Towards practical kesterite photovoltaics: ab initio thermodynamics
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Global photovoltaic (PV) electricity generation is currently of the order 7GW, while
global energy consumption (including liquid fuels) is of the order 15TW. In order to
make a significant contribution to the energy mixture, PV generation must be hugely
expanded. Abundant thin-film absorbers such as Cu2ZnSnS4 (CZTS) offer one way
forward.

A number of synthesis routes have been identified, but whether the precursors are
binary compounds, salts in solution, metal alloys or pre-formed CZTS nanoparticles,
film formation typically takes place in a high-temperature annealing process with
sulfur vapour. This critical step involves complex phase equilibria and is suited to a
thermodynamic study.

Ab initio thermodynamics

The structures and energies of moderately complex crystalline
materials (~100 atoms in a unit cell) may be studied with some
confidence using density functional theory (DFT). These methods
employ the variational principle to identify the ground state;
however, this is not representative of typical usage conditions,
and lies even further from industrial reaction conditions.
Temperature and pressure effects can be introduced by
calculating key bulk properties including the heat capacity and
vibrational entropy. By using this data to estimate the chemical
potential ($\nu$) for each compound of interest, the Gibbs free
energy ($\Delta G$) may be calculated for arbitrary reactions and
conditions:

$$\Delta G = \sum \nu_i \mu_i - E_{elect} - E_{chem,prod} + \int_0^T C_p \, dT + PV - TS$$

In the solid state, full phonon spectra may be computed from a
series of structures with small displacements to form a set of
approximate harmonic normal modes. By filling these modes
according to the Boltzmann distribution, free energies can be
calculated. Industrial gases are largely well-described in
the literature; the challenge lies in bringing the data together to form
a consistent model of gas-vapour equilibrium.

Computational details

Calculations are primarily carried out using the FH-aims quantum chemistry code with
the PBEsol functional for exchange and correlation. This
offers a balance of efficiency and accuracy, while being readily scalable across
thousands of computing cores.

Phonon calculations are set up and processed with the
"Phonopy" package, and
thermodynamic modelling is executed with Scientific Python and Matlab.

The University of Bath’s 800-
core Aquila cluster is used for
structure optimisation and
testing; demanding phonon
calculations are carried out on
national-scale Cray and
Bluegene/Q facilities.

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The sulfur equilibrium

Solid sulfur is an attractive industrial reagent as it is cheap,
abundant and relatively safe. However, it is less reactive than
some alternatives including H2S, and forms a complex phase
equilibrium. A set of calculated free energies is presented here (drawn
from standard data tables) showing the solid
phase (α and β) phases, as well as the major gas
phases. In fact a range of
cyclic compounds SxSy exist in equilibrium at the
raised temperatures and low pressures which are
preferred for deposition processes.