Calculation of point defect concentration in $\text{Cu}_2\text{ZnSnS}_4$, insights into the high-temperature equilibrium and quenching.

V. Kosyak,^{1,a)} A.V. Postnikov,² J. Scragg,¹ M.A. Scarpulla^{3,4} and C. Platzer-Björkman¹

¹Department of Engineering Sciences, Solid State Electronics, Ångström Solar Center, Box 534, 751 21, Uppsala, Sweden.

²LCP-A2MC, Institut Jean Barriol, University of Lorraine, ICPM, 1 Bd Arago, Metz F-57078, France

³Materials Science and Engineering, University of Utah, Salt Lake City, UT-84112, USA

⁴Electrical and Computer Engineering, University of Utah, Salt Lake City, UT-84112, USA

^{a)}Electronic mail: volodymyr.kosyak@angstrom.uu.se

Abstract

Herein we study the native point defect equilibrium in $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) by applying a statistical thermodynamic model. The stable chemical-potential space (SCPS) of CZTS at elevated temperature was estimated directly, on the basis of deviations from stoichiometry calculated for the different combinations of chemical potential of the components. We show that the SCPS is narrow due to high concentration of $(V_{\text{Cu}}^- - \text{Zn}_{\text{Cu}}^+)$ complex which is dominant over other complexes and isolated defects. The CZTS was found to have p-type conductivity for both stoichiometric and Cu-poor/Zn-rich composition. It is established that the reason for this is that the majority of donor-like Zn_{Cu}^+ antisites are involved in the formation of $(V_{\text{Cu}}^- - \text{Zn}_{\text{Cu}}^+)$ complex making Cu_{Zn}^- dominant and providing p-type conductivity even for Cu-poor/Zn-rich composition. However, our calculation reveals that the hole concentration is almost insensitive to the variation of the chemical composition within the composition region of the single-phase CZTS due to nearly constant concentration of dominant charged defects. The calculations for the full equilibrium and quenching indicate that hole concentration is strongly dependent on the annealing temperature and decreases substantially after the drastic cooling. This means that precise control of annealing temperature and post-annealing cooling rate are critical for the tuning of electrical properties of CZTS.

I. INTRODUCTION

The past decade's intensive study of the CZTS and $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ compounds as a promising earth-abundant material for solar cell applications enabled the record efficiencies of 12.6 %¹ and 9.2%² for the $\text{Cu}_2\text{ZnSnSe}_4$ and pure CZTS, correspondingly. However, this is still much lower than the theoretically predicted maximum efficiency for CZTS-based solar cells, that is, about 30 %.³ It is well known that Zn-rich/Cu-poor composition is favorable for the high-efficiency CZTS solar cells.⁴⁻⁶ As an off-stoichiometric material is expected to contain high concentration of point defects and their complexes, further progress in CZTS-based solar cells is hardly possible without improving the crystal quality and compositional homogeneity

of thin films; moreover it would demand optimizing the concentration of native point defects. These defects could act as shallow impurity levels or deep traps, affecting the conductivity and recombination losses in the absorber layer and hence the device efficiency.^{5,7}

The highly disordered crystal structure of CZTS was confirmed experimentally.^{8–13} The experimental works^{14–16} focused on electrical and optical characterization of CZTS reveal a number of energy levels in the band gap. In many cases, these levels were associated with different charged native point defects based on results of density functional theory (DFT) calculations of formation energies and ionization levels.^{17–19} Nowadays, the common opinion is that, depending on chemical composition, the Zn_{Cu}^+ is dominant shallow donor while Cu_{Zn}^- and V_{Cu}^- are dominant shallow acceptors, and the Sn_{Zn}^{2+} and Zn_{Sn}^{2-} antisites were considered to be most probable deep traps.^{17–20} These defects can easily form complexes with each other, such as $(Cu_{Zn}^- - Zn_{Cu}^+)$, $(2Cu_{Zn}^- - Sn_{Zn}^{2+})$, $(2Zn_{Cu}^+ - Zn_{Sn}^{2-})$ and $(V_{Cu}^- - Zn_{Cu}^+)$.^{17,18} The opinions regarding the presence of the V_S^{2+} as a mid-gap trap are divided.^{18,19,21}

The theoretical works^{17,18,20,22} contributed significantly to the understanding of the composition-dependent behavior of the point defects and their complexes. In particular, it was established¹⁸ that concentration of charged point defects in CZTS is sensitive to chemical composition. Therefore in the best-case scenario, the electrical properties of the material could be tuned by changing the precursor composition and the growth conditions. But since the synthesis of the CZTS implies high-temperature annealing under sulfur pressure with subsequent cooling to room temperature, it is difficult to make any prediction regarding the point defect concentration by considering only formation energies calculated by DFT for 0 K.

Thus it is necessary to develop a model for calculating the point defect concentration for the material with different chemical composition at a high temperature and after cooling to room temperature. Such a model was developed in our previous work.²³ However, in that work, the concentration of point defects was calculated depending on the chemical potentials of the components, whereas the effect of chemical composition on the point defects' equilibrium was only roughly estimated, by assuming that different sets of the metals' chemical potentials corresponded to deficiency or excess of one or another component.

Later in Refs.^{24,25} the results for calculation of point defect concentrations as a function of chemical composition were reported for the first time. In these studies, the formation energies of point defects were assumed to be constant. However, according to theory outlined in Refs.^{17,18}, the formation energies of the defects are dependent on the chemical potentials of the components and hence should be varied with chemical composition. In addition, the contribution of the vibrational free energy to the total formation energy of the defects was not taken into account. As was shown in Ref.²³, this contribution could be substantial at high temperature. Also, in Ref.^{24,25}, the calculations were done only for the case of high-temperature equilibrium without considering cooling to room temperature, while our results for CZTS²³ show dramatic changes in the concentration of free carriers and point defects after cooling. Moreover, experimental works^{8–10} reveal that the rate of post-growth cooling has a great effect on the order-disorder transition and hence on overall concentration of defects in CZTS.

The main aim of the present study is to estimate SCPS of CZTS at high temperature, and further calculate the concentration of native point defects and free carriers for high-temperature conditions as well as to investigate the influence of cooling on the point defect equilibria. In order to allow direct comparison to experimental data on the effect of growth

conditions on properties of CZTS, the concentration of the point defects and free carriers will be presented as a function of chemical composition and temperature.

II. CALCULATION MODEL

In this study, analogously to our previous work,²³ we consider one-zone annealing of the CZTS under sulfur vapor. This chapter gives a brief description of the main equations and focuses on improvements in the model and calculation procedure.

The point defect equilibrium was described with the help of a quasi-chemical formalism under the assumption of dilute conditions (i.e. number of lattice sites $\gg$ number of defects). In the case of a multi-compound material consisting of several elements $ABCD$..etc., the concentration of the defect X_k^q ($k=ABCD$..etc.) with a charge state q (e.g. $q = 0$ for neutral defect, and $q = -1$ for single charged acceptor) at an elevated temperature can be calculated according to an Arrhenius-type law, expressed as follows (see Refs.^{26–28}):

$$[X_k^q] = g_{electr} g_{struct} [N_k] \exp\left(-\frac{H_{total}^q}{k_b T}\right). \quad (1)$$

Here, g_{electr} is the electronic degeneracy factor, i.e. number of possible spin configurations (numerical values were taken from our work²³), g_{struct} is the structural degeneracy factor, i.e. number of equivalent configurations in which the defect can be incorporated ($g_{struct}=1$ for the isolated vacancies and antisites), $[N_k]$ is the concentration of available lattice sites, i.e. concentration of lattice sites in a stoichiometric material (for example, $[N_k]=[N_{Cu}]=1.247 \cdot 10^{22} \text{ cm}^{-3}$ for the defects in the Cu sub-lattice of CZTS) and H_{total}^q is total formation energy of the defect with a charge state q . The total formation enthalpy of the neutral defects H_{total}^0 can be written analogously to,²⁹ adding the vibrational free energy,

$$H_{total}^0 = F_{vib}^0 + E_{el}^0 + \sum_k n_k \mu_k, \quad (2)$$

here, F_{vib}^0 is the vibrational free energy of the neutral defect, E_{el}^0 is the electronic formation energy of the neutral defect (i.e. sum of the energies of pure elemental constituent in solid state, perfect supercell and supercell with defect), n_k is the number of atoms transferred to ($n_k = -1$) or from ($n_k = 1$) the supercell, and μ_k is the reference chemical potential of the constituent.

By taking into account the transition energy level for the charged defects ε and assuming that vibrational free energies of the neutral and charged defects are equal, it is possible to express H_{total}^q similarly to Refs.^{17,18,30}

$$H_{total}^q = F_{vib}^0 + E_{el}^0 + q(E_F - \varepsilon) + \sum_k n_k \mu_k, \quad (3)$$

where E_F is the Fermi energy referenced to the valance band maximum.

The Fermi energy and hence concentration of point defects can be calculated self-consistently as a function of temperature and the chemical potentials by using the equation of electroneutrality,

$$p - n + \sum_k q [X_k^q] = 0, \quad (4)$$

where p and n are the concentrations of holes and electrons, respectively, which can be expressed by Fermi statistics analogously to Ref.²³

Then, the concentration of neutral complexes may be computed by using known concentrations of involved defects $[X_A]$ and $[X_B]$:²⁶

$$[(X_A - X_B)] = \frac{g_{struct}[X_A][X_B]}{[N_k]} \exp\left(-\frac{H_{int}}{k_b T}\right), \quad (5)$$

where H_{int} is the interaction energy of the involved defects.

In a case of defect complexes, g_{struct} can be determined by considering multiple equivalent configurations as was carried out in Refs.^{24,25}

A concentration of component A in a compound is the sum of the stoichiometric concentration of lattice sites $[N_A]$ and deviation from stoichiometry. The latter is represented by a combination of different point defects (isolated and involved in the formation of complexes) related to the corresponding component,^{31,32} which gives,

$$[A] = [N_A] + [A_i^q] - [V_A^q] + \sum_{m=B,C,D..} [A_m^q] - \sum_{m=B,C,D..} [m_A^q], \quad (6)$$

where A_i^q is the interstitial atom, V_A^q is the vacancy in A sub-lattice, A_m^q and m_A^q are antisite defects.

The concentration of any other component could be calculated similarly to Eq.(6). Thus, the chemical composition in the off-stoichiometric CZTS can be given in the usual form as a ratios of various components, for example $[Cu]/[Sn]$, $[Zn]/([Cu]+[Sn])$ and $S/([Cu]+[Zn]+[Sn])$.

It should be noted that similar to our previous work²³ we focused only on lowest-formation-energy defects such as Cu_{Zn} , V_{Cu} , V_{Zn} , Zn_{Cu} , Zn_{Sn} , and V_S . In the present study, we also include the Sn_{Zn} antisite, since this defect was predicted to be an important deep trap.¹⁸ In a case of defect complexes we considered those having highest interaction energy H_{int} , namely $(Cu_{Zn}^- - Zn_{Cu}^+)$, $(2Cu_{Zn}^- - Sn_{Zn}^{2+})$, $(2Zn_{Cu}^+ - Zn_{Sn}^{2-})$ and $(V_{Cu}^- - Zn_{Cu}^+)$.¹⁸ Thus, we have chosen point defects based on their DFT calculated formation energies. However, a recent experimental study¹³ shows the significant concentration of copper interstitials, and hence the formation of this defect requires further careful theoretical analysis.

The key problem of the calculation of point defects is the determination of the input parameters, first of all, formation energies of the isolated defects H_{total}^q . According to Eq.(3) the H_{total}^q consists of several contributions, discussed in the following.

The vibrational free energies F_{vib}^0 for the most probable defects in CZTS were calculated by us in,²³ and were used in the present work. The contribution from F_{vib}^0 for the additional Sn_{Zn} defect was neglected.

The charge transition level ε and electronic formation energies E_{el}^0 were taken from Ref.³³ As follows from Eq.(2), analogously to our work,²³ the E_{el}^0 and μ_k are considered independently rather than in combination at a discrete point in the chemical potential space.¹⁸

The numerical values for the input parameters of Eqs. 1, 3 and 5 discussed above are summarized in Table I.

The chemical potentials of the components μ_k should be limited by the SCPS of CZTS which, in turn, can be constructed according to formation reaction of secondary phases and of the CZTS itself. The calculation of the SCPS of CZTS was performed in Refs.^{17,18} for the T=0 K conditions. However, formation enthalpies of CZTS (ΔH_{CZTS}) reported in different works are significantly different. The identification of the SCPS of CZTS at real annealing conditions is more complicated than at T=0 K, since it requires to know the formation enthalpies of CZTS and secondary phases (metal sulfides) at a certain pressure and temperature. In fact, the first theoretical paper in this field³⁴ reveals a strong effect of temperature and pressure on enthalpies of CZTS formation reactions. Therefore the SCPS of CZTS identified T=0 K can only serve as an estimate of the boundary conditions while modeling the point defect equilibria at high temperature.

It is difficult to calculate chemical potentials of metals in the case of high-temperature annealing of CZTS, since the equilibrium pressures of the Cu, Zn and Sn are unknown. On the other hand, the temperature-equilibrium pressure dependence of pure sulfur is well defined experimentally; here we used an empirical formula from Ref.³⁵ This makes it possible to determine chemical potentials of the elemental sulfur in terms of standard thermodynamic equations. For instance, in Ref.²³ we have calculated the chemical potential of sulfur vapor, assumed, for simplicity, to be represented by the S_2 molecules only. A recent theoretical study³⁶ reports a universal chemical potential function for the sulfur vapor, which can provide more accurate calculations by considering the sulfur gas as a mixture of the S_2 and S_8 molecules. Therefore, in the present study we calculated the chemical potential of sulfur vapor as a function of pressure and temperature by using equations from Ref.³⁶ In the case of one-zone annealing of CZTS, the chemical potential of sulfur is constant at constant temperature. This gives a starting point for the further determination of the SCPS at high temperature and suggests that this task can be achieved by considering the reactions involving the secondary phases and the CZTS formation, similarly to how it was done at T=0 K conditions in Refs.^{17,18} However, as was mentioned above, this requires to know the formation enthalpies of CZTS and secondary phases at high temperature.

As follows from Eq.1-5, the chemical composition of CZTS at constant temperature can be changed only by varying the metal chemical potentials. This leads to the conclusion that every set of chemical potentials corresponds to a particular concentration of point defects (Eq.1, 3) and hence to a particular chemical composition (Eq.6). One can expect that at high chemical potentials the concentration of the point defects could reach extreme values close to the concentration of the lattice sites giving an approach to set the boundary of the SCPS. Thus, we speculate that it is possible to construct the SCPS of the stable CZTS not only by considering

the reaction of the secondary phase formation but also by calculation of the point defects concentration and consequently chemical composition for the different combination of the metals chemical potentials. This way, the problem reduces to a selection of the sets that match reasonable chemical composition.

To determine the point defect concentration under different temperature conditions we consider two distinct cases:

- 1) Full equilibrium of the point defects at a given temperature. With the purpose to study temperature evolution of the point defects' equilibrium, we will calculate the concentration of the point defects at several trial temperatures within the range 550 down to 27 °C, assuming that the point defects would equilibrate even at low-temperature conditions. For instance, the room-temperature equilibrium of the point defects in CZTS was considered in Ref.¹⁸ It is not clear what is the minimal temperature required for the equilibrium conditions. It is thought³⁷ that point defect equilibrium takes place under high temperature, namely >0.5 melting point of the material (about 490 °C for the CZTS³⁸).
- 2) Quenching of the defects, i.e. a rapid cooling from high to room temperature. Quenching means that while the total concentration of the defects is determined by the annealing temperature, and remains constant during instantaneous cooling, the concentration of free carriers is variable.^{23,39–42} Consequently, one can expect a shift in the Fermi energy and a redistribution of concentrations of neutral and charged defects. The defects' concentration on quenching was calculated analogously to Ref.,²³ namely the total concentration of the defects was defined at high temperature and, then the concentrations of free carriers and ionized defects were recomputed at room temperature.

It is not obvious which of the above approximations is more suitable to describe point defect equilibria in real samples, the decision would depend on annealing conditions and post-annealing cooling. However, in our opinion, the quenching of the defects seems more realistic, especially in a case of thin films annealing when the cooling rate is rather high.

The calculations were done using a self-made Matlab script which allows operating with large input arrays.

III. RESULTS AND DISCUSSION

First of all, we determined the SCPS at $T=550$ °C. For this purpose, the chemical potential of sulfur (μ_S) was calculated at this temperature and kept constant. In particular, the calculation of sulfur vapor pressure at $T=550$ °C yields 3.72×10^5 Pa, which sets the chemical potential of sulfur at -0.385 eV. The chemical potentials of the metals were varied with a step of 0.01 eV in a range from $\mu_k=0$ eV ($\mu_k=0$ corresponds to the formation of pure phase of the component¹⁷) to -0.7, -1.9 and -1.45 eV for Cu (μ_{Cu}), Zn (μ_{Zn}) and Sn (μ_{Sn}) chemical potentials, correspondingly. Then, the point defect concentrations were calculated for all possible combinations of chemical potentials. While scanning throughout the output array, the sets showing extremely high concentrations of the point defects i.e. $[N_k] < [X_k^q]$ were excluded. It should be noted that $[N_k] < [X_k^q]$ condition is not consistent with the dilute limit (i.e. $[N_k] \gg$

$[X_k^q]$) and could be used only for the preliminary estimate of the SCPS. Then we found the combinations of chemical potentials for which the values of $[Cu]/[Sn]$, $[Zn]/([Cu]+[Sn])$ and $S/([Cu]+[Zn]+[Sn])$ do not exceed the limits of 1.75-2, 0.33-0.46 and 1-1.3, correspondingly. The results of this calculation are plotted in Fig.1 (a) and (b) as a map of the $[Zn]/([Cu]+[Sn])$ and $S/([Cu]+[Zn]+[Sn])$ composition ratios in a two-dimensional space of the chemical potentials.

Fig.1. The distribution of composition ratios $[Zn]/([Cu]+[Sn])$ (a) and $S/([Cu]+[Zn]+[Sn])$ (b) in metals chemical potentials space at $T=550$ °C.

Note that in Ref.¹⁸ the chemical potential of sulfur was varied and hence it is difficult to compare our results with this work. Nevertheless, we denoted points by (A, P, etc.) corresponding to the same Sn chemical potentials (-0.29, -0.49 eV, etc.) as in Refs.^{17,18} As follows from Fig. 1(a), the region of reasonable values of $[Zn]/([Cu]+[Sn])$ is rather narrow, less than 1 eV in the broadest part at high metal chemical potentials, but extends from -1.4 to 0 eV, from -1.85 to -1.14 eV and from -0.6 to -0.18 eV for μ_{Sn} , μ_{Zn} and μ_{Cu} , correspondingly. These results correlate with¹⁸ where the bottom limits for μ_{Zn} and μ_{Cu} were found to be -1.75 and -0.55 eV (near the G point), correspondingly. The chemical potential of tin μ_{Sn} is limited only at the low range of chemical potentials by -1.4 eV, whereas even at $\mu_{Sn}=0$ eV the value of $[Zn]/([Cu]+[Sn])$ is close to stoichiometric.

We speculate that this is due to underestimated formation energy of the Sn_{Zn} antisite, since one can expect high concentrations of this defect at extremely high μ_{Sn} close to 0 eV (from the A point to 0 eV) and hence deviation from stoichiometry toward Sn-rich compositions. Thus the direct determination of the SCPS of CZTS immediately from the deviation from stoichiometry requires precisely defined formation energies of the point defects. Therefore, the formation enthalpies of secondary phases and of CZTS should be also taken into account for a more refined calculation.

The presence of Zn and Sn-related secondary phases in a region of high μ_{Sn} and μ_{Zn} (from point A to 0 eV) is not confirmed by our calculations. However theoretical works^{18,34} show that the formation of ZnS , SnS and SnS_2 phases is thermodynamically favorable, since their enthalpies of formation (ΔH) are rather low. In particular, in standard conditions ΔH_{ZnS} , ΔH_{SnS} and ΔH_{SnS_2} are -1.62, -1.01 and -1.25 eV, correspondingly.³⁴ The upper limit of the Zn

and Sn chemical potentials could be estimated by taking into account a calculated sulfur chemical potential μ_S of -0.385 eV and that, to avoid formation of the secondary phases, the relations $\mu_{Zn} + \mu_S < \Delta H_{ZnS}$, $\mu_{Sn} + \mu_S < \Delta H_{SnS}$ and $\mu_{Sn} + 2\mu_S < \Delta H_{SnS_2}$ must be satisfied.¹⁸ This yields the following chemical potential limits: of -1.24 and -0.63 eV for μ_{Zn} and μ_{Sn} , correspondingly. It should be noted that the formation enthalpies of the Cu-related secondary phases are comparatively high,^{18,34} for example $\Delta H_{Cu_2S} = -0.47$ eV,³⁴ this makes it unlikely that such phases would be formed even at maximal μ_{Cu} of -0.18 eV. We denote the point which corresponds to a maximum limit of μ_{Sn} by F because of similar chemical potentials of the components as for point F in Ref.¹⁷ Considering only the upper limit for μ_{Zn} it is possible to conclude that A, N-N1 and P-P1 points could be included to the SCPS of CZTS analogously to Ref.¹⁸ This seems especially possible for the N-N1 and P-P1 points because the CZTS formation enthalpy at these points is close to the theoretically predicted value of about -4.2 eV.¹⁸ However the position of the F point suggests that the upper limit for μ_{Zn} is about -1.47 eV and the N-N1 and P-P1 points must be excluded. Thus, F is considered as a border point of the SCPS, indicating an upper limit for the metal chemical potentials. At the same time, it is necessary to estimate a bottom limit for the metal chemical potentials. The distribution of the $S/([Cu]+[Zn]+[Sn])$ ratio in Fig.1 (b) gives additional useful information about the lower limits in the SCPS. As could be seen from Fig.1 (b), the decrease in metal chemical potentials leads to gradual increase in $S/([Cu]+[Zn]+[Sn])$ values indicating sulfur excess. This trend is clearly visible at low ranges of the metal chemical potentials. Therefore the chemical-potential space along the M-Q-G line corresponds to metal loss, most likely Cu and Sn, because the map in Fig.1 (a) shows high values of $[Zn]/([Cu]+[Sn])$ ratio at this range. The region around M, Q, and G points can be excluded from the stable chemical-potential region. This implies that the bottom limit is situated between the F and M points. However, it is reasonable to consider a range at which $S/([Cu]+[Zn]+[Sn])$ ratio and hence probability of the metal loss is minimal. Therefore we focused on the analysis of point defect equilibria for the SCPS close to the F-F1 line.

For a more accurate determination of the SCPS near the F-F1 line, the concentration of point defects and free carriers was recalculated by using the same approach as above but for constant μ_{Sn} of -0.63 eV and for μ_{Zn} and μ_{Cu} varied with a smaller step of 0.001 eV in narrow ranges from -1.45 to -1.5 eV and -0.4 to -0.35 eV, respectively. The results of this calculation are presented in Fig. 2(a) as a map of hole concentration in a composition ratio scale for full equilibrium at $T=550$ °C and quenching to room temperature. As was mentioned before, the total concentration of defects is not changed after the rapid cooling, and hence SCPS for full equilibrium and quenching coincide.

The F2-F5 points represent boundary values in the SCPS. It follows from Fig. 2(a) that a small variation of the chemical potentials near the F-F1 line leads to a significant deviation from stoichiometry. The maximal deviation from stoichiometry, i.e. $[Zn]/([Cu]+[Sn])=0.33$ and $[Cu]/[Sn]=2$, calculated in compliance with the $[N_k] < [X_k^q]$ conditions are 0.39 and 1.79 for the $[Zn]/([Cu]+[Sn])$ and $[Cu]/[Sn]$ ratios, correspondingly. However the mapping of the $S/([Cu]+[Zn]+[Sn])$ ratio (Fig.2(b)) shows high sulfur excess at very Cu-poor conditions (F4-F5-F6 triangle area) suggesting that the SCPS is limited by the F4-F2, F4-F6, F6-F3 and F3-F2 lines. As could be seen from Fig. 2 (a) the hole concentration only slightly decreases with

increasing deviation from stoichiometry. In particular, along the F2-F5 line, the hole concentration is varied from about 1×10^{19} to $1.26 \times 10^{19} \text{ cm}^{-3}$ and from about 2×10^{16} to $2.58 \times 10^{16} \text{ cm}^{-3}$, in a case of full equilibrium and quenching, correspondingly. Thus our calculations show that the hole concentration is not very sensitive to chemical composition, but drastically decreases throughout three orders of magnitude after the quenching.

Fig.2. The distribution of hole concentration (a) and S/([Cu]+[Zn]+[Sn]) ratio (b) over chemical composition at $T=550^\circ\text{C}$.

To explore the cause of such behavior, we plot composition dependencies of the point defect and hole concentrations for the cases of full equilibrium and of quenching. Similar to Fig. 2(a), the concentration map can be constructed for any point defect. Here, in order to present all concentration curves on the same, more conventional, concentration-chemical composition plot, the concentration of each point defect was plotted as a function of $[Zn]/([Cu]+[Sn])$ and $[Cu]/[Sn]$ ratios only for some points of the chemical-potential region (Fig. 2(a)). By keeping in mind the preferable chemical composition of the CZTS solar cells,⁴⁻⁶ we selected points which correspond to Zn-rich/Cu-poor and, for the comparison, to stoichiometric composition. Namely, we consider points on the F2-F6 line and for Cu-poor conditions points on the perpendicular line from F6 to the intersection with x-axis at $[Cu]/[Sn]=1.90$. The plots are presented in Figs. 3 and 4.

Fig.3. The composition dependencies of the Fermi energy, holes and point defects concentration for the points on F2-F6 line of chemical potentials space, full equilibrium at $T=550$ °C (a) and quenching to the room temperature (b).

As follows from Fig.3 (a), regardless of composition, the Fermi energy is almost constant at 0.05 eV; this is reflected in an insignificant decrease in hole concentration from 1.26×10^{19} to 1.06×10^{19} cm $^{-3}$ with deviation from stoichiometric to Zn-rich/Cu-poor composition. This could be explained by similar differences in concentrations between the dominant Cu_{Zn}^- acceptor and Zn_{Cu}^+ donor, which leads to Fermi level pinning. In particular, the concentration of the Cu_{Zn}^- acceptors is about 10^{20} cm $^{-3}$ and it is always only slightly higher than the concentration of the Zn_{Cu}^+ donors. Much lower concentrations of the V_{Cu}^- of about 1×10^{17} cm $^{-3}$, even at Cu-poor composition, indicates small effect of the copper vacancy on doping level. The acceptor-like V_{Zn}^0 shows much lower concentration than V_{Cu}^0 of about 3×10^{13} cm $^{-3}$, while concentrations of charged Zn vacancies are even less than 10^{13} cm $^{-3}$.

The concentrations of shallow defects are much higher than concentrations of the Sn_{Zn}^{2+} , Sn_{Zn}^+ and V_S^{2+} deep donors of 2×10^{16} cm $^{-3}$, 9×10^{13} and 1×10^{13} cm $^{-3}$, correspondingly. The reason of the relatively high concentration of the Sn_{Zn}^+ is that the μ_{Zn} is much lower than the μ_{Sn} for all points of the SCPS (Fig.2). According to Eq.(3), this leads to decreases in the total formation energy and hence increases in the defect concentration. Although, the Sn_{Zn}^{2+} was found to be clearly dominant over other deep donors, one should bear in mind that, unlike the rest of the defects, we neglected the contribution from F_{vib}^0 to the total formation energy of the Sn_{Zn} , which could significantly change its concentration.

Fig.4. The composition dependencies of the Fermi energy, hole and point defects concentration for the points in chemical potentials space corresponding to constant $[Cu]/[Sn]=1.90$ and $[Zn]/([Cu]+[Sn])$ varied from 0.33 to F6 point, full equilibrium at $T=550$ °C (a) and quenching to the room temperature (b).

Thus, it is possible to conclude that the formation of the defects related to Cu-Zn disorder mainly influences the hole concentrations and the dominance of the Cu_{Zn}^- acceptor over Zn_{Cu}^+ donor provides p-type conductivity of the CZTS.

In general, the concentration of the neutral complexes is higher than the concentration of the charged defects, indicating a high level of complexation. Moreover, the $(V_{Cu}^- - Zn_{Cu}^+)$ complex shows highest concentration among all defects, increasing from 8×10^{20} to $9 \times 10^{20} \text{ cm}^{-3}$ with a deviation from stoichiometry toward Zn-rich/Cu-poor composition. At stoichiometric composition, the concentration of the $(2Zn_{Cu}^+ - Zn_{Sn}^{2+})$ complex of $0.5 \times 10^{20} \text{ cm}^{-3}$ is almost the same as $(2Cu_{Zn}^- - Sn_{Zn}^{2+})$, while it is expectedly higher, but not significantly, at Zn-rich/Cu-poor composition. Such a high concentration of defect complexes, especially $(V_{Cu}^- - Zn_{Cu}^+)$, makes them responsible for deviation from stoichiometry of composition along with Cu_{Zn}^0 , Cu_{Zn}^- and Zn_{Cu}^+ dominant defects.

It should be noted that the calculations reveal unrealistically high concentrations of the $(Cu_{Zn}^- - Zn_{Cu}^+)$ complex of $6 \times 10^{23} \text{ cm}^{-3}$ at 550 °C (not shown in Fig.3 (a)). This is due to the high concentration of involved defects and high interaction energy. The presence of the $(Cu_{Zn}^- - Zn_{Cu}^+)$ complex has no influence on deviation from stoichiometry and, in general, on the determination of the stable potential region of the CZTS as well as on compositional dependencies of Fermi energy and point defect concentration. However, an extremely high concentration of the $(Cu_{Zn}^- - Zn_{Cu}^+)$ complex implies complete rearrangement of the atoms in

the Cu and Zn sub-lattices and hence the use of the DFT formation energies calculated under assumption of the dilute solution case becomes questionable.

Here we ignore possible effects of the $(Cu_{Zn}^- - Zn_{Cu}^+)$ complex high concentration on formation energies of the defects. However one should bear in mind that, if the concentration of isolated defects or complexes is close to the density of lattice sites, the formation energies of the defects must be reconsidered.

As can be seen from Fig. 3(b), the rapid cooling leads to a shift in Fermi level towards the conduction band, by about 0.14 eV, and hence to a redistribution of neutral and charged defects. For instance, as compared to full equilibrium, the concentration of the V_{Cu}^- is twice as high and in the case of the V_{Cu}^0 it drops by one order of magnitude after quenching. Also the difference between the concentration of the Cu_{Zn}^- and Zn_{Cu}^+ is reduced, which indicates a higher level of compensation in quenched material. This results in a dramatic decrease in hole concentration by about three orders of magnitude.

The concentration of the Sn_{Zn}^{2+} and V_S^{2+} remains almost the same after the rapid cooling, namely of about $2 \times 10^{16} \text{ cm}^{-3}$ and $1 \times 10^{13} \text{ cm}^{-3}$, correspondingly, while the concentration of the Sn_{Zn}^+ increases to the level of Sn_{Zn}^{2+} . Hence, as in a case of high temperature equilibrium, these defects have little effect on the doping level. However, these donor-like deep traps, especially Sn_{Zn}^{2+} and Sn_{Zn}^+ , could significantly affect the transport or recombination of photogenerated electrons.

The calculation of the hole and point defect concentrations for $[Cu]/[Sn]=1.90$ and $[Zn]/([Cu]+[Sn])$ varied from 0.33 to the F6 point shows no significant difference between stoichiometric and Cu-poor conditions. As follows from comparison of Fig.3 and Fig.4, the trends in compositional behavior of point defect concentration for stoichiometric and Cu-poor conditions are very similar, except that the concentration of $(V_{Cu}^- - Zn_{Cu}^+)$ is higher in Cu-poor samples.

A high concentration of the $(V_{Cu}^- - Zn_{Cu}^+)$ and $(2Zn_{Cu}^+ - Zn_{Sn}^{2-})$ complexes implies the existence of so-called A-type and B-type substitutions, correspondingly. Moreover, our calculations show that the A-type substitution is dominant. This is consistent with experimental results obtained by Raman spectroscopy showing presence of the A-type and B-type complexes in Zn-rich/Cu-poor CZTS.¹⁰ At the same time, the concentration of the $(2Cu_{Zn}^- - Sn_{Zn}^{2+})$ is also rather high and the presence of this complex could have a significant effect on material properties. According to theoretical work,¹⁸ the formation of the $(V_{Cu}^- - Zn_{Cu}^+)$ and $(2Zn_{Cu}^+ - Zn_{Sn}^{2-})$ clusters leads to band-gap fluctuation by about 100 meV, which could affect light absorption and energy band alignment in CZTS-based solar cells. However such fluctuations are much lower than for the $(2Cu_{Zn}^- - Sn_{Zn}^{2+})$ clusters, namely the band gap could shrink to about 1.15 eV.¹⁸ Thus the dominance of the $(V_{Cu}^- - Zn_{Cu}^+)$ and $(2Zn_{Cu}^+ - Zn_{Sn}^{2-})$ complexes over $(2Cu_{Zn}^- - Sn_{Zn}^{2+})$ could be the reason why Zn-rich/Cu-poor composition was found to be beneficial for high-efficiency solar cells.⁴³ We note that the $(Cu_{Zn}^- - Zn_{Cu}^+)$ complex is at high concentration in all chemical potential regions, and is also thought to introduce large band gap fluctuations.¹⁸

Experimental structural analysis of the CZTS shows that the substitution of Cu atoms by Zn atoms significantly prevails in both Zn-rich/Cu-poor (A-type) and Cu-poor/Sn-poor (B-type) materials.^{12,13} Thus one can expect a dominance of the Zn_{Cu}^+ shallow donor over other

charged defects which, in turn, could lead to n-type conductivity. But according to our calculations, the major amount of the Zn_{Cu}^+ is involved in formation of the $(V_{Cu}^- - Zn_{Cu}^+)$ and $(Cu_{Zn}^- - Zn_{Cu}^+)$ neutral complexes. This makes the Cu_{Zn}^- shallow acceptor dominant and explains the p-type conductivity of Zn-rich/Cu-poor CZTS.

The high concentration of the defect complexes and Cu_{Zn}^0 , Cu_{Zn}^- and Zn_{Cu}^+ dominant defects explains high sensitivity of the $[Zn]/([Cu]+[Sn])$ and $[Cu]/[Sn]$ ratios to the variation of the metal chemical potentials, consequently, the SCPR of CZTS is very narrow. This, in turn, restricts variation of the acceptors and donors. As a result the hole concentration is hardly changed with chemical composition. Thus, we speculate that large variation of doping level with chemical composition observed experimentally⁴⁴⁻⁴⁶ is rather related to formation of the secondary phases than due to changes in concentration of the native point defects.

In contrast to the full equilibrium conditions, in which the hole concentration is very high at $1.2 \times 10^{19} \text{ cm}^{-3}$ (which means that the material is nearly a degenerate semiconductor), the hole concentration of $2.2 \times 10^{16} \text{ cm}^{-3}$ determined for the case of quenching is in a good correlation with experimental observations of the doping level in CZTS solar cells.⁴⁷⁻⁵⁰ However, this comparison is not quite appropriate since the electrical properties of CZTS(Se) strongly depend on the presence of sodium^{51,52} which typically diffuses from the soda-lime glass substrate.

The temperature dependencies of the point defect concentrations under full equilibrium conditions for material with composition $[Zn]/([Cu]+[Sn])=0.345$ and $[Cu]/[Sn]=1.9$ are presented on Fig. 5(a).

Fig.5. Temperature dependencies of the point defects under full equilibrium conditions (a) and hole concentration (b) for the material with composition of $[Zn]/([Cu]+[Sn])=0.345$ and $[Cu]/[Sn]=1.9$; points 1, 2 and 3 represents hole concentration for the cases of full equilibrium at annealing temperature (823 K), full equilibrium at room temperature and after the quenching from annealing to room temperature, correspondingly. The dashed red line at $T=763 \text{ K}$ (0.5 of melting point of CZTS) indicates possible critical temperature below which point defect equilibrium can hardly be reached.

As could be seen from Fig. 5(a), the concentrations of defects significantly decrease with temperature. However, the rate of decrease is different for different defects. For example,

the rate of decrease of Zn_{Cu}^+ is much higher than of Cu_{Zn}^- , especially in the low-temperature range of 550-300 K. This makes Cu_{Zn}^- a clearly dominant charged defect which solely determines the doping level in the material. The concentrations of the defect complexes are also dropping drastically with temperature, except $(V_{Cu}^- - Zn_{Cu}^+)$ complex. This leads to the conclusion that at low-temperature equilibrium (if it was to be reached), the deviation from stoichiometry mainly depends on the presence of $(V_{Cu}^- - Zn_{Cu}^+)$ complexes.

The temperature behavior of the hole concentration, curve 1-2 in Fig. 5(b), is similar to that of the dominant Cu_{Zn}^- , namely its rate of decrease is higher in the low-temperature range. As follows from Fig. 5(b), the hole concentration after the quenching (point 3) is about five times higher than in a case of full equilibrium at room temperature (point 2). This could be explained by the different mechanism of doping, in particular in a case of quenching the concentration of dominant charged defects is high and concentration of holes determined by compensation of Cu_{Zn}^- by Zn_{Cu}^+ (Fig. 4 (b)). On the contrary, under low-temperature equilibrium the hole concentration depends only on Cu_{Zn}^- (Fig. 5). Thus, we claim that the concentration of the free carriers in CZTS is strongly related to annealing and cooling conditions. In other words, it matters whether the annealing temperature is high enough to maintain equilibrium conditions, as well as whether the cooling rate is sufficient to provide an efficient quenching of the defects.

IV. CONCLUSIONS

The proposed approach allows estimation of the SCPS of CZTS at high temperature directly from calculated deviation from stoichiometry. However, more reliable analysis requires accurate values of the formation energies of the point defects.

It was shown that crystal structure of CZTS is highly disordered, which manifests itself in high concentration of the Cu_{Zn}^0 , Cu_{Zn}^- and Zn_{Cu}^+ dominant defects as well as $(V_{Cu}^- - Zn_{Cu}^+)$, $(2Zn_{Cu}^+ - Zn_{Sn}^{2-})$ and $(2Cu_{Zn}^- - Sn_{Zn}^{2+})$ complexes. As a result the deviation from stoichiometry is very sensitive to the metal chemical potentials. On the other hand the hole concentration is weakly dependent on chemical composition due to compensation of Cu_{Zn}^- by Zn_{Cu}^+ and because of the very narrow SCPS, which limits variation of concentration of the dominant acceptors and donors. It should be noted that the predicted hole concentration of about $2.2 \times 10^{16} \text{ cm}^{-3}$ for quenched material is much more reasonable than $1.2 \times 10^{19} \text{ cm}^{-3}$ as found in a case of full equilibrium at $T=550^\circ\text{C}$.

The so-called A-type $(V_{Cu}^- - Zn_{Cu}^+)$ complex was found to be dominant for Zn-rich/Cu-poor and stoichiometric composition, with a concentration of about $8 \times 10^{20} \text{ cm}^{-3}$. Thus we speculate that even in case of small deviation from stoichiometry the formation of large clusters of the $(V_{Cu}^- - Zn_{Cu}^+)$ complexes and hence fluctuations in band-gap energy are possible. This is also the case for the $(Cu_{Zn}^- - Zn_{Cu}^+)$, which occurs in high concentration at all compositions. The presence of the $(V_{Cu}^- - Zn_{Cu}^+)$ complexes suppresses formation of Zn_{Cu}^+ isolated defects and makes the Cu_{Zn}^- dominant over all other charged defects at even Zn-rich/Cu-poor conditions.

The calculations show that donor-like tin antisites S_{Zn} and sulfur V_S vacancy with concentration of about 10^{16} and 10^{13} cm^{-3} , correspondingly, could act as important deep traps.

It was determined that the concentration of holes in samples quenched from high to room temperature is significantly higher than in samples under low-temperature equilibrium conditions. This leads to the conclusion that the concentration of the free carriers is equally dependent on annealing (temperature and vapor pressure) and post-annealing conditions (e. g. cooling rate).

ACKNOWLEDGMENTS

Financial support from the Swedish Research Council and Wallenberg Academy Fellows program is acknowledged.

References

- ¹W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, and D.B. Mitzi, *Adv. Energy Mater.* **4**, 1301465 (2014).
- ²K. Sun, C. Yan, F. Liu, J. Huang, F. Zhou, J.A. Stride, M. Green, and X. Hao, *Adv. Energy Mater.* **6**, 1600046 (2016).
- ³W. Shockley and H.J. Queisser, *J. Appl. Phys.* **32**, 510 (1961).
- ⁴C. Platzer-Björkman, J. Scragg, H. Flammersberger, T. Kubart, and M. Edoff, *Sol. Energy Mater. Sol. Cells* **98**, 110 (2012).
- ⁵X. Liu, Y. Feng, H. Cui, F. Liu, X. Hao, G. Conibeer, D.B. Mitzi, and M. Green, *Prog. Photovoltaics Res. Appl.* **24**, 879 (2016).
- ⁶Y. Feng, B. Yu, G. Cheng, T. Lau, Z. Li, L. Yin, Q. Song, C. Yang, and X. Xiao, *Energy Environ. Sci.* **6**, 3171 (2013).
- ⁷A. Polizzotti, I.L. Repins, R. Noufi, S.-H. Wei and D.B. Mitzi, *Energy Environ. Sci.* **6**, 3171 (2013).
- ⁸J.J.S. Scragg, L. Choubrac, A. Lafond, T. Ericson, and C. Platzer-Björkman, *Appl. Phys. Lett.* **104**, 41911 (2014).
- ⁹K. Rudisch, Y. Ren, C. Platzer-Björkman, and J. Scragg, *Appl. Phys. Lett.* **108**, 231902 (2016).
- ¹⁰M. Paris, L. Choubrac, A. Lafond, C. Guillot-Deudon, and S. Jobic, *Inorg. Chem.* **53**, 8646 (2014).
- ¹¹A. Ritscher, M. Hoelzel, and M. Lerch, *J. Solid State Chem.* **238**, 68 (2016).
- ¹²A. Ritscher, A. Franz, S. Schorr, and M. Lerch, *J. Alloys Compd.* **689**, 271 (2016).
- ¹³L.E. Valle Rios, K. Neldner, G. Gurieva, and S. Schorr, *J. Alloys Compd.* **657**, 408 (2016).
- ¹⁴P.A. Fernandes, A.F. Sartori, P.M.P. Salomé, J. Malaquias, A.F. Da Cunha, M.P.F. Graça, and J.C. González, *Appl. Phys. Lett.* **100**, 233504 (2012).
- ¹⁵M.J. Romero, H. Du, G. Teeter, Y. Yan, and M.M. Al-Jassim, *Phys. Rev. B* **84**, 165324

- (2011).
- ¹⁶E. Kask, T. Raadik, M. Grossberg, R. Josepson, and J. Krustok, *Energy Procedia* **10**, 261 (2011).
- ¹⁷S. Chen, J.-H. Yang, X.G. Gong, A. Walsh, and S.-H. Wei, *Phys. Rev. B* **81**, 245204 (2010).
- ¹⁸S. Chen, A. Walsh, X.-G. Gong, and S.-H. Wei, *Adv. Mater.* **25**, 1522 (2013).
- ¹⁹D. Han, Y.Y. Sun, J. Bang, Y.Y. Zhang, H.-B. Sun, X.-B. Li, and S.B. Zhang, *Phys. Rev. B* **87**, 155206 (2013).
- ²⁰P. Sarker, M.M. Al-Jassim, and M.N. Huda, *J. Appl. Phys.* **117**, 35702 (2015).
- ²¹X. Zhang, M. Han, Z. Zeng, and H.Q. Lin, *RSC Adv.* **6**, 15424 (2016).
- ²²K. Yu and E.A. Carter, *Chem. Mater.* **28**, 4415 (2016).
- ²³V. Kosyak, N.B. Mortazavi Amiri, A. V. Postnikov, and M.A. Scarpulla, *J. Appl. Phys.* **114**, 124501 (2013).
- ²⁴D. Mutter and S.T. Dunham, *IEEE J. Photovoltaics* **5**, 1188 (2015).
- ²⁵D. Mutter and S.T. Dunham, in *2014 IEEE 40th Photovolt. Spec. Conf.* (IEEE, 2014), pp. 2384–2389.
- ²⁶C.G. Van de Walle and J. Neugebauer, *J. Appl. Phys.* **95**, 3851 (2004).
- ²⁷Gaddy Benjamin Erik, *Predictive Calculations of Defects in Thin-Film Heterostructures*, North Carolina State University, 2013.
- ²⁸P. Pichler, *Intrinsic Point Defects, Impurities, and Their Diffusion in Silicon* (Springer, 2004), p. 367.
- ²⁹S.B. Zhang, S.-H. Wei, A. Zunger, and H. Katayama-Yoshida, *Phys. Rev. B* **57**, 9642 (1998).
- ³⁰C.G. Van de Walle, D.B. Laks, G.F. Neumark, and S.T. Pantelides, *Phys. Rev. B* **47**, 9425 (1993).
- ³¹M. Hagen and M.W. Finnis, *Philos. Mag. A* **77**, 447 (1998).
- ³²J. Rogal, S. V. Divinski, M.W. Finnis, A. Glensk, J. Neugebauer, J.H. Perepezko, S.

- Schuwalow, M.H.F. Sluiter, and B. Sundman, *Phys. Status Solidi* **251**, 97 (2014).
- ³³S. Chen, A. Walsh, X.-G. Gong, and S.-H. Wei, *Adv. Mater.* **25**, 1522 (2013).
- ³⁴A.J. Jackson and A. Walsh, *J. Mater. Chem. A* **2**, 7829 (2014).
- ³⁵H. Rau, T.R.N. Kutty, and J.R.F. Guedes de Carvalho, *J. Chem. Thermodyn.* **5**, 291 (1973).
- ³⁶A.J. Jackson, D. Tiana, and A. Walsh, *Chem. Sci.* **7**, 1082 (2016).
- ³⁷C. Freysoldt, B. Grabowski, T. Hickel, J. Neugebauer, G. Kresse, A. Janotti, and C.G. Van de Walle, *Rev. Mod. Phys.* **86**, 253 (2014).
- ³⁸I.D. Olekseyuk, I.V. Dudchak, and L.V. Piskach, *J. Alloys Compd.* **368**, 135 (2004).
- ³⁹F.A. Kröger, *The Chemistry of Imperfect Crystals*. (North-Holland Pub. Co, 1973), p.998
- ⁴⁰J. Maier, *Solid State Ionics* **173**, 1 (2004).
- ⁴¹C. Persson, Y.-J. Zhao, S. Lany, and A. Zunger, *Phys. Rev. B* **72**, 35211 (2005).
- ⁴²Y.S. Yee, B. Magyari-Köpe, Y. Nishi, S.F. Bent, and B.M. Clemens, *Phys. Rev. B* **92**, 195201 (2015).
- ⁴³J.J.S. Scragg, J.K. Larsen, M. Kumar, C. Persson, J. Sandler, S. Siebentritt, and C. Platzer Björkman, *Phys. Status Solidi* **253**, 189 (2016).
- ⁴⁴G. Brammertz, M. Buffière, Y. Mevel, Y. Ren, A.E. Zaghi, N. Lenaers, Y. Mols, C. Koeble, J. Vleugels, M. Meuris, and J. Poortmans, *Appl. Phys. Lett.* **102**, 13902 (2013).
- ⁴⁵J.K. Larsen, J.J.S. Scragg, C. Frisk, Y. Ren, and C. Platzer-Björkman, *Phys. Status Solidi* **212**, 2843 (2015).
- ⁴⁶E. Garcia-Hemme, A. Fairbrother, L. Calvo-Barrio, E. Saucedo, and I. Martil, *IEEE J. Photovoltaics* **6**, 990 (2016).
- ⁴⁷J.J. Scragg, P.J. Dale, L.M. Peter, G. Zoppi, and I. Forbes, *Phys. Status Solidi* **245**, 1772 (2008).
- ⁴⁸C. Frisk, T. Ericson, S.-Y. Li, P. Szaniawski, J. Olsson, and C. Platzer-Björkman, *Sol. Energy Mater. Sol. Cells* **144**, 364 (2016).

- ⁴⁹S. Levchenko, J. Just, A. Redinger, G. Larramona, S. Bourdais, G. Dennler, A. Jacob, and T. Unold, Phys. Rev. Appl. **5**, 24004 (2016).
- ⁵⁰M.M. Islam, M.A. Halim, T. Sakurai, N. Sakai, T. Kato, H. Sugimoto, H. Tampo, H. Shibata, S. Niki, and K. Akimoto, Appl. Phys. Lett. **106**, 243905 (2015).
- ⁵¹A. Nagaoka, H. Miyake, T. Taniyama, K. Kakimoto, Y. Nose, M.A. Scarpulla, and K. Yoshino, Appl. Phys. Lett. **104**, 152101 (2014).
- ⁵²J. V. Li, D. Kuciauskas, M.R. Young, and I.L. Repins, Appl. Phys. Lett. **102**, 163905 (2013).

Table I. Parameters of the point defects formation.

Type of defect	degeneracy factor
----------------	-------------------

		electronic formation energy of the neutral defects E_{el}^0 , (eV)	vibrational free energy F_{vib}^0 ($T=550$ °C) (eV)	charge transition level ε , VBM=0 (eV)	electronic g_{electr}	structural g_{struct}	interaction energy H_{int} , (eV)
Cu_{Zn}	$q=0$	1.42	-0.101		1	1	
	$q=-1$			0.146	2	1	
V_{Cu}	$q=0$	1.14	0.058		1	1	
	$q=-1$			0.0368	2	1	
V_{Zn}	$q=0$	2.9	-0.085		1	1	
	$q=-1$			0.12	2	1	
	$q=-2$			0.256	2	1	
Zn_{Sn}	$q=0$	0.73	0.029		1	1	
	$q=-1$			0.136	2	1	
	$q=-2$			0.28	2	1	
Zn_{Cu}	$q=0$	1.0	-0.422		1	1	
	$q=+1$			1.356	0.5	1	
Sn_{Zn}	$q=0$	2.63	0.0		1	1	
	$q=+1$			0.5	0.5	1	
	$q=+2$			0.5	0.5	1	
V_S	$q=0$	2.86	-0.27		1	1	
	$q=+2$			0.77	0.5	1	
$(Cu_{Zn}^- - Zn_{Cu}^+)$						4	-2.22
$(2Cu_{Zn}^- - Sn_{Zn}^{2+})$						28	-2.11
$(2Zn_{Cu}^+ - Zn_{Sn}^{2-})$						6	-4.66
$(V_{Cu}^- - Zn_{Cu}^+)$						4	-2.32