

# Hybrid halide perovskites: Doping vs stability

## Structural and electronic properties of hybrid halide perovskites: $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$

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### In Short

- improve stability of the hybrid halide perovskite formamidinium lead triiodide (FAPbI<sub>3</sub>) by doping with Cs
- lattice strain upon doping stabilises cubic perovskite structure
- large supercell calculations are needed to investigate small doping concentrations
- contribute to in-depth atomistic understanding of alloy formation in hybrid halide perovskites

Hybrid halide perovskites have shown huge potential as possible solar cell materials for the third generation of photovoltaic devices. This is mainly due to their proven ability to reach high light-to-electricity conversion efficiencies and their low production costs [1].

However, similar to the most investigated hybrid halide perovskite, methylammonium lead triiodide (MAPbI<sub>3</sub>), formamidinium lead triiodide (FAPbI<sub>3</sub>) faces stability issues as well, which have hindered a large scale application as solar cell material in photovoltaic devices. Both hybrid halide perovskites can exist in the cubic perovskite structure  $\text{APbI}_3$ , where the *A*-site cations comprise an organic methylammonium cation  $\text{CH}_3\text{NH}_3^+$  ( $\text{MA}^+$ ) or a formamidinium cation  $\text{CH}(\text{NH}_2)_2^+$  ( $\text{FA}^+$ ), respectively.

At room temperature, FAPbI<sub>3</sub> crystallises in a hexagonal non-perovskite  $\delta$  phase of space group  $P6_3mc$ , and an unstable cubic perovskite  $\alpha$  phase. Therein, the organic  $\text{FA}^+$  cations show a complex distribution pattern. However, it has been suggested that small doping on the *A*-site with inorganic Cs<sup>+</sup> cations, can stabilise the cubic perovskite structure [2].

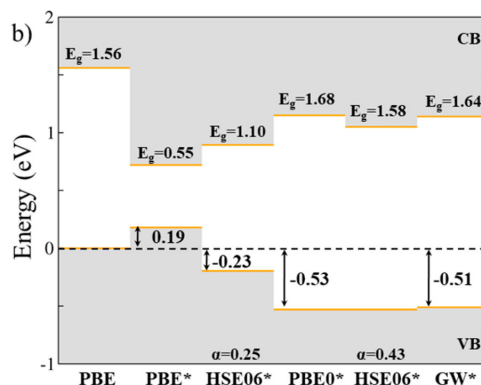
Another issue that strongly affects the applicability of a material for photovoltaic devices concerns the defect characteristics. In order to obtain an atomic scale insight into structural properties and a subsequent defect characterisation in FAPbI<sub>3</sub> and  $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ , first-principles calculations based on density functional theory (DFT) are the method of choice. The best practices for first-principles modelling of defects in lead halide perovskites have been summarised by Meggiolaro and De Angelis [3]. They

state that an accurate description of defects in those materials requires geometry optimisations based on hybrid functionals, e.g. HSE06 [4], with spin-orbit coupling effects taken into account. The huge influence of the level of theory on the band edge energies is exemplary shown for MAPbI<sub>3</sub> in Fig. [1].

Another issue relates to the description of bonds between the inorganic cage and the organic molecules. The incorporation of Cs<sup>+</sup> cations into FAPbI<sub>3</sub> results in structural distortions, which influence the hydrogen bonding interactions between the  $\text{FA}^+$  cations and the  $[\text{PbI}_6]$  framework. These hydrogen bonding interactions lead to an increased stability of the perovskite  $\alpha$  phase, and have to be taken into account by additional dispersion corrections in the calculations.

Here, we want to address the structural properties of the parent compound FAPbI<sub>3</sub> and Cs-doped systems  $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$  ( $x \leq 0.1$ ), keeping in mind the requirements for a subsequent analysis of the defect characteristics. To this end, we employ DFT calculations utilising different versions of the exchange-correlation functional, namely the standard generalised gradient approximation (GGA) in the parameterisation of Perdew, Burke and Ernzerhof (PBE) [5], the parameterisation revised for solids (PBEsol) [6], and the more accurate hybrid functional HSE06 [4]. Calculations based on hybrid functionals have been shown to yield improved structural and electronic properties compared to the standard GGA parameterisations [7].

The results obtained in this project will contribute to an atomic scale insight into structural and electronic properties of  $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$ , and pave the way for a subsequent investigation of the defect characteristics.



**Figure 1:** Band edge energies of MAPbI<sub>3</sub> calculated at different levels of theories (in eV), where asterisks \* denote calculations including spin-orbit interaction [3].

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## More Information

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