Hybrid halide perovskites: Doping vs stability

Structural and electronic properties of hybrid halide perovskites: $FA_{1-x}Cs_xPbI_3$

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In Short

- improve stability of the hybrid halide perovskite formamidinium lead triiodide ($FAPbI_3$) 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 ($MAPbI_3$), formamidinium lead triiodide ($FAPbI_3$) 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 $A\mathrm{PbI}_3$, where the A-site cations comprise an organic methylammonium cation $CH_3NH_3^+$ (MA^+) or a formamidinium cation $CH(NH_2)_2^+$ (FA^+), respectively.

At room temperature, $FAPbI_3$ crystallises in a hexagonal non-perovskite δ phase of space group $P6_3mc$, and an unstable cubic perovskite α phase. Therein, the organic FA^+ cations show a complex distribution pattern. However, it has been suggested that small doping on the A-site with inorganic Cs^+ 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 $FAPbI_3$ and $FA_{1-x}Cs_xPbI_3$, 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 $MAPbI_3$ in Fig. [1].

Another issue relates to the description of bonds between the inorganic cage and the organic molecules. The incorporation of Cs^+ cations into $FAPbI_3$ results in structural distortions, which influence the hydrogen bonding interactions between the FA^+ cations and the $[PbI_6]$ framework. These hydrogen bonding interactions lead to an increased stability of the perovskite α 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 $FAPbI_3$ and Cs-doped systems $FA_{1-x}Cs_xPbI_3$ ($x \leq 0.25$), 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 parametrisation of Perdew *et al.* revised for solids (PBEsol) [5], the newly introduced SCAN functional [6], which shows superior behaviour for the structural properties of hybrid perovskites over combinations of GGA-based functionals plus various additional dispersion-correction schemes [7], 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 parametrisations [8].

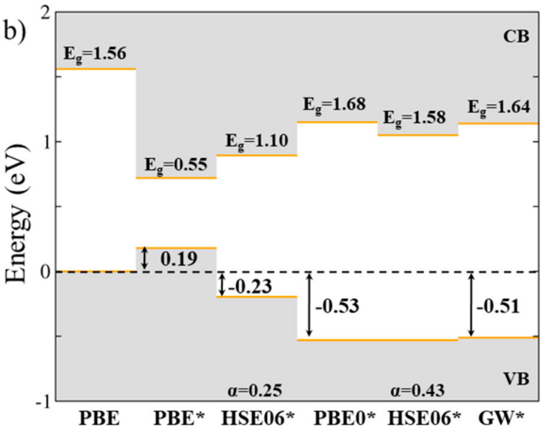

Figure 1: *Band edge energies of $MAPbI_3$ calculated at different levels of theories (in eV), where asterisks * denote calculations including spin-orbit interaction [3].*

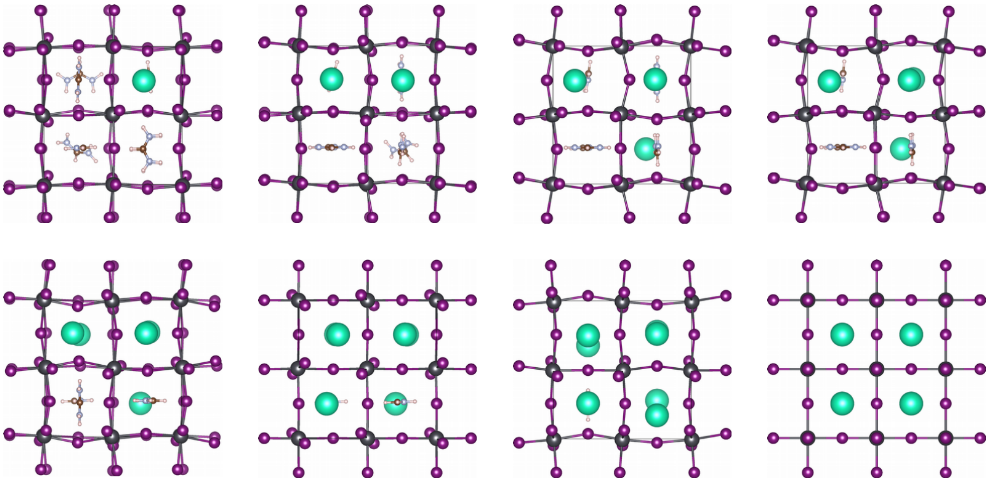

Figure 2: *Relaxed lowest-energy structures for $FA_{1-x}Cs_xPbI_3$ obtained for the $2 \times 2 \times 2$ unit cells out of 10 different random arrangements of Cs^+ and FA^+ cations including a random orientation of FA^+ molecules.*

One particular difficulty in the modelling of these alloy systems lies in the (random) distribution of the Cs^+ cations in the $FA_{1-x}Cs_xPbI_3$ supercell. In case of the hybrid halide perovskites we additionally face the problem of the random orientation of the FA^+ molecules. This leads to the generation and structural optimisation of a vast amount of different supercells for each chosen x value for the $FA_{1-x}Cs_xPbI_3$ alloy system, allowing for the study of different (random) distributions of Cs^+ cations and orientations of the FA^+ molecules. This is exemplary given in Fig. [2] for smaller $2 \times 2 \times 2$ supercells of the whole $FA_{1-x}Cs_xPbI_3$ alloy system, where only the lowest energy structures for each x value are shown. Further analyses will yield information on the electronic properties, e.g. band structures, and optical properties, e.g. dielectric functions, of the whole $FA_{1-x}Cs_xPbI_3$ alloy system, respectively.

The results obtained in this project will contribute to an atomic scale insight into structural and electronic properties of $FA_{1-x}Cs_xPbI_3$, and pave the way for a subsequent investigation of the defect characteristics.

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More Information

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