$\beta-In_2S_3$ for photovoltaic devices: unravelling the properties from *ab initio* investigation of the native and alkali point defects

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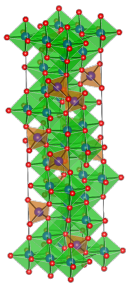
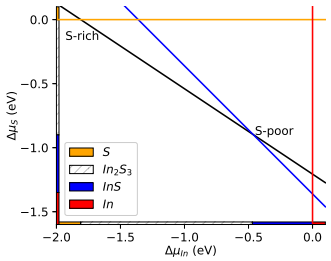
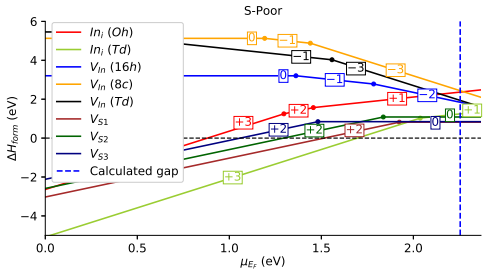
Fine tuning material properties for device applications requires a deep understanding of the origin of the desired properties. In the case of materials involved in photovoltaic solar cells, one can rightfully ask the question: where does the conductivity of the material come from? The general answer is simple: lattice point defects. However, they are really difficult to investigate experimentally. In this study, we show how Density Functional Theory (DFT) calculations can help rationalise the optoelectronic properties of applicative materials by taking the example of $\beta-In_2S_3$, a material used as buffer in chalcopyrite thin film solar cells.[1] Our simulations led to unambiguous results concerning the incapability for this material to be a p-type semiconductor. Furthermore, it is demonstrated that the insertion of indium into a Td interstitial site seems to be the driving force leading to natural n-type conductivity. Our calculations took into account different atmospheres in order to be directly comparable with experimental data, in particular the competitive InS structure was considered. It is shown that the S-poor condition strongly lesser the defect formation energy and should be privileged to achieve high free electron concentrations for potential applications. Subsequently, we develop a methodology to tackle extrinsic point defects and to address the issue of the effect of alkali (A) Post-Deposition Treatment (PDT) on the In_2S_3 buffer layer.[2] Our simulations prove that the migration of alkali from the soda-lime glass substrate to the buffer and additionally suggest the PDT step may trigger the decomposition of $\beta-In_2S_3$ into $AInS_2$ and InS at the grain boundaries. All the post-treatments were performed using the PyDEF 2.0 package.[3]



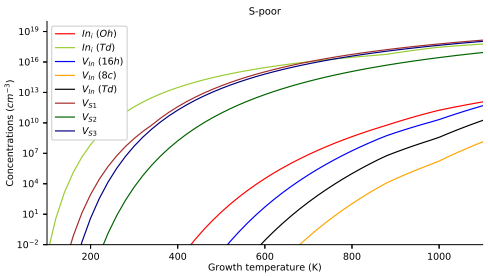
(a) $\beta-In_2S_3$ structure.



(b) Stability domain in $(\Delta\mu_{In}, \Delta\mu_S)$ plane.



(c) Intrinsic defects formation enthalpies.



(d) $\beta-In_2S_3$ intrinsic defect concentrations.

[1] A. Stoliaroff et al., **Theor. Chem. Acc.** (2018) 137, 102.
[2] A. Stoliaroff et al., **Comput. Mat. Sci.** (2019) 168, 221.
[3] A. Stoliaroff et al., **J. Comput. Chem.** (2018) 26, 2251.