DESIGN OF QUATERNARY CHALCOGENIDE PHOTOVOLTAIC ABSORBERS THROUGH CATION MUTATION

Aron Walsh
Materials Chemistry, Department of Chemistry, University College London, UK

Su-Huai Wei
National Renewable Energy Laboratory, Golden, CO, 80401, USA

Shiyou Chen and X. G. Gong
Surface Science Laboratory and Department of Physics, Fudan University, Shanghai 200433, China

ABSTRACT

Design of chalcogenide photovoltaic absorbers is carried out systematically through sequential cation mutation, from binary to ternary to quaternary compounds, using first-principles electronic structure calculations. Several universal trends are identified for two classes of quaternary chalcogenides (I_2-II-IV-VI_4 and I-III-II_2-VI_4 systems). For example, the lowest-energy structure always has larger lattice constant *a*, smaller tetragonal distortion parameter $\eta = c/2a$, and larger band gap than the metastable structures for common-row cation mutations. The band structure changes on mutation illustrate that although the band gap decreases from binary II-VI to ternary I-III-VI_2 are mostly due to the p-d repulsion in the valence band, the decreases from ternary I-III-VI_2 to quaternary I_2-II-IV-VI_4 chalcogenides are due to the downshift in the conduction band caused by the wavefunction localization on the group IV cation site. We find that I_2-II-IV-VI_4 compounds are more stable in the kesterite structure, whereas the widely-assumed stannite structure reported in the literature is most likely due to partial disorder in the I-II (001) layer of the kesterite phase. Ten compounds are predicted have band gaps close to the 1 to 2 eV energy window suitable for photovoltaics.

INTRODUCTION

The design and synthesis of high-efficiency materials to convert solar to electrical energy is becoming an increasingly important research field. Zinc-blende chalcogenide semiconductors, such as ZnX, CdX, $CuBX_2$, their alloys $CuIn_xGa_{1-x}X_2$ and $Zn_{2-2x}(CuB)_xX_2$ (B=Ga, In and X=S, Se, Te), have been widely studied for photovoltaic applications[1]. Although these chalcogenides have shown some promising properties, it is important to develop systematic design principles that accelerate the discovery of novel materials with lower cost and higher efficiency to satisfy the need for wide-range photovoltaic applications [2-4]. Furthermore, we must also keep in mind the cost, abundance and environmental impact of the elemental components, criteria that could be improved upon for current thin film absorber materials, e.g. the scarcity and high cost of indium and gallium in $Cu(In,Ga)(S,Se)_2$ based cells and the high toxicity of cadmium in CdTe based cells.

Cation cross-substitution (mutation) from zinc-blende II-VI and III-V binary semiconductors to form ternary and quaternary zinc-blende superlattices was pioneered by Goodman and Pamplin in the 1950's and 60's[5,6]. A schematic of the cross-substitutional steps to form I_2-II-IV-VI_4 and I-III-II_2-VI_4 compounds is shown in Figure 1. Relative to the binary II-VI chalcogenides, ternary I-III-VI_2 compounds can be generated by mutating the group II atoms into pairs of group I and III atoms, with the octet rule still obeyed, i.e. each anion is coordinated to two group I and two group III cations (Fig. 2).

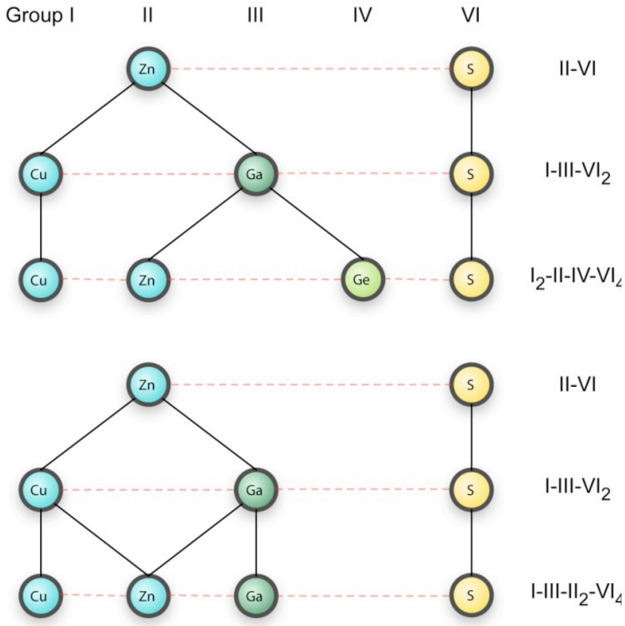

Fig. 1. Schematic cation mutation to form ternary and quaternary charge neutral semiconductors, starting from binary zinc-blende II-VI parents.

Ternary semiconductors exhibit more flexible properties arising from their enhanced chemical and structural freedom [7]. For example, the band gap of $CuGaSe_2$ (1.68 eV), being lower than that of ZnSe (2.82 eV), is more suitable for application in thin-film solar cells, especially when alloying with $CuInSe_2$ to lower the gap. However, due to the high cost of In and Ga, it is desirable to find alternatives with appropriate band gaps and lower material costs than $Cu(Ga,In)(S,Se)_2$. One way to design novel chalcogenides is to follow the mutation concept to further split the ternary I-III-VI_2 systems into quaternary compounds (Fig. 1). There are two methods for this cation mutation: (i) to replace two group III atoms by one II and one IV atom, forming a I_2-II-IV-VI_4 compound (Fig. 2); (ii) to replace one group I atom and one III by two II atoms, forming a I-III-II_2-VI_4 compound, which can also be taken as the $II_{2x}(I\text{-}III)_{1-x}VI_2$ alloy at x = 0.5. Through this ternary-to-quaternary mutation and control of the atomic configuration, one can perform band engineering to tailor the material properties for a specific photovoltaic application.

In this paper, we report a systematic investigation of the properties (crystal and electronic structure) of the quaternary chalcogenides, from a cation mutation perspective to elucidate the underlying chemical trends [2], and identify potential candidate photovoltaic absorber materials.

METHOD OF CALCULATION

The electronic structure and total energies are calculated within the density functional theory formalism[8] as implemented in the plane-wave code VASP[9]. For the exchange-correlation potential, we use the generalized gradient approximation (GGA) of Perdew and Wang (PW91). The interaction between the core electrons and the valence electrons is included by the standard frozen-core projector augmented-wave potentials[10]. An energy cutoff of 300 eV was applied in all cases. For the Brillouin-zone integration, we used *k*-point meshes that are equivalent to the 4×4×4 Monkhorst-Pack meshes for an 8-atom cubic unit cell. All lattice vectors and atomic positions were fully relaxed by minimizing the quantum mechanical stresses and forces.

RESULTS

Our main findings may be summarized as follows:

(i) For common-row-cation I_2-II-IV-VI_4 compounds, the low-energy kesterite (KS) structure, derived from the ternary chalcopyrite structure (Fig. 2), has a tetragonal distortion parameter $\eta < 1$, a negative crystal field splitting and the largest band gap.

(ii) The valence band offsets between II-VI and I_2-II-IV-VI_4 compounds are positive and large, while those between I-III-VI_2 and I_2-II-IV-VI_4 are always small (Fig. 3), because the p-d coupling between group I and VI cations raises the valence band maximum (VBM) in both the I-III-VI_2 and I_2-II-IV-VI_4 systems [5].

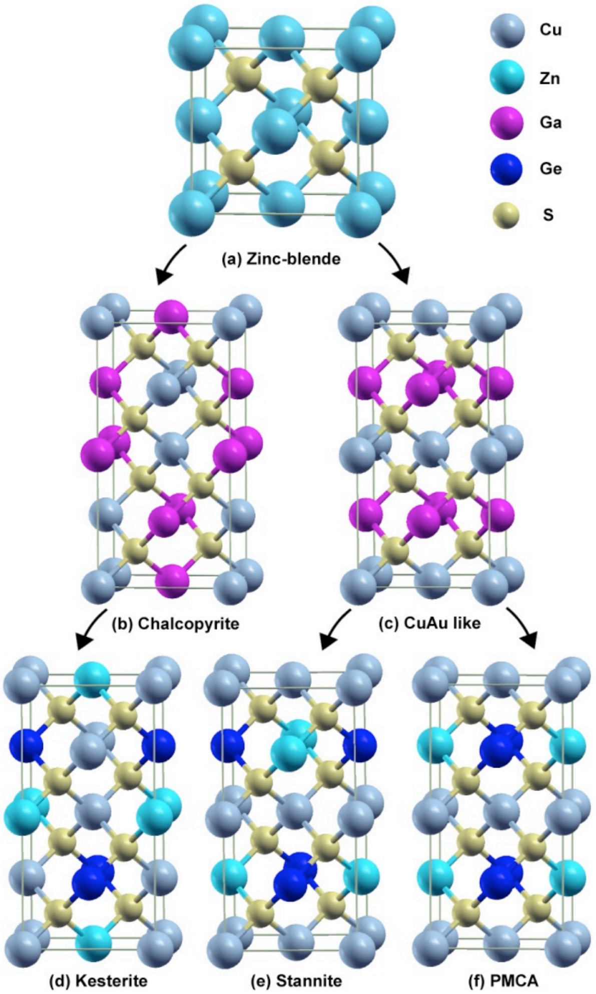

Fig. 2. Crystal structure representations of: (a) zinc-blende ZnS, (b) chalcopyrite $CuGaS_2$, (c) CuAu-like $CuGaS_2$, (d) KS-Cu_2ZnGeS_4, (e) ST-Cu_2ZnGeS_4, and (f) PMCA-Cu_2ZnGeS_4.

(iii) The conduction band minimum (CBM) level of the I_2-II-IV-VI_4 compounds is lower than that of the parent I-III-VI_2 systems as a result of the lower cation s level of the group IV cations (e.g. Ge, Sn) compared to III (e.g. Ga, In), which determines the band gap decrease in the ternary to quaternary mutation (Fig. 4).

(iv) Similarly for the common-row-cation I-III-II_2-VI_4 compounds, the lowest energy stannite (ST) structure is also derived from chalcopyrite and has $\eta < 1$, a negative crystal field splitting and the largest band gap.

(v) Cross-row cation mutation from the ternary to quaternary chalcogenides shows more complicated trends in both the crystal structure and electronic band structure, depending on the relative sizes and chemical nature of the I, II, III and IV elements.

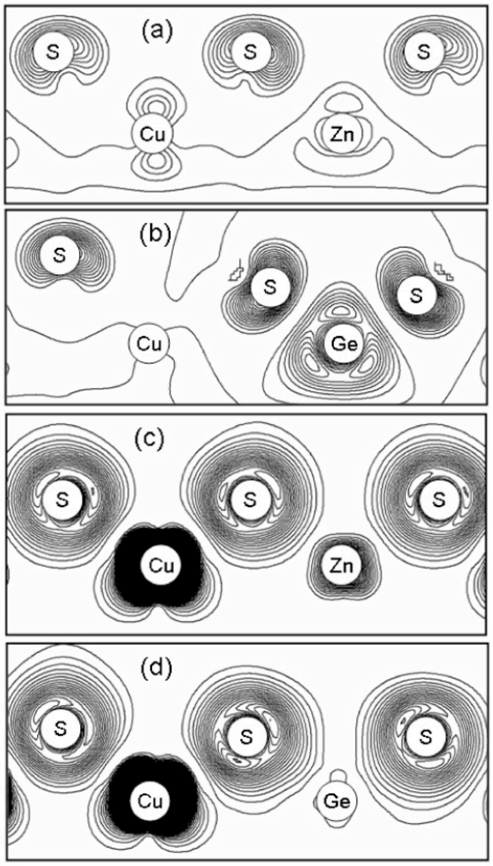

Fig. 3. Band and *k*-point decomposed charge density plots of the KS−Cu_2ZnGeS_4 conduction band minimum in the (a) Cu−S−Zn plane and (b) Cu−S−Ge plane, and the valence band maximum in the (c) Cu−S−Zn plane and (d) Cu−S−Ge plane.

(vi) In comparison to the experimental literature, our analysis highlights a possible long-standing misunderstanding in the crystal structure determination of I_2-II-IV-VI_4 quaternary chalcogenides. We suggest that the widely-assumed stannite structure reported in the literature for experimental samples is in fact a partially-disordered kesterite structure (PDKS). This confusion most likely arose from the similarity of the crystal symmetries; the space groups are no. 121 I/42m (ST) and no. 82 I/4 (KS). For the PDKS structure, disorder occurs between the group I and II cations in the (001) planes, which XRD will have difficulty distinguishing for some systems (e.g. Cu and Zn). First-principles supercell calculations simulating random displacement of the Cu/Zn layers along the <110> direction predict that the total energy loss is only on the order of 10 meV relative to the thermodynamic ground state, e.g. 9.1 meV/atom for Cu_2ZnSnS_4.

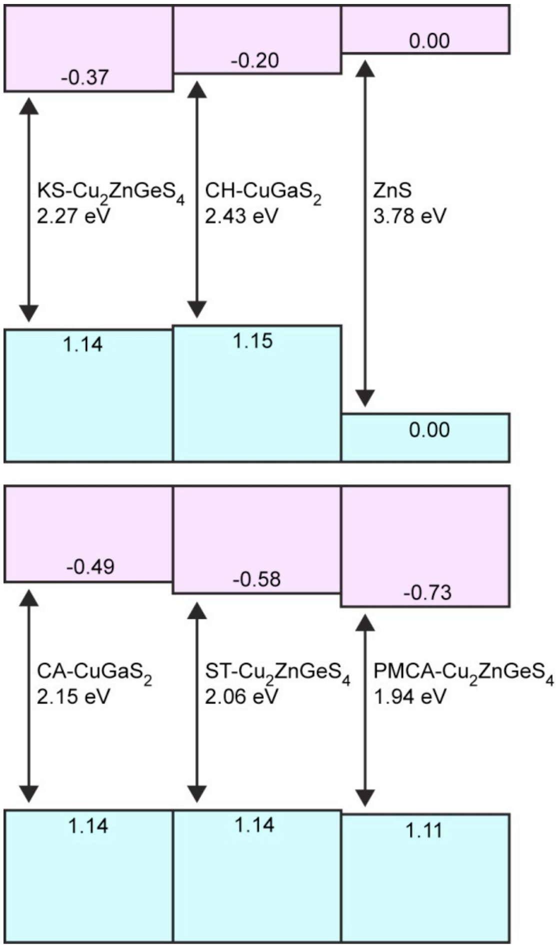

Fig. 4. The predicted valence band alignment of ZnS, $CuGaS_2$ and Cu_2ZnGeS_4 calculated using a core level reference[11], and employing the GGA-corrected band gaps[2] to obtain the conduction band offsets. KS, CH, CA, ST and PMCA refer to the kesterite, chalcopyrite, CuAu-like, stannite and primitive-mixed CuAu structures, respectively.

For I_2-II-IV-VI_4 compounds, band gaps in the 1 – 2 eV range are predicted for $Cu_2ZnSnSe_4$ (1.0 eV), $Ag_2CdSnSe_4$ (1.2 eV), Cu_2CdSnS_4 and $Cu_2ZnGeSe_4$ (1.5 eV), Cu_2ZnSnS_4 (1.6eV), Ag_2CdSnS_4 (1.9 eV), and Ag_2ZnSnS_4 (2.0 eV). For I-III-II_2-VI_4 compounds, $AgInCd_2Se_4$ (1.4 eV), $CuInCd_2S_4$ (1.8 eV), $CuGaZn_2Se_4$ (2.1 eV) fall within this energy window. In both cases the effect of alloy ordering on the band gap is found to be small (± 0.2 eV between the kesterite and stannite phases), and the onset of the optical absorption coefficient is found to be strong, similar to the ternary chalcopyrite materials.

CONCLUSIONS

In summary, using first-principles calculations, a series of quaternary (I_2-II-IV-VI_4 and I-III-II_2-VI_4) chalcogenides have been studied from a cation mutation perspective. From our analysis, we identified common trends in the crystal and electronic structure of these multiternary chalcogenides. Our results provide insights into searching new chalcopyrite absorber materials for future solar cell applications. In particular, we identified kesterite as the lowest energy phase for the I_2-II-IV-VI_4 compounds with Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$ and Cu_2ZnGeS_4 offering the promising combination of low band gaps (1 – 1.5 eV), low-cost elemental components and strong optical absorption.

ACKNOWLEDGEMENTS

The work at NREL is supported by the U.S. DOE under contract No. DE-AC36-08GO28308. Computing resources of the National Energy Research Scientific Computing Center were employed, which is supported by DOE under Contract No. DE-AC02-05CH11231. The work in Fudan University (FU) is partially supported by the National Sciences Foundation of China, the Basic Research Program of MOE and Shanghai, the Special Funds for Major State Basic Research, and Postgraduate Innovation Fund of FU.

REFERENCES

[1] M. A. Green, K. Emery, Y. Hisikawa, and W. Warta, *Prog. Photovoltaics: Res. Appl.* **15**, 425 (2007).

[2] S. Chen, X. G. Gong, A. Walsh, and S.-H. Wei*, Phys. Rev. B* **79**, 165211 (2009).

[3] S. Chen, X. G. Gong, A. Walsh, and S.-H. Wei, *Appl. Phys. Lett.* **94**, 041903 (2009).

[4] S. Schorr, G. Wagner, M. Tovar, and D. Sheptyakov, *MRS Symp. Proc.* **1012**, Y03 (2007).

[5] C. H. L. Goodman, *J. Phys. Chem. Solids* **6**, 305 (1958).

[6] B. R. Pamplin, *J. Phys. Chem. Solids* **25**, 675 (1964).

[7] S.-H. Wei and A. Zunger, *J. Appl. Phys.* **78**, 3846 (1995).

[8] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).

[9] G. Kresse and J. Furthmuller, *Phys. Rev. B* **54**, 11169 (1996); G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).

[10] P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).

[11] S.-H. Wei and A. Zunger, *Phys. Rev. Lett.* **59**, 144 (1987).