

# Thin-film solar cells: Defects vs performance

## Intrinsic point defects in kesterite-type $\text{Cu}_2\text{ZnGeSe}_4$ compound semiconductors

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### In Short

- improve performance of thin-film solar cells based on new materials, e.g. kesterite-type  $\text{Cu}_2\text{ZnGeSe}_4$
- 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  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) and  $\text{Cu}_2\text{ZnSnSe}_4$  (CZTSe) have been shown to reach very high light-to-electricity conversion efficiencies [1].

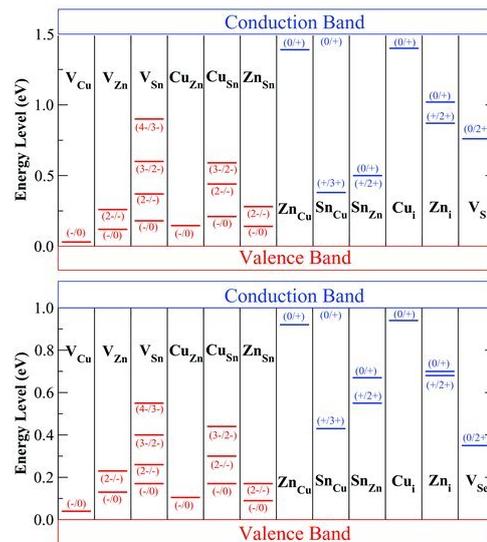
Compared to simpler binary and ternary compound semiconductors the quaternary kesterite-type CZT(S,Se) semiconductors contain more elements which give rise to a larger number of intrinsic point defects, some of which have been identified as source of a reduced performance. The intrinsic point defects 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. 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."

The obtained formation energies allow to determine the defect levels within the band gap of the materials and their position with respect to the Fermi energy, typically measured from the valence band maximum. Fig. 1 exemplary shows the ionisation levels of intrinsic point defects in the band gap for

$\text{Cu}_2\text{ZnSnS}_4$  (upper panel) and  $\text{Cu}_2\text{ZnSnSe}_4$  (lower panels) [2].

Another important quantity for solar cell absorber materials is the band gap of the material. Here, a recent work by our group showed that substituting  $\text{Ge}^{4+}$  for  $\text{Sn}^{4+}$  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  $\text{Cu}_2\text{ZnGeSe}_4$  (CZGSe) compound semiconductor. To this end, we employ density functional theory to calculate the total energies of large supercells (containing up to 64 atoms) with and without intrinsic defects to subsequently obtain the formation energies and ionisation levels (similar to the ones shown in Fig. 1). We employ two different parameterisation of the density functional, namely the GGA functional after Perdew, Burke and Ernzerhof (PBE), and the more accurate hybrid functional HSE06. In particular, calculations based on hybrid functionals have been shown to yield improved electronic properties compared to the standard PBE parameterisation [2,3,5]. 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.



**Figure 1:** Ionisation levels of intrinsic defects in the band gap of  $\text{Cu}_2\text{ZnSnS}_4$  (upper panel) and  $\text{Cu}_2\text{ZnSnSe}_4$  (lower panel) calculated using density functional theory [2].

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**More Information**

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