

Title: Tight-Binding modeling of CsPbI₃ in several perovskite phases

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Content:

Among perovskite solar cells, fully inorganic perovskite solar cells can compete as a stable and efficient alternative to hybrid cousins, with the recent report of a 13.4% efficient CsPbI₃ perovskite quantum dot solar cell. Using synchrotron X-ray powder diffraction (SXRD), the detailed experimental structures of the three perovskite-phases of CsPbI₃ (gamma at 325K, beta at 510K and alpha at 645K) have been recently reported. Based on these experimental results, we investigate the electronic properties of all three phases using a recently developed symmetry-based tight-binding (TB) model [1] as well as DFT calculations including both spin-orbit coupling (SOC) and many-body (GW approximation) effects.

In fact, TB models afford an atomic-scale description to computing various properties, including distorted structures, at a significantly reduced computational cost compared to first-principles approaches. It allows tackling more difficult issues in terms of size, with complex heterostructures, nanostructures or composite materials, as well as properties with a great diversity of physical phenomena.

The original empirical sp³ tight-binding (TB) model has been built for the reference Pm3m cubic phase of halide perovskite structures of general formula ABX₃ and the TB parameters have been calibrated using available experimental and theoretical data for MAPbI₃ (MA=CH₃NH₃⁺) [1]. To investigate less symmetric structure, such as the beta and gamma phases of CsPbI₃, we show that this model can be extended by means of a simple d²-Harrison law, which allows tackling bond length variation. Given that very few experimental results are available on these phases of CsPbI₃, we used the initial parameterization performed on MAPbI₃. In order to gauge the quality and performances of this TB model, we further performed DFT calculations including both self-consistent GW corrections and relativistic effects (SOC). The band structure obtained with our TB model agrees nicely with results obtained from first-principles calculations. The model is then further exploited to inspect effect related to anharmonicity and results support the hypothesis of dynamical Rashba effects in CsPbI₃. We may expect that such a model will be as relevant to the future of perovskite device modeling, as it has proved efficient for conventional semiconductors.

References: [1] S. Boyer-Richard et al., J. Phys. Chem. Lett. 2016, 7, 3833.

This project has received funding from the European Union's Horizon 2020 programme, through a FET Open research and innovation action under the grant agreement No 687008.