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Crystal structure and defect reactions in the kesterite solar cell absorber Cu_2ZnSnS_4 (CZTS): Theoretical insights

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Abstract. Cu_2ZnSnS_4 (CZTS) is one of the most promising quaternary absorber materials for thin-film solar cells. Light to electricity conversion efficiencies in CZTS devices have recently reached 9.6%, making it a competitive and more sustainable replacement for existing CdTe and $Cu(In,Ga)Se_2$ (CIGS) thin-film technologies. We review our recent insights into the structural, electronic and defect properties of this topical material. We have found that the stable crystal structure of CZTS is kesterite, which is derived from the ternary chalcopyrite structure. Examination of the thermodynamic stability of CZTS reveals that the stable chemical potential region for the formation of the stoichiometric compound is small. Under these conditions, the dominant defect will be p-type Cu_{Zn} antisite, which has an acceptor level deeper than the isolated Cu vacancy. The dominant self-compensated defect pair is $[Cu_{Zn}+Zn_{Cu}]$, which leads to the formation of various polytype structures. We propose that to maximize the solar cell performance, growth of CZTS under Cu-poor/Zn-rich conditions will be optimal, if the precipitation of ZnS can be avoided. This theoretical guidance can provide new directions for improving the conversion efficiencies of kesterite based solar cells.

Keywords: Kesterite, Stannite, CZTS, Solar Cells
PACS: 61.50.Ah, 71.20.Nr, 71.55.Ht, 72.40.+w

Solar cells involving direct band-gap light absorbing materials offer a clear advantage over silicon based technologies: thin films can be utilized, which use substantially less material and energy to fabricate. While the two prototypal thin-film photovoltaic absorbers (CdTe and $Cu(In,Ga)Se_2$) can achieve solar conversion efficiencies of up to 20% and are now commercially available, the presence of toxic (Cd) and expensive elemental components (In, Te) is a real issue as the demand for photovoltaics rapidly increases. To overcome these limitations, there has been substantial interest in developing viable alternative materials, with Cu_2ZnSnS_4 (CZTS) being one of the most suitable candidate due to its combination of sustainable components and attractive physical properties[1, 2, 3, 4]. It is worth noting that the efficency of CZTS based solar cells has increased from 0.66% in 1996 to almost 10% in 2010.[4]

The details of our simulations have been presented elsewhere[5, 6, 7, 8, 9, 10]. Here, we highlight the key insights that we have provided for this system, in addition to reviewing recent theoretical results from other research groups[11, 12]:

- The lowest energy structure of CZTS is kesterite (space group $I\bar{4}$), which is derived from the ternary chalcopyrite structure[5]. The stannite crystal structure lies higher in energy. We suggest that the experimentally observed "stannite" structure is actually the kesterite structure with disorder in the Cu-Zn sublattice[5].
- The band gaps of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ are close to 1.5 eV and 1.0 eV, respectively[5]. We have called for earlier experimental reports of a 1.5 eV band gap for $Cu_2ZnSnSe_4$ to be re-examined. Moreover, we predict that $Cu_2ZnGeSe_4$ with a band gap of 1.5 eV could be a better absorber material in terms of its expected defect properties[8, 9].
- In the stable chemical potential range, Cu_{Zn} is the dominant p-type defect, lower in energy than the Cu vacancy[6].
- Due to the presence of three cations in the quaternary system, many possible defect complexes exist. Of particularly low energy is the bound anti-site pair between Cu and Zn, which can result in the existence of CZTS polytype structures[9].
- Formation of the $[V_{Cu}^{-}+Zn_{Cu}^{+}]^0$ pair under Zn-rich and Cu-poor conditions should be beneficial for maximizing solar cell performance; however, the precipitation of ZnS has to be avoided[6, 9].
- Type-II band alignment exists for the CdS/Cu_2ZnSnS_4 heterojunction, different from that of $CuInSe_2/CdS$.[9].

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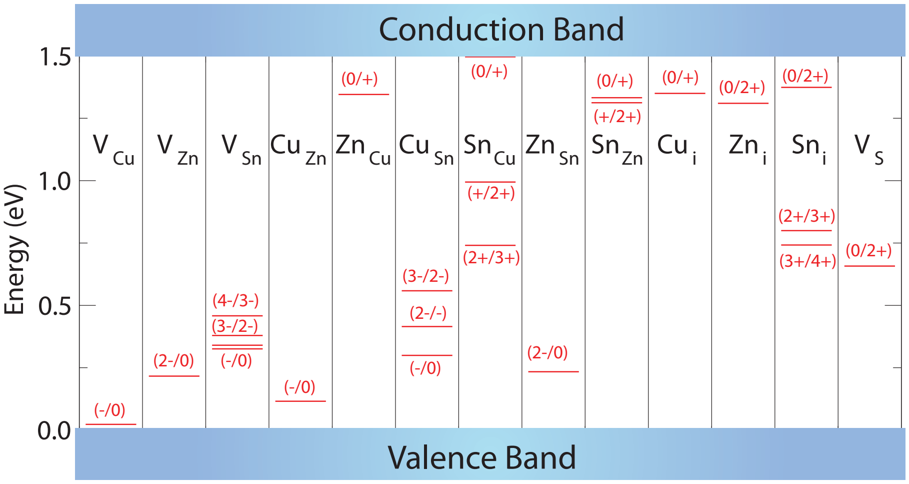

FIGURE 1. Calculated transition energy levels of intrinsic defects in the band gap of Cu_2ZnSnS_4.

The calculated values of the intrinsic defect ionization levels within the band gap of Cu_2ZnSnS_4 are summarized in Fig. 1.

In the study of Nagoya *et al*, performed at a similar level of theory, consistent ionization levels can be found, and their results further support our conclusion that the stable chemical potential range for CZTS is small[12]. The work of Biswas *et al* focused on the higher energy (less abundant) defects involving Sn, and highlighted that the associated donor states are deep, arising from the accessibility of both Sn(II) and Sn(IV) oxidation states[11]. The existence of both oxidation states is well understood, and is associated with the fact that Sn has a low energy 5*s* and two higher energy 5*p* valence states[9, 13, 14]. When the Sn 5*p* state is occupied, its level will be higher in energy. This explains why Sn_{Cu} (0/+) is a shallow donor level and why it is higher than the Sn_{Zn} (0/+) level, although the valence difference, thus the electronegativity difference, between Sn and Cu is larger than that between Sn and Zn[8, 9]. However, this shallow level and its origin are not discussed in Ref. 11.

We hope that our theoretical guidance relating to the structure, band gap and defect physics of CZTS will aid the improvement of light conversion efficiencies in kesterite based solar cells.

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