2.5 g of material were pressed into pellets and sealed in evacuated silica tubes for annealing. For the annealing, both ampoules were placed in the same one-zone furnace, in order to have the same thermal history. First, the temperature was increased with 50 K/h until 300 °C and held at that temperature for 48 h. At the end of this period, one of the samples was taken out of the furnace and quenched in ice water. This sample, the “disordered” one, is called 5NQ in the following. The other sample was left in the furnace, and the temperature was gradually reduced. The temperature was reduced with the speed of 5 K/h at each step, and the longer the temperature, the longer the holding time. A very detailed scheme of the annealing procedure can be found in Fig. 6. The resulting slowly cooled sample, the “ordered” one, is called 5NS in the following.

The chemical composition and phase content of the three 5N samples: the initial 5N, the 5NQ quenched, and the 5NS, the “ordered” sample were determined using WDX

spectroscopy. The 5N sample was remeasured to have a reference point within these samples. As can be seen in Fig. 7, the resulting composition of the initial 5N sample is very close to the one measured the second time; it is within the 1% error, which allows us to directly compare the changes in the original, quenched, and “ordered” sample. The main quaternary CZTSSe phase of the 5NQ and 5NS samples is homogeneous with slightly off-stoichiometric composition (see Fig. 7). Also, the composition of these samples is extremely similar and very similar to the composition of the initial 5N sample. The difference is within the error of the measurement for all three samples (5N, 5NQ, and 5NS). The Cu/(Zn+Sn), Zn/Sn, and S/(S+Se) ratios of the CZTSSe monograins as well as the off-stoichiometry type information and final formulas of the quaternary compounds, calculated in the same way as for the initial 5N and 6N samples, are presented in the second half of Table I. The secondary phase $\text{ZnS}_{0.8}\text{Se}_{0.2}$ is also still present. All of these allow us to conclude on the fact that neither quenching from 300 °C nor slow low-temperature annealing introduces significant changes in chemical composition or phase content of CZTSSe.

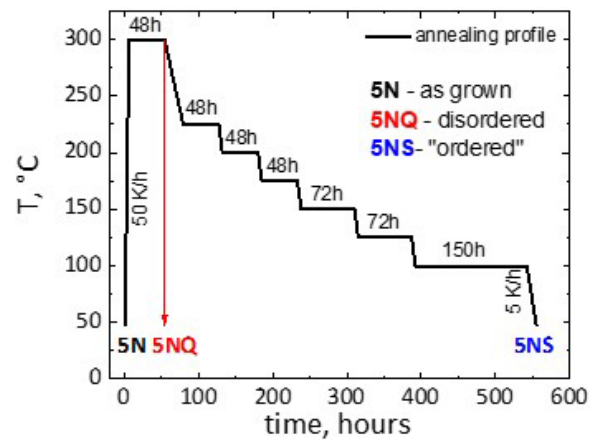


FIG. 6. The scheme of the “ordering” slow annealing procedure. The point where the 5NQ “disordered” sample was taken out of the furnace is marked with the red arrow.

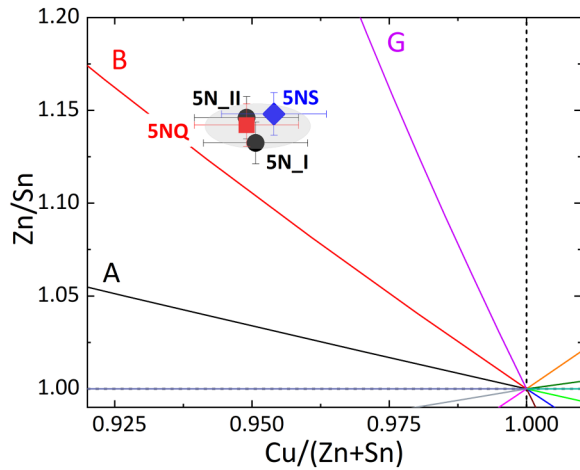


FIG. 7. The cation ratio plot showing the main quaternary CZTSSe phase of the 5N sample measured twice and the 5NQ and 5NS samples. The resulting cation ratios are located in the Cu-poor Zn-rich region corresponding to the B-G type off-stoichiometry [14] for all of the CZTSSe monograin samples.

Applying average neutron scattering length analysis to the SOF obtained from Rietveld refinement of the neutron diffraction data of 5NQ and 5NS CZTSSe monograins in the same way as for the 5N and 6N samples results in a very similar figure. The resulting cation distribution in general is very similar, but the absolute values of the intrinsic point defect concentrations are changing. In this way, the $2b$ site is the least affected—it is still occupied mainly by Sn, with the presence of a Zn_{Sn} antisite, resulting from the Sn-poor composition, with Zn_{Sn} antisite belonging to both B and G off-stoichiometry types. The average neutron scattering length of the $2a$ site is slightly dropping for both 5NQ and 5NS samples in comparison to the 5N sample. This is a hint for the split of the Zn_{Cu} antisite resulting from the B-type off-stoichiometric composition on both the $2c$ and the $2a$ crystallographic site without significant changes in the amount. Such a behavior

for kesterites close to the B-type line was already reported earlier [14]. This change can be clearly seen in Fig. 8(b), where the resulting cation distribution of 5N, 5NS, and 5NQ is compared. Comparing the fractions of the Zn_{Cu} defect correlated to the off-stoichiometric composition (Table III) becomes clear that neither quenching nor slow cooling introduces significant changes in this defect, which is in very good agreement with the fact that no changes in composition happened either. The $2c$ and $2d$ sites in the same way as in the parent 5N sample and previously mentioned 6N sample are dominated by Cu/Zn disorder, which increases for the 5NQ sample, and significantly decreases in the 5NS sample. This is in agreement with a previously published study by anomalous x-ray diffraction [9], and confirms the assumption that thermal annealing used in this work allows us to control the Cu/Zn disorder in CZTSSe in a very targeted way. Analysing the Q value shows that quenching increases the Cu/Zn disorder with almost a factor of 2, while the slow, low temperature annealing decreases the Cu/Zn disorder, bringing the value of the order parameter Q almost to the value of the 6N sample. A detailed overview of the final modelled cation distribution for each of the sites, the point defect fractions, and the quantitative measure of Cu/Zn disorder Q is presented in Table III. All these trends are maintained, or even highlighted, when changing from site fractions to defect concentrations (see Fig. 9).

The optical properties were deduced in the same way as for the as-grown monograin samples. A shift of the spectra in the Tauc plot in the direction of high wavelengths for the 5NQ samples can be observed, while for the 5NS samples, the changes are rather small, hardly detectable in the opposite direction. The obtained band gap energy can be found in Table IV. Similar results on the band gap variation in ordered and disordered samples have been published for the CZTSSe polycrystalline thin films with $\text{S}/(\text{S} + \text{Se}) = 0.92$ and $x = 1.0$ [10,12], although in those reports the order parameter has not been determined experimentally. The PL properties of the annealed CZTSSe monograins are similar to those of the as-grown: a broad PL emission with FWHM of about 0.2 eV

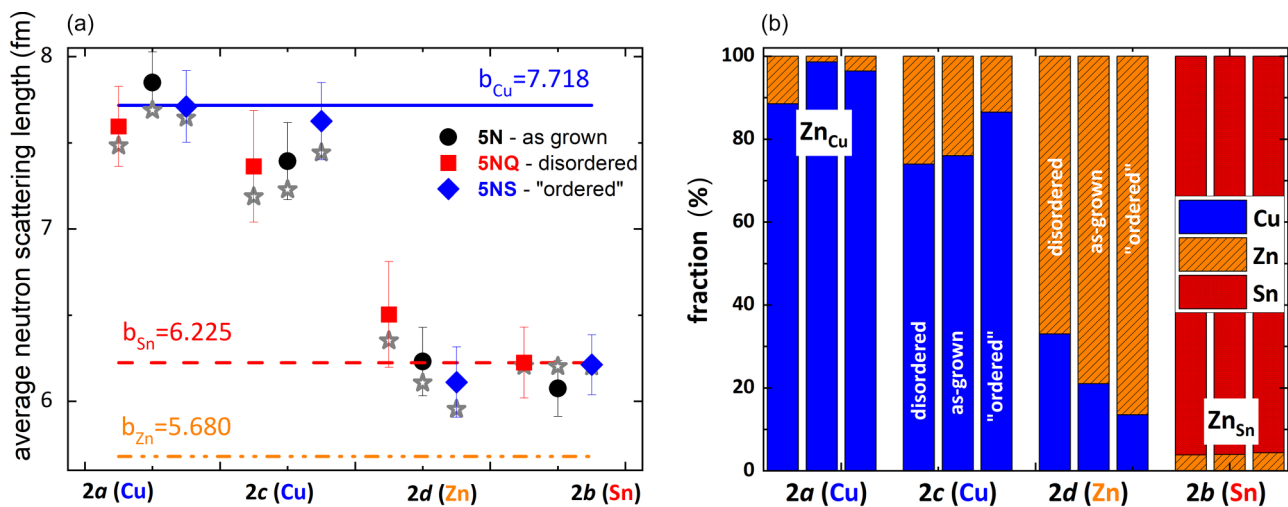


FIG. 8. (a) Average neutron scattering length $\bar{b}$ of the cation sites $2a$, $2c$, $2d$, and $2b$ for 5N, 5NQ, and 5NS powders, (full symbols—experimental values; star—calculated values from best distribution model; lines—pure elements). (b) The resulting cation distribution on the structural sites $2a$, $2b$, $2c$, and $2d$ for 5N, 5NQ, and 5NS samples, obtained from the in-depth analysis of neutron diffraction data.

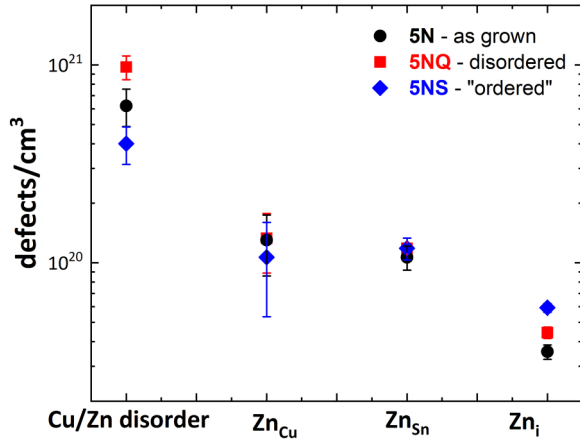


FIG. 9. Concentration of Cu_{Zn} and Zn_{Cu} antisites related to Cu/Zn disorder as well as Zn_{Cu} , Zn_{Sn} , and Zn_{i} point defects related to the off-stoichiometric composition (defects/ cm^3) obtained from neutron diffraction for annealed samples.

[Fig. 10(b)]. The PL emission maximum associated with the band-to-acceptor transition energy follows the change of the band gap energy for the disordered sample (5NQ). However, a slightly different increase (~ 0.03 eV) of the defect transition energy is observed in the ordered sample (5NS). This most likely indicates either that ordering (less Cu/Zn disorder) moves the defect states toward the valence band or that it reduces the formation of the tail states near the conduction band minimum [35]. Earlier works have not found any clear influence of the order-disorder treatment on the band tailing in CZTSSe thin film samples [10,36]. Also noting a larger uncertainty (~ 0.02 eV) involved in our estimate of the PL emission shift compared to band gap energy for the 5NS sample, we conclude that a more direct measurement is needed to probe band tailing in ordered monograin samples. Figure 10(b) also shows that the PL intensity of the defect transition is higher by a factor of 2 in the disordered sample (5NQ), which might be related to a higher doping [37].

Unfortunately, it was impossible to produce solar cells from the annealed material, which does not allow us to

make a statement on the changes in the performance of these monograins.

IV. CONCLUSIONS

Neutron diffraction, wavelength-dispersive x-ray spectroscopy, diffuse reflectance spectroscopy, and photoluminescence were used to investigate the influence of the purity of copper used for the synthesis of CZTSSe monograins on structural, optical, and PV device parameters. These studies showed a very similar chemical composition and phase content as well as optoelectronic properties in CZTSSe monograins grown with 5N and 6N copper, respectively, while the Cu/Zn disorder and the device efficiency change drastically. The monograin where the 6N purity of Cu was used shows less Cu/Zn disorder and a higher efficiency. After “ordering” and “disordering,” annealing procedures were applied to the CZTSSe monograin grown from 5N pure copper; no significant changes in the chemical composition or phase content were detected. But the Cu/Zn disorder follows the trend reported previously—the “ordered” CZTSSe shows a decrease in Cu/Zn disorder, while in the “disordered” CZTSSe, the Cu/Zn disorder increases drastically. Such an “ordering” procedure brings the quality of the 5N monograin very close to the 6N one, concerning the Cu/Zn disorder. The optoelectronic properties of these compounds initially show no difference for both E_g determined from DRS and PL_{max} . The changes after the annealing procedures follow the same trend in both methods—the E_g and PL_{max} are shifting to the lower energy values for “disordered” CZTSSe. There is almost no change in E_g for the “ordered” CZTSSe, while the PL_{max} slightly shifts to the higher energy. Such a behavior is most likely an indication of the ordering either moving the defect states toward the valence band or that it reduces the formation of the tail states near the conduction band minimum. These results, obtained on CZTSSe monograins, allow us to bridge the gap between the fundamental understanding of the Cu/Zn disorder and the performance of these materials in solar cells.

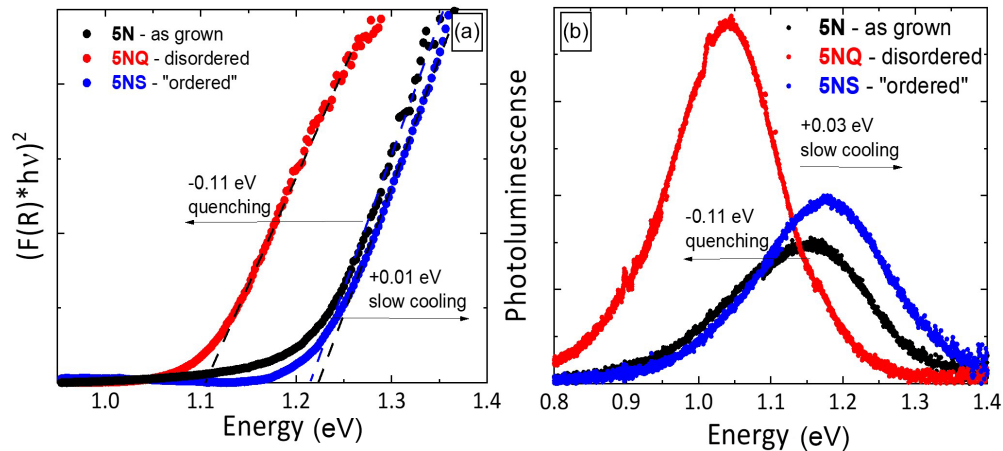


FIG. 10. The (a) Tauc plots for the bandgap determination of the powders. (b) PL of 5N, 5NQ, and 5NS monograin samples at room temperature.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available upon publication because it is not technically feasible and/or the cost of preparing, depositing, and hosting the data would be prohibitive within the terms of this research project. The data are available from the authors upon reasonable request.

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