Crystal and electronic band structure of Cu$_2$ZnSnX_4 (X=S and Se) photovoltaic absorbers: First-principles insights

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The structural and electronic properties of Cu$_2$ZnSnS$_4$ and Cu$_2$ZnSnSe$_4$ are studied using first-principles calculations. We find that the low energy crystal structure obeys the octet rule and is the kesterite (KS) structure. However, the stannite or partially disordered KS structures can also exist in synthesized samples due to the small energy cost. We find that the dependence of the band structure on the (Cu,Zn) cation ordering is weak and predict that the band gap of Cu$_2$ZnSnSe$_4$ should be on the order of 1.0 eV and not 1.5 eV as was reported in previous absorption measurements. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3074499]

An ideal thin-film solar cell absorber material should have a direct band gap around 1.3–1.5 eV with abundant, inexpensive, and nontoxic elements. Cu(In,Ga)Se$_2$ (CIGS) is one of the most promising thin-film solar cell materials, demonstrating an efficiency of about 20%.[1] However, In and Ga are expensive components, and the band gap is usually not optimal for high efficiency CIGS solar cells. Currently, designing and synthesizing novel, high-efficiency, and low cost solar cell absorbers to replace CIGS has attracted much attention. Among the materials that have been investigated, quaternary Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSe) compounds have drawn significant interest because they contain only abundant and nontoxic elements Cu, Zn, Sn, S, and Se, and the reported band gaps for both materials are about 1.5 eV (Table I),[2–15] which is ideal for solar cell application.

Unfortunately, the fundamental physical properties of these materials are not well understood. For example, what are the ground state structures, and how does the crystal structure affect their band structure and optical properties. From a theoretical point of view, it is also difficult to understand why the recently reported band gap of CZTSe at about 1.5 eV is basically the same as that of CZTS. Selenides (ZnSe, CuGaSe$_2$ with band gaps of 2.82 and 1.68 eV, respectively), with larger lattice constants and higher p orbital energies, usually have much smaller band gaps than sulfides (ZnS, CuGaS$_2$ with band gaps of 3.78 and 2.43 eV, respectively).

In this paper, we systematically investigate the structural and electronic properties of these two quaternary compounds using first-principles total energy and band structure calculations within the density functional formalism as implemented in the VASP code.[16] For the exchange-correlation potential, we used the generalized gradient approximation (GGA) of Perdew and Wang, known as PW91.[17] The projector augmented-wave pseudopotentials[18] with an energy cutoff of 300 eV for plane waves in the $4 \times 4 \times 4$ Monkhorst–Pack k-point meshes were employed to give converged results.

It has been shown that the ternary CuGaX_2, CuInX_2, and the quaternary Cu$_2$ZnSnX_4 compounds can be obtained through cation mutation of their II-VI analogs.[19] For example, by mutating two Zn in ZnS to Cu+Ga, we obtain CuGaS$_2$. There are two fundamental I-III-VI$_2$ structures that obey the octet rule: chalcopyrite (CH) and CuAu-like (CA) structures. Previous studies have shown that due to smaller strain energy and more negative Coulomb energy, the CH structure with larger band gap is always more stable than the CA structure.[20] Further mutation can be carried out by replacing, e.g., Ga+In in Cu(Ga,In)X_2, by Zn+Sn to form Cu$_2$ZnSnX_4 quaternary compounds. In this case, there are three fundamental crystal structures that obey the octet rule. One is the kesterite structure (KS) [space group $I\bar{4}$, Fig. 1(a)], which is derived from the CH structure. The other two are the stannite structure (ST) [space group $I\bar{4}2m$, Fig. 1(b)] and the primitive mixed CA structure (PMCA) [space group $P\bar{4}2m$, Fig. 1(c)], both derived from the CA structure.

The calculated properties of CZTS and CZTSe in the three structures are listed in Table II. We find that KS is the ground state structure for both CZTS and CZTSe, whereas the ST and PMCA structures have higher total energies. This follows the same trend as their ternary parent structures, i.e., CH is more stable than CA. Indeed, similar to the ternary analogs, we find the KS structure has lower strain energy[21] and also lower Madelung energy,[22] relative to ST and PMCA. However, although the KS structure possesses a lower energy, the energy difference between the KS and ST structures is small, about 3 meV/atom. This indicates that KS and ST ordering may coexist in the synthesized samples.[11,12,20]

Experimentally, samples of CZTS and CZTSe are observed to crystallize in either KS or ST structures (Table I). Recently, Schorr and co-workers, using neutron diffraction
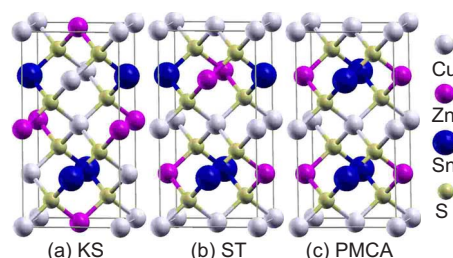

FIG. 1. (Color online) The crystal structure of Cu$_2$ZnSnS$_4$ in (a) KS, (b) ST, and (c) PMCA structures.

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TABLE I. The measured lattice constant a, tetragonal distortion parameter η, and band gap of samples in different structures. In the PD-KS structure, the atoms in the Cu+Zn layer are assumed to be randomly distributed.

Sample	Structure	a (Å)	η	E_g (eV)	References
CZTS	KS	5.427	1.002		2
CZTS	KS			1.5	3–6
CZTS		5.44	1.001	1.49	7 and 8
CZTS	ST	5.436		1.46,1.51	9 and 10
CZTS	PD-KS	5.428	1.001		11 and 12
CZTSe	ST	5.606	0.995	1.44	13
CZTSe	ST	5.776	1.011	1.5	14
CZTSe	KS	5.68	1.00	1.40–1.65	15

measurements, also showed that a partially disordered KS (PD-KS) structure can exist, in which the atoms in the Cu+Zn (001) layer in the KS structure are disordered, while atoms in the Cu+Sn layer reside in their original positions.[11,12] To see the effect of the partial-disorder, we have calculated physical properties of CZTS in the PD-KS structure using a 64 atom special quasirandom structure (SQS) supercell.[23] The calculation shows that the randomization energy is 9.1 meV/atom for the Cu+Zn layer, whereas it is much higher, 77.8 meV/atom, for the Cu+Sn layer. Furthermore, the disorder in the Cu+Zn layer causes a volume expansion of 0.3%, whereas the disorder in the Cu+Sn layer causes a 1.8% volume expansion. The different randomization energies originate from the large chemical and size mismatch between Cu and Sn, compared to Cu and Zn. Our results agree with the observation[11,12] that only the Cu+Zn layer is disordered during certain growth conditions. It is interesting to point out that (i) PD-KS has higher energy than the ST and PMCA structures because the PD-KS structure does not obey the octet rule, and (ii) for PD-KS, its crystallographic symmetry is equivalent to ST, thus some of the experimental samples that have been identified as ST may be the PD-KS structure, instead.

The calculated lattice constants for both KS and ST structures are in good agreement with experimental values. For both CZTS and CZTSe, the lattice constant a of the KS structure is slightly larger than those of ST and PMCA, whereas the tetragonal distortion parameter, $\eta = c/2a$, of KS is slightly smaller. The crystal field splitting, $\Delta_{CF} = \Gamma_{5v} - \Gamma_{4v}$,[24] which is determined partially by η,[25] follows the same trend, that is KS has a smaller and negative Δ_{CF} while ST and PMCA have larger and positive values. The distortion preferences of KS, ST, and PMCA result from the different Cu-X, Zn-X, and Sn-X bond lengths. Similar trends are observed for CuGaSe$_2$ and CuInSe$_2$ in CH and CA structures.[20] This is not surprising because KS can be derived from CH, while ST and PMCA are derived from CA; therefore, these trends are inherited.

We also calculated the partial and total density of states (DOS) of CZTS in the KS and ST structures, as shown in Fig. 2. From the partial DOS, we find that the upper valence band is derived mainly from the hybridization of S p and Cu d states, similar to CuInSe$_2$ and CuGaSe$_2$, because Cu has higher d orbital energy than Zn, Ga, In, and Sn, while the low conduction band is mainly from the hybridization of S s,p and Sn s states, which is due to the lower s orbital energy of Sn than the other cations. We find that the total DOS has similar shape for KS, ST, and even the PD-KS (not shown) structures, which indicates that the dependence of the band structure on the distribution of Cu and Zn is weak for this class of compounds.

The ground state KS structure has the largest band gap within the different cation configurations. For example, the band gap of KS-CZTS is about 0.12 eV larger than that of ST-CZTS. The disorder also has effect on the band gap of PD-KS-CZTS and our SQS calculation shows that its band gap is 0.04 eV smaller than the stable KS-CZTS. The calculated GGA band gap of CZTSe is about 0.4 eV smaller than CZTS in the same crystal structure, which is consistent with our common expectation that the selenides have smaller band gaps than the corresponding sulfides but disagrees with the interpretation of experimental adsorption data (Table I),

TABLE II. Calculated lattice constant, tetragonal distortion parameter, crystal field splitting, energy difference per atom relative to the lowest-energy structure, and direct band gap using GGA. The corrected band gaps according to HSE06 calculation are given in parenthesis.

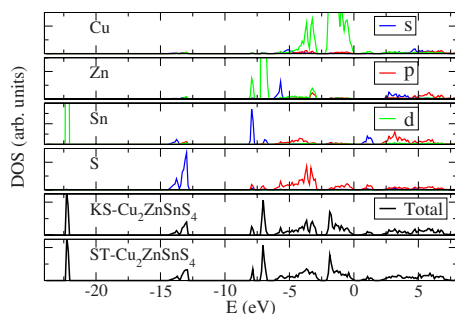| Structure	a (Å)	η	Δ_{CF} (eV)	ΔE (meV)	E_g (eV)
			CZTS		
KS	5.467	0.999	−0.065	0	0.09 (1.50)
ST	5.458	1.004	0.138	2.86	−0.3 (1.38)
PMCA	5.459	1.005	0.128	3.15	−0.06 (1.35)
			CZTSe		
KS	5.763	0.998	−0.031	0	−0.30 (0.96)
ST	5.762	1.000	0.066	3.79	−0.44 (0.82)
PMCA	5.753	1.004	0.065	5.53	−0.47 (0.79)

FIG. 2. (Color online) The partial and total DOS of Cu_2ZnSnS_4 in KS and ST structures and the partial DOS in the KS structure.

showing that the band gaps of CZTSe are nearly the same as CZTS at about 1.5 eV.[13–15] As the GGA underestimates the band gaps, we have performed hybrid functional calculations [HSE06 (Ref. 26)] at experimental lattice constants, where 25% of the GGA exchange potential is replaced by screened Fock exchange. From the HSE06 calculation, we find that the band gap of stoichiometric KS-CZTS is 1.50 eV, whereas the band gap of KS-CZTSe is 0.96 eV. The corrected band gap according to the HSE06 calculation are also given in Table II. Similar band gaps are obtained if we estimate the band gap for CZTX (X = S and Se) by adding the corresponding GGA band gap errors for $CuGaX_2$ and $CuInX_2$ to the calculated GGA band gaps for CZTX.[19] Our results suggest that experimental data[13–15] for the band gap of CZTSe should be re-examined. The discrepancy between our prediction and experiment could be either poor sample quality or incorrect linear interpolation in determining the band gap. Indeed, a recent photoluminescence (PL) measurement[27] showed that the difference in PL peak energies between CZTS (1.3 eV) and CZTSe (0.8 eV) is about 0.5 eV, which is consistent with our calculated results and an earlier transmission measurement.[28] Using the same approach,[19] we estimate that KS-$Cu_2ZnGeSe_4$ should have a band gap of 1.5 eV and is thus also suitable for solar cell application.

In conclusion, using first-principles density functional methods, we studied the structural and electronic properties of CZTS and CZTSe and compared our results with the available experimental data. We find that (i) although the KS structure has the lowest total energy, the ST and PD-KS structures are also possible to form due to the low energy cost, (ii) the dependence of the band structure on the (Cu,Zn) cation ordering is weak, and (iii) we predict that the band gap of CZTSe is around 1.0 eV and not 1.5 eV as was reported in some of the previous literature.

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