Solar cell materials: Doping vs efficiency

Structure-property relations in the (Cu,Ag)$_2$Zn(Si,Ge,Sn)(S,Se)$_4$ solar cell materials

D. Fritsch[1] ***and S. Schorr***[1,2], *[1] Helmholtz-Zentrum Berlin für Materialien und Energie, [2] Freie Universität Berlin, Institut für Geologische Wissenschaften*

In Short

- (Cu,Ag)$_2$Zn(Si,Ge,Sn)(S,Se)$_4$ solar cell materials
- investigate structural, electronic, and optical properties of structural polymorphs
- employ *special quasirandom structures* to investigate Cu$_2$Zn(Ge$_{1-x}$Si$_x$)(S,Se)$_4$ solid solutions
- contribute to in-depth material understanding and their potential as key materials in future photovoltaic devices

Quaternary chalcogenide materials based on A_2ZnCX_4 (A = Cu, Ag, C = Si,Sn,Ge, X = S, Se) are building blocks for the third generation of thin film photovoltaic devices. A prime example is based on Cu$_2$ZnSnS$_4$ which has been studied extensively in the past, reaching a power conversion efficiency of 12.6 % [1]. However, stability issues and a not-yet-ideal band gap for photovoltaic device efficiency has triggered research into solid solutions with adjacent cations.

Experimental research efforts employing a plethora of growth techniques, tools for structural characterisation, and subsequent analyses into electronic and optical properties, allowed for a much improved understanding of material properties in general. On the theoretical side, the development of ever more capable exchange and correlation functionals to be employed in density functional theory (DFT) calculations, and the wide-spread availability of high-performance computing facilities, led to an in-depth understanding of structure-property relations in a wide range of material classes.

Here, we're concerned with the (Cu,Ag)$_2$Zn(Si,Ge,Sn)(S,Se)$_4$ solar cell materials, crystallising in a variety of structural polymorphs. Some of those structural polymorphs can be derived from a simpler zinc blende crystal structure applying successive pairwise cation substitutions. This is exemplary shown in Fig. [1]. In order to shed some light on the intricate balance of the underlying crystal structure on the electronic and optical properties, we will perform DFT calculations employing different exchange and correlation functionals, as well as subsequent quasiparticle calculations for a better description of the optical properties.

We employ two different parameterisation of the density functional, namely the newly introduced SCAN functional [2], and the more accurate hybrid functional HSE06 [3]. While the SCAN functional satisfies all known possible exact constraints for the exact density functional and has been claimed to match or improve on the accuracy of computationally more demanding hybrid functionals [4], calculations based on hybrid functionals have been shown to yield improved structural and electronic properties compared to standard parametrisations [5]. In order to get a better grasp of the optical properties, additional quasiparticle calculations based on the GW method introduced by Hedin [6] will be performed as well.

We can draw from our experiences of an earlier project on Cu$_2$ZnSnSe$_4$ and Ag$_2$ZnSnSe$_4$, where we already identified a suitable procedure to perform DFT calculations with a combination of exchange and correlation functionals for the structural and electronic properties, and additional quasiparticle calculations for the optical properties, leading to very good agreement with available experimental results [7]. Exemplary, Fig. [2] shows (a) the electronic band structure and (b) the dielectric functions of kesterite Cu$_2$ZnSnSe$_4$. The dashed lines in (b) present experimental results of León *et al.* [8], obtained via spectroscopic ellipsometry on bulk Cu$_2$ZnSnSe$_4$ crystals, and showing overall good agreement with the theoretical results.

Once the structural, electronic, and optical properties of the structural polymorphs in the quaternary (Cu,Ag)$_2$Zn(Si,Ge,Sn)(S,Se)$_4$ solar cell materials have been obtained, additional calculations will investigate two particular

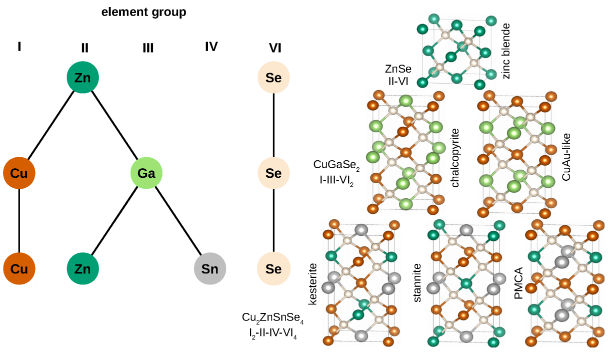
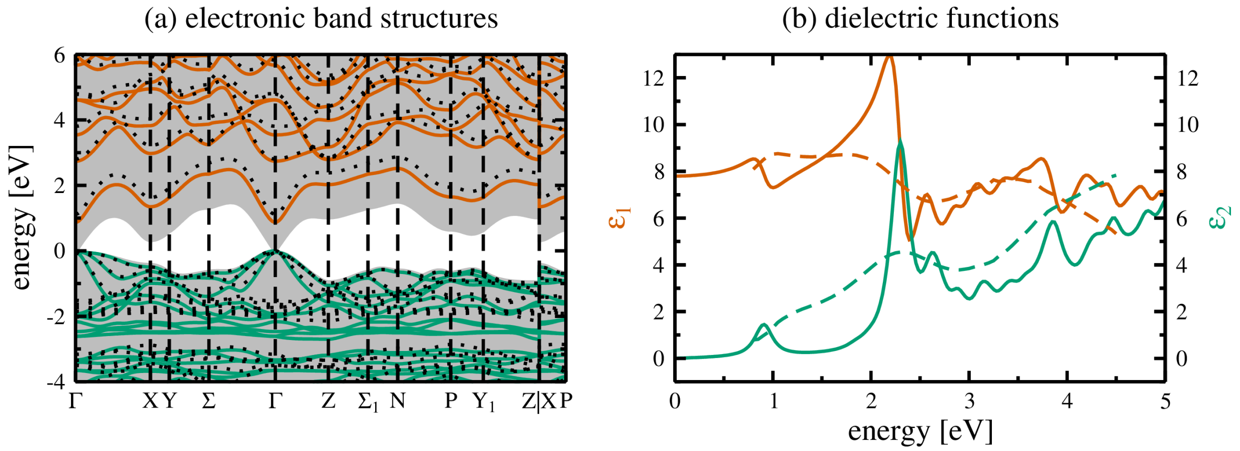


Figure 1: *Possible pathways from a basic crystal structure for zinc blende ZnSe towards various derivative crystal structures for the quaternary Cu$_2$ZnSnSe$_4$ (kesterite, stannite, and primitive-mixed CuAu-like (PMCA) crystal structures), obtained via successive pairwise cation substitutions.*


(a) electronic band structures

(b) dielectric functions

Figure 2: *(a) Electronic band structures for the kesterite crystal structure of $Cu_2ZnSnSe_4$, with zero energy at the top of the valence bands [7]. Shown are the valence (green) and conduction bands (orange), calculated using the hybrid HSE06 [3] functional. The dotted lines and the shaded grey backgrounds show the results from the G_0W_0 and SCAN [2] calculations, respectively. (b) Real (orange) and imaginary (green) parts of the dielectric functions for the kesterite crystal structure of $Cu_2ZnSnSe_4$, obtained by hybrid HSE06 calculations. The dashed lines in (b) present experimental results of León et al. [8], obtained via spectroscopic ellipsometry on bulk $Cu_2ZnSnSe_4$ crystals.*

solid solutions, namely $Cu_2Zn(Ge_{1-x}Si_x)S_4$ and $Cu_2Zn(Ge_{1-x}Si_x)Se_4$. Here, we will make use of so-called *special quasirandom structures*, introduced by Zunger *et al.* [9], to sample the whole composition range within the solid solutions. Thereby, the concept of *special quasirandom structures* allows to identify only symmetry-inequivalent cation distributions within the solid solutions, ultimately leading to an efficient use of provided computational resources.

The results obtained in this project will contribute to an atomic scale insight into structural, electronic, and optical properties of chalcogenide solar cell materials, and will allow for the identification of prospective materials for future photovoltaic devices.

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More Information

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