Optimising and Tuning the Band Gap of Hybrid Perovskites for Solar Cells

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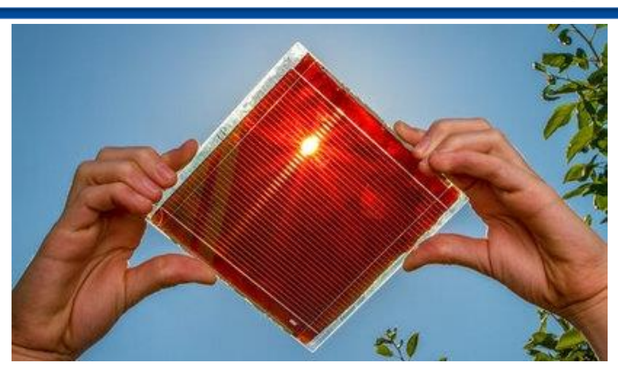
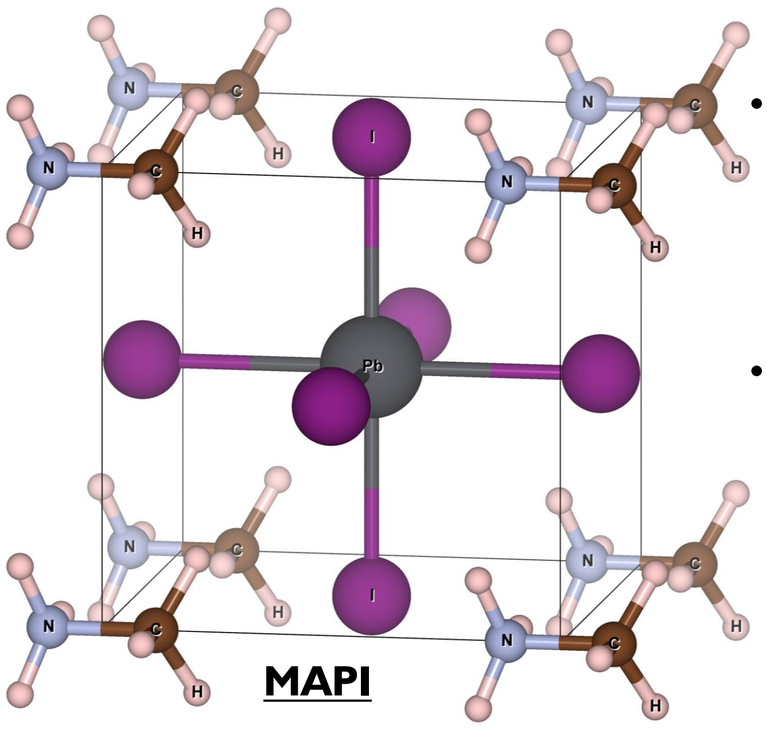
We investigated the highly efficient organic-inorganic hybrid perovskite solar cell's composition and orientation that lead to the maximum theoretical efficiency limit. We find that less than 50% Br in Br–I and mixing organic molecules can reduce band gap towards 1.34 eV required for the efficiency limit. We also find various orientations coexist in experiment and improve absorption and carriers' mobility.

Introduction

- Perovskite solar cells have demonstrated a power conversion efficiency (PCE) of 23.7% [1] and theoretically could achieve 33.7%.



Source: Renewable Energy Magazine



MAPI

Figure 1. Cubic MAPI Crystal

- Perovskites (ABX_3) have customisable bandgaps, long carrier diffusion lengths, low recombination losses.
- Here we consider a hybrid perovskite (organic A = $CH_3NH_3^+$, (**MA**), or $CH(NH_2)_2^+$, (**FA**), inorganic B = **P**b^{2+} and halide X = **I**$^-$ or **B**r$^-$).

- Hybrid perovskites are easy and cheap to fabricate, but stability and structural issues remain.

Methodology

- Electronic and geometric properties of **MAPI**, **MAPB**, **FAPI** & **FAPB** are calculated using density functional theory (DFT).
- DFT exactly solves the many body Schrödinger equation from first principles. Thus it is a predictive theory with no parameter fitting.

Atomic Geometry and Energetics

- Asymmetry of MA or FA favours rotation until equilibrium.

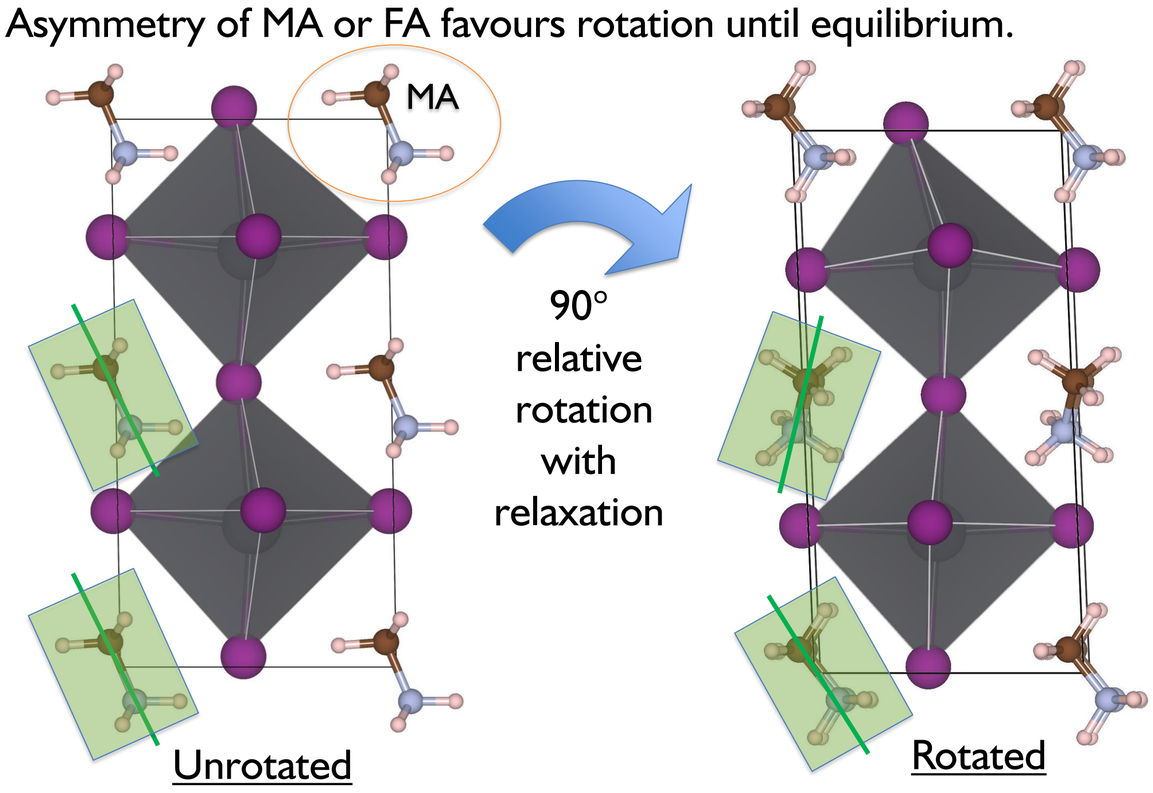


Figure 2. Terminated MAPI Structures of 2-unit-cell in (001) Plane.

$$\Delta E_{formation} = E_{rotated} - E_{unrotated} = -20\ \text{meV}\ (\sim \text{thermal fluctuations})$$

- Rotated structure is more energetically favourable (0.01 eV per formula unit).

Rotational Effect

- Band gap changes depending on orientation.
- Excellent absorption up to 3 eV range / UV spectrum.
- Rotated structure also shows better electron mobility in band structure and vice versa.

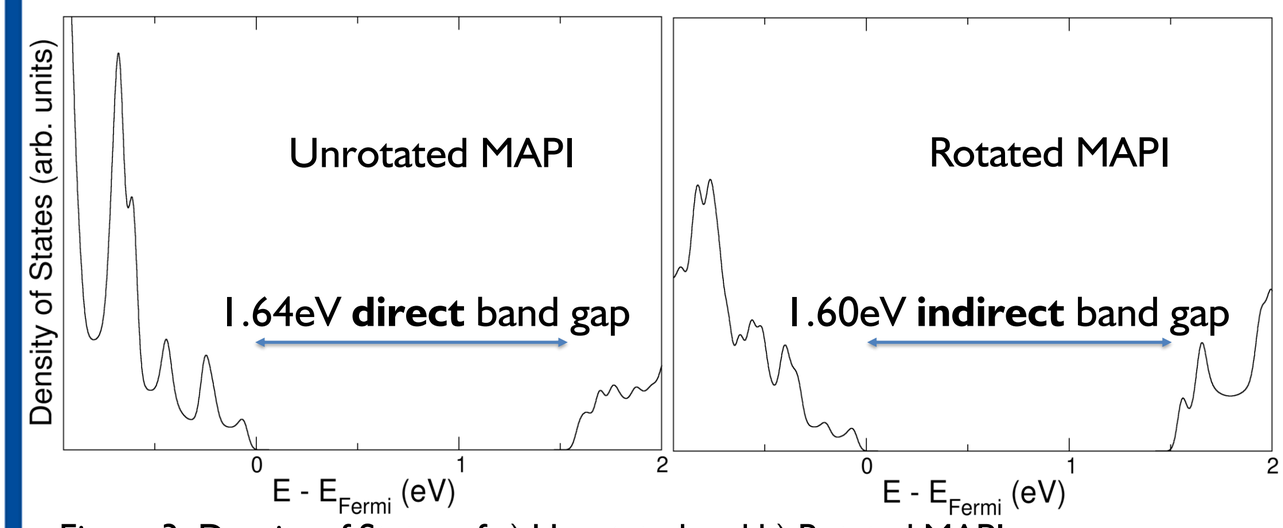


Figure 3. Density of States of a) Unrotated and b) Rotated MAPIs

Composition

- We explore the effect of composition of halide and the orientation of the organic molecule.
- We find that we can tune the bandgap by changing the composition of $CH_3NH_3Pb(I_{1-y}Br_y)_3$.

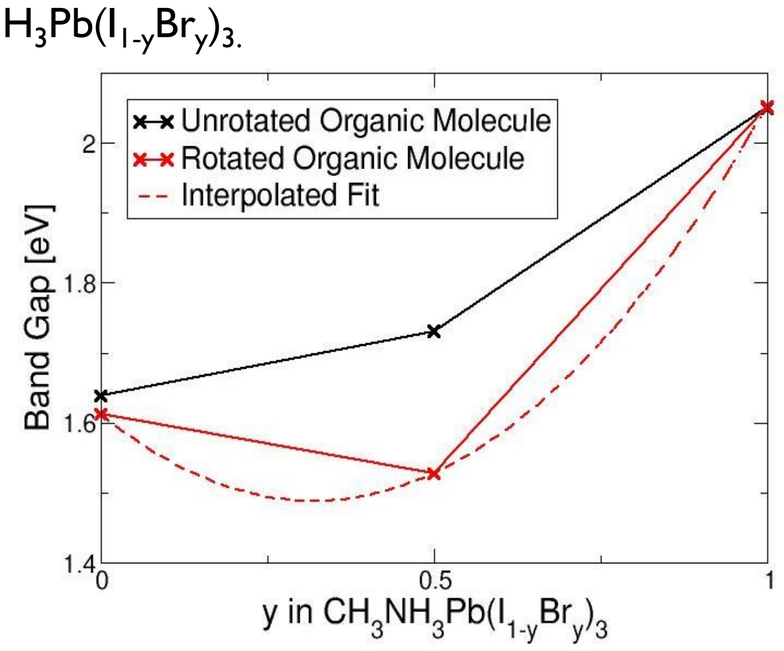


Figure Band gap with change of I-Br proportion in MAPI

- Minimum band gap is predicted between 0% and 50% Br in MAPI structure.
- We also find there is a difference in band gap for different orientations of the organic molecule.
- Thermal fluctuations can cause variations in the orientation of the organic molecule, therefore the band gap can fluctuate between the minimum and the maximum values.
- Rotated $FA_{0.5}MA_{0.5}PbI_3$ results in a PBE band gap of ~1.45 eV

Conclusion

- Hybrid perovskite properties are dominated rotation of molecule.
- This rotation is within the energy of a thermal fluctuation.
- Different rotation can enhance the charge carriers' mobility.
- 0–50% Br doping and FA-MA molecule mixing will optimise band gap of perovskite solar cell towards 1.34 eV to achieve 33.7% theoretical PCE.
- Next step is to look into stability, including clustering.

Reference

[1]"A decade of perovskite photovoltaics," *Nat. Energy*, **4**, 1, 1, 2019.

[2] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, **77**, 18, 3865–3868, 1996.

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