Pressure on solar cells

Calculation for equilibrium material properties and high-pressure-behaviour of solar cell materials

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In Short

- Kesterites (Cu_2ZnSnS_4) are a promising material class for a cost-effective sustainable electrical power production with thin film solar cells from solar radiation.
- The structural and electronic properties of Cu_2ZnSnS_4 bulk systems have been theoretically studied extensively, showing good agreement with experimental data regarding structural and electronic properties.
- We successfully modelled the high pressure phase of Cu_2ZnSnS_4 and predicted the structural phase transition to be in the experimentally observed range of 14 to 16 GPa.
- We were able to predict the Cd content in $Cu_2Zn_{1-x}Cd_xSnS_4$ for which the structure changes from kesterite to stannite.
- We want to investigate how the material's properties change upon exchange of the cations.
- We aim to investigate: Ag_2ZnSnS_4, Cu_2MnSnS_4 and Cu_2FeSnS_4.

The impending exhaustion of fossil fuel has prompted the exploration and exploitation of alternative energy resources, with the solar energy harvesting through photovoltaic devices spearheading these efforts. In an attempt to overcome the restraints of Si-based materials, the direct optical band gap of chalcogenide-based solar cells offers the benefit of higher absorption in comparison to silicon. Given that the employed chalcogenides are composed of multiple elements, one can additionally optimize the photovoltaic properties of the respective material by appropriate metal or chalcogenide substitution. Among the various chalcogenides investigated for this purpose, the quaternary semiconductor Cu_2ZnSnS_4 has attracted considerable attention in recent years. [1] The suitability of this material for solar cell applications stems from its almost optimal band gap ($E_g \approx$ 1.5 eV), its high absorption coefficient (maximum around 1000 nm), and its earth-abundant, low-cost, and non-toxic constituents. [2]

At ambient conditions, Cu_2ZnSnS_4 crystallizes in the tetragonal kesterite (KS) structure (SG $I\bar{4}$, Z = 2, Fig. 1). [3] This phase, which is structurally related to the sphalerite- and chalcopyrite-type structures, is composed of alternating cationic (Cu/Sn or Cu/Zn) layers along the c-axis interrupted by sulfur anions, with all of the cations tetrahedrally coordinated with respect to anions. Even though the KS phase represents an ordered cationic arrangement, i.e. each cation occupies a unique Wyckoff site, cationic disorder is quite common in this material. [3] Such disorder can affect the photovoltaic properties of this system. For example, a mixed occupancy between Cu and Zn in the z = 1/4 and z = 3/4 cationic layers results in a disordered kesterite (DKS) configuration (SG $I\bar{4}2m$, Z = 2, Fig. 1) and a reduction of E_g. [4]

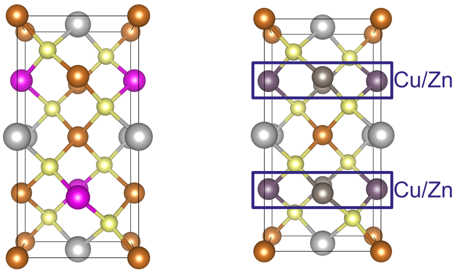

***Figure 1:** Unit cell of the kesterite-type Cu_2ZnSnS_4 (KS, SG $I\bar{4}$, Z =2, left) and the disordered-KS (DKS, SG $I\bar{4}2m$, Z =2, right) phases. The copper, pink, grey, and yellow spheres represent Cu, Zn, Sn, and S ions, respectively; the dark spheres in the DKS phase depict the mixed Cu/Zn occupancy.*

In our computational studies, the electronic und structural properties of the systems are obtained by periodic density functional theory calculations. In the first step we use the GGA functional PBE for the structure optimisations. The PBE functional yields sufficiently accurate results for the structural parameters in comparison to experimental data. Since the PBE functional fails to accurately describe the electronic structure, we use the hybrid functional HSE06 to calculate the electronic properties. The calculations are performed with a plane wave basis set using the Vienna Ab Initio Simulation Package [5] , which is known to benefit from the parallelisation over several nodes and hundred processors with sufficiently large unit cells. Only the availability of computational resources like the ones provided by HLRN allows us to investigate the described systems.

In the course of this project we have shown that Cu_2ZnSnS_4 adapts a distorted rocksalt structure beyond 16 GPa (Fig. 2). [6] This result matches the experimental XRD (X-ray diffraction) observations of our collaborators which indicate the transition in a pressure range of 14 to 16 GPa. We carried out volume scans for both structural models and fit a Birch-Murnaghan equation of state (EOS). To determine the pressure as a function of the unit cell volume, we derived the EOS with reference to the volume ($p(V) = -\left(\frac{\delta E}{\delta V}\right)$). Finally we calculated the enthalpy ($H = E + pV$) of both structural models. We also investigated the electronic structure of both structures. At the transition pressure we observe a drastic change. The band gap of KS at 16 GPa is 2.5 eV. After the transition it closes completely; the distorted rocksalt structure has metallic character. This prediction was confirmed by our experimental colleagues by UV-vis measurements.

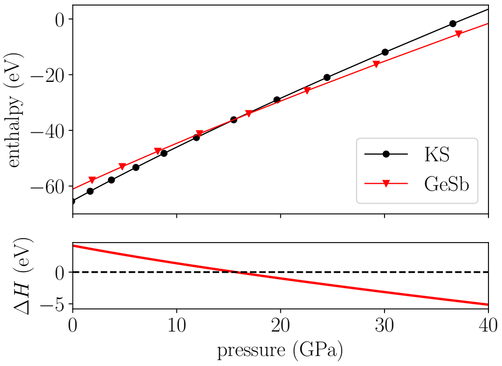

Figure 2: *Calculated enthalpy of structural models for kesterite (KS) and the distorted rocksalt (GeSb, SG $I4/mmm$, c<a) at the PBE level of theory. The relative enthalpy of GeSb in the bottom panel is printed with reference to KS.*

In our latest study we examined Cu_2ZnCdS_4. Unlike Cu_2ZnSnS_4 it crystallizes in the stannite (ST, SG: $I\bar{4}2m$) structure. Through partial exchange of Zn with Cd we can gradually transition between the two structures ($Cu_2Zn_{1-x}Cd_xSnS_4$). In collaboration with our experimental colleagues we wanted to reveal at which Cd content the structure flips from KS to ST. We also included differently disordered KS structures to understand the influence of disorder for the transition. We used 2x2x1 super cells and considered all symmetry inequivalent substitution patterns for each Cd content and averaged their total energies to compare to the energy of the equally substituted ST phase (Fig. 3). For the fully ordered KS structure we predict the KS-to-ST transition at 0.51 Cd content. In the experiment the transition is observed at 0.38 Cd content. We observe that disorder destabilizes the KS structure with reference to the ST structure. Therefore we conclude that the deviation from our prediction to the experiment could be due to a small disorder (well below 12.5 %) in the sample.

Next we will turn to similar materials where one cation of Cu_2ZnSnS_4 is exchanged. Thereby we aim to study Ag_2ZnSnS_4, Cu_2MnSnS_4 and Cu_2FeSnS_4. In collaboration with our experimentalist colleagues we want to identify the equilibrium ground state structure and determine the band gap. For selected materials we also will identify the high-pressure phase and the corresponding electronic structure.

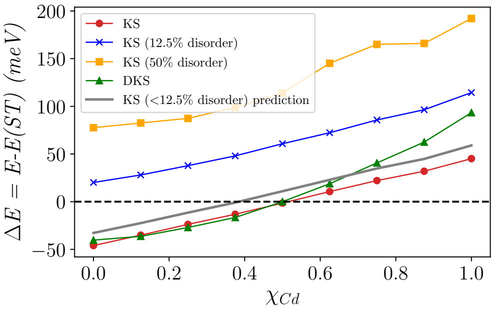

Figure 3: *Relative energy of the kesterite phases (solid lines) with respect to the stannite phase (black dotted baseline) for different Cd substitution fractions. Energies below zero means the KS phase is more stable.*

WWW

http://userpage.fu-berlin.de/agpaulus/

More Information

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