Multivalency of Sn in Cu$_2$ZnSnS$_4$. KOUSHIK BISWAS, STEPHAN LANY, ALEX ZUNGER, National Renewable Energy Laboratory — The highly efficient ternary chalcopyrites such as 2(CuInSe$_2$) = Cu$_2$In$_2$Se$_4$ can be replaced as absorber materials in photovoltaic cells by Cu$_2$ZnSnS$_4$ (band gap $\sim$ 1.5 eV) in order to avoid the costly element In. Yet, the question remains whether a Fermi-level pinning defect can form spontaneously in these quaternary materials just as the In$_{Cu}$ intrinsic DX centers in CuInSe$_2$ [1]. Here we study theoretically the deep gap levels introduced by the Sn$_{Cu}$ and Sn$_{Zn}$ defects in Cu$_2$ZnSnS$_4$. We find that these originate from the multi-valency of Sn, which can change into a +II oxidation state instead of the normal +IV state. Such a transition can even occur for Sn on its native site. Thus, we compare to the respective defect behavior in the kesterite Cu$_2$ZnGeSe$_4$, which has a similar band gap, but a less pronounced multi-valency of the respective IV-valent element Ge.


This work is supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy.