Thin-film solar cells: Defects vs performance

Intrinsic point defects in kesterite-type Cu$_2$ZnGeSe$_4$ compound semiconductors

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In Short

- improve performance of thin-film solar cells based on new materials, e.g. kesterite-type Cu$_2$ZnGeSe$_4$

- strong influence of material defects on electronic and optical properties, which ultimately limit the performance as absorber material

- large supercell calculations are needed to determine defect properties from first-principles methods

- contribute to the microscopic understanding of non-radiative recombination mechanisms in kesterite-type materials

Thin-film solar cells have attracted much attention because they require less materials and energy compared to the industry standard of silicon-based technologies. Moreover, solar cells based on kesterite-type semiconductors such as Cu$_2$ZnSnS$_4$ (CZTS) and Cu$_2$ZnSnSe$_4$ (CZTSe) have been shown to reach very high light-to-electricity conversion efficiencies [1].

Compared to simpler binary and ternary compound semiconductors the quaternary kesterite-type CZT(S,Se) semiconductors contain more elements which give rise to a larger number of intrinsic point defects, some of which have been identified as source of a reduced performance. The intrinsic point defects include various vacancies, where atoms are simply missing in the crystal lattice, antisite defects, where the elements swap places within the crystal lattice, and some interstitial vacancies, where atoms are build into the crystal lattice away from their ideal position, respectively. In addition, there exist also defect complexes, which can combine any of the above mentioned intrinsic defects, leading to off-stoichiometric samples and even more complex defect characteristics. All these defects can be characterised by their formation energy, which in turn can be calculated from first-principles methods such as density functional theory [2,3]. More generally, the authors of Ref. [3] also note that "a microscopic understanding of the non-radiative recombination mechanisms in kesterites is still unclear."

Another important quantity for solar cell absorber materials is the so-called band gap of the material. Here, a recent work by our group showed that substituting Ge^{4+} for Sn^{4+} enhances the band gap of CZT(S,Se) materials and improves the optoelectronic properties [4].

This project addresses the computational modelling of intrinsic point defects in the kesterite-type Cu$_2$ZnGeSe$_4$ (CZGSe) compound semiconductor. To this end, we employ density functional theory utilising two different parametrisation of the density functional, namely the PBEsol functional revised for solids [5] based on the generalised gradient approximation (GGA), and the more accurate hybrid functional HSE06 [6]. In particular, results based on hybrid functionals have been shown to yield improved electronic properties compared to plain GGA calculations [2,3,7]. This can be seen from the electronic band structure, shown in the upper panel of Fig. 1, where we obtain very good agreement with the experimentally determined band gap, and from the real and imaginary dielectric functions, shown in comparison to experimental results from our group [8] in the lower panel of Fig.1, respectively. The calculated dielectric functions subsequently give access to experimentally much easier to determine quantities, such as absorption and reflectivity spectra.
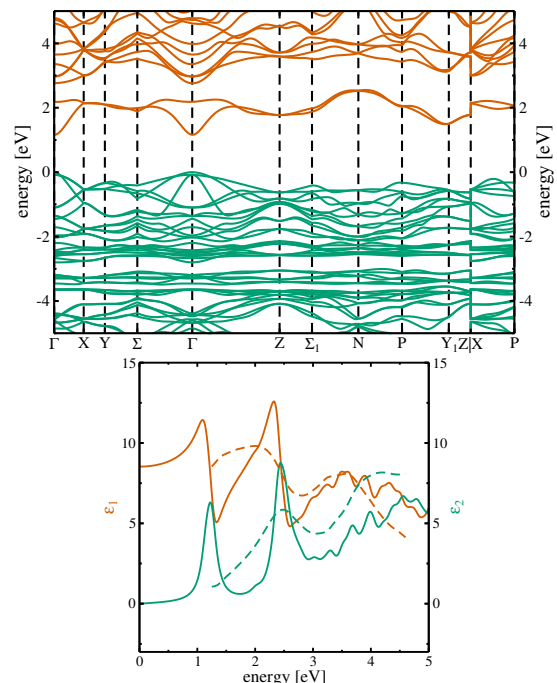
Figure 1: *Upper panel: electronic band structure of Cu$_2$ZnGeSe$_4$ calculated with the hybrid HSE06 functional [6]. Lower panel: real (orange) and imaginary (green) dielectric functions in comparison to experimental results utilising spectroscopic ellipsometry (dashed lines) [8].*
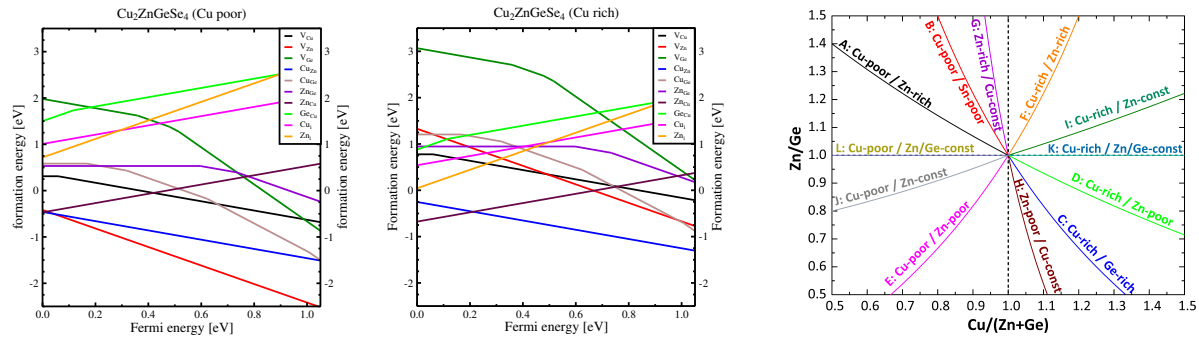
Figure 2: *Left panels: defect formation energies for intrinsic point defects in $Cu_2ZnGeSe_4$ compound semiconductor for Cu-poor (left panel) and Cu-rich (middle panel) experimental growth conditions (adjusted by different values for the chemical potentials of the constituent atomic species). Right panel: cation ratio plot indicating different off-stoichiometry types present in $Cu_2ZnGeSe_4$ [4].*

In order to estimate the defect formation energies one has to calculate the total energies of large supercells (containing up to 64 atoms) with and without intrinsic defects. These supercells have to undergo computationally demanding structural relaxations in order to provide reliable total energies, and have to account for the different possible charge states of the intrinsic defects. The total energies of the relaxed structures including defects have to be supplemented by different values for the chemical potentials of the constituent atomic species to take into account different experimental growth conditions. Preliminary results for the defect formation energies of CZGSe are shown in the left and middle panels of Fig. 2 for Cu-poor and Cu-rich experimental growth conditions, respectively. A subsequent analysis allows to identify defect levels within the band gap of CZGSe and their position with respect to the Fermi energy, typically measured from the valence band maximum (shown as zero energy in the formation energy diagrams of Fig. 2).

The final results on intrinsic point defects in CZGSe will be compared to already published investigations on CZT(S,Se) materials, in order to understand the influence of the Ge^{4+} substitution on the defect formation energies and in particular the suitability of CZGSe as solar cell absorber material. At a later stage, also several defect complexes and their respective formation energies will be investigated. Here, we will be guided by the already available experimental data on the different possible defect complexes and their off-stoichiometry types from an accurate neutron powder diffraction study from our group [4].

With the results obtained in this project we can make detailed statements about the defect characteristics in CZGSe in particular, and provide more inside in the as of yet unknown microscopic understanding of non-radiative recombination mechanisms in kesterite-type compound semiconductors in general.

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More Information

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