Defects Activity in Lead Halide Perovskites: a Computational Perspective

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Outline

- **Defects modelling** in Lead-Halide Perovskites *(ACS Energy Lett.* ***2018****, 3, 2206-2222)*

- **Defects chemistry** and **Defects Tolerance** of Lead-Halide Perovskites *(Energy Environ. Sci.* ***2018****, 11, 702-713)*

- **Role of surfaces** and defects reactivity *(ACS Energy Lett.* **2019**, 4, 779-785*)*

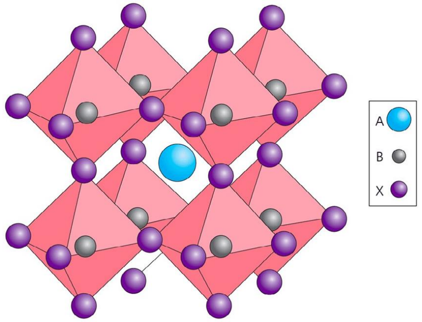
Introduction – Perovskites Solar Cells

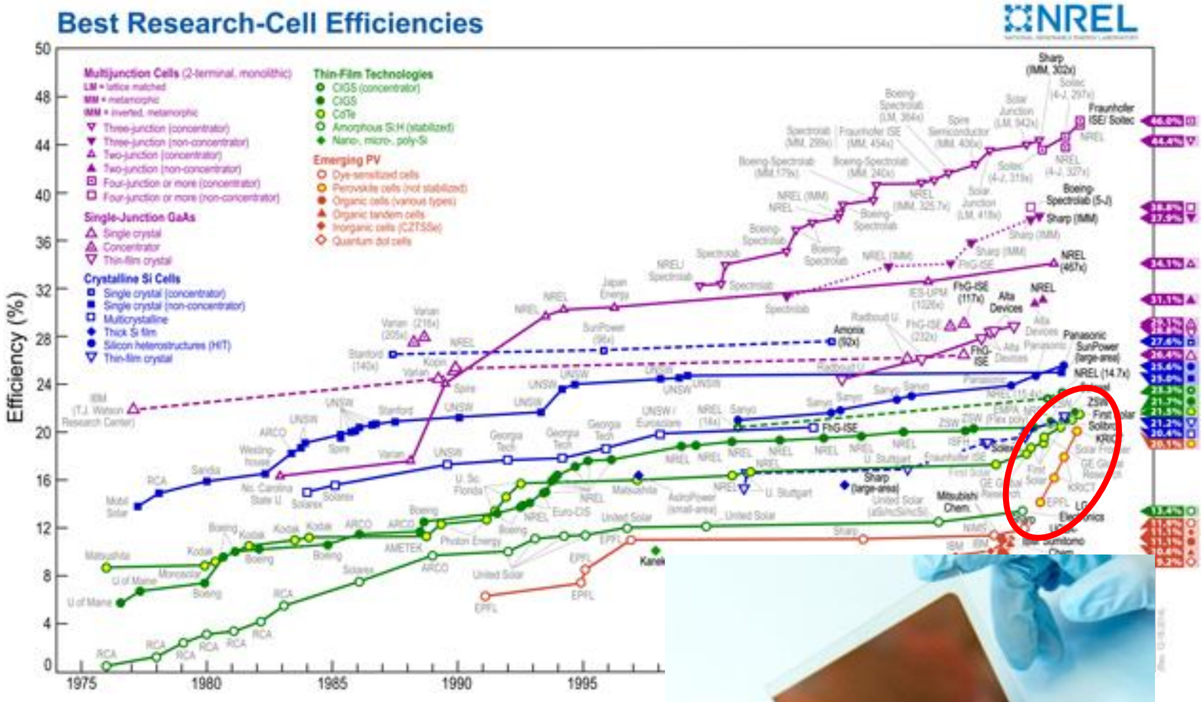
- **Structure ABX_3**

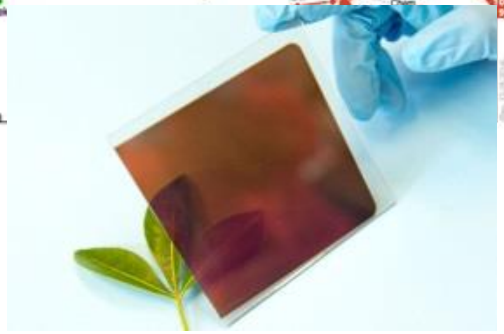
  A = organic/inorganic cation

  B = metal (Pb)

  X = halide (I, Br, Cl)



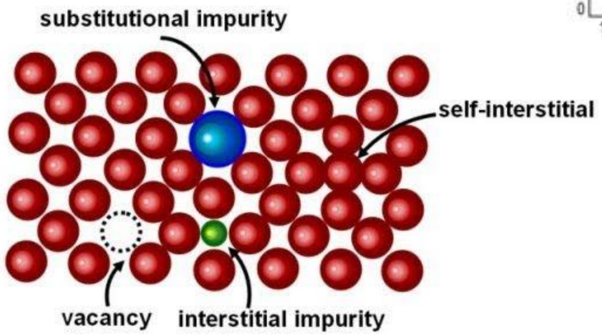




- **Direct band-gap semiconductor (1.2 to 1.6 eV)**
- **Low cost manufacturing (solution chemistry)**
- **Thin films technology (high defects densities)**

High efficiencies (24%)

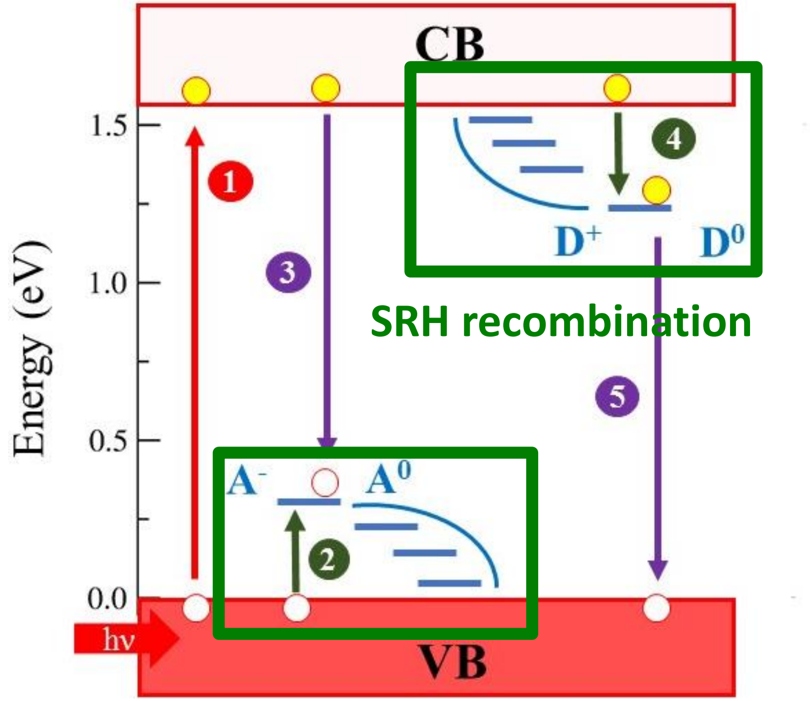
- **Long-lived carriers**
- **High defects tolerance**



Green et al. *Nat. Photon.* **2014**, 8, 506-514

Defects and Charge Traps in Perovskites

$MAPbI_3$ (SC)



Charge Traps: loss of efficiency

- Native defects play a prominent role in PL properties of HOIP (*Shockley et al. Phys. Rev.* ***1952****, 87, 835-842*)
- Defects tolerance: PL properties not strongly affected even in polycrystalline HOIP (~ 10^{16} cm^{-3}) (*Leijtens et al. Energy Environ. Sci.* ***2016****, 9, 3472-3481*)

Defects activity both in the bulk and on the surface of LHP

First-principles DFT modelling

Defects - Essentials

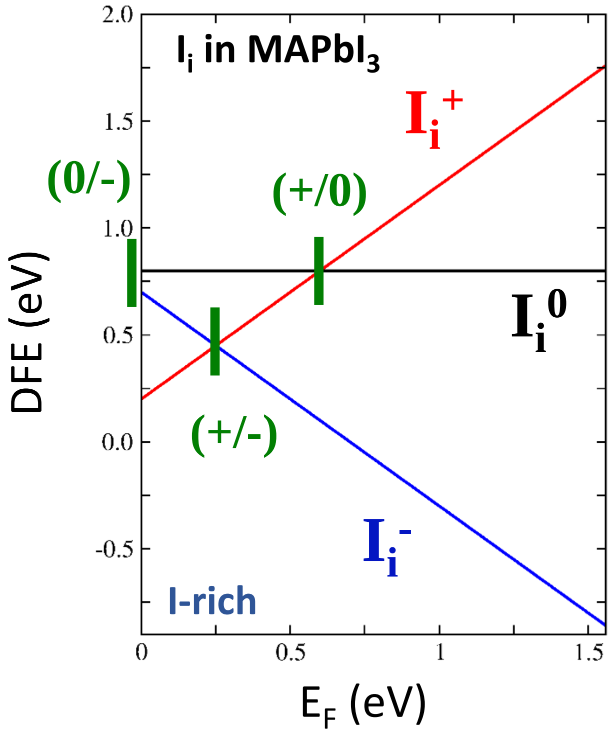
- **Native defects:** natural products of crystal growth (**entropy gain**)

$$\Delta G_{def} = \Delta H_{def} - T\Delta S_{def} \qquad \Delta H_{def}>0 \qquad \Delta S_{def}>0$$

- **Defects stability: Defects formation energies (DFE)**

$$DFE(X^q) = E(X^q) - E(bulk) - \boxed{\sum_i n_i \mu_i} + \boxed{q(E_F + VBM + \Delta V)} + E^q$$

Different states of charge



Different conditions of growth

- **Thermodynamics ionization levels (TIL)**

$$\boldsymbol{\varepsilon(q/q') = \frac{DFE(D^q, E_F=0) - DFE(D^{q'}, E_F=0)}{q' - q}}$$

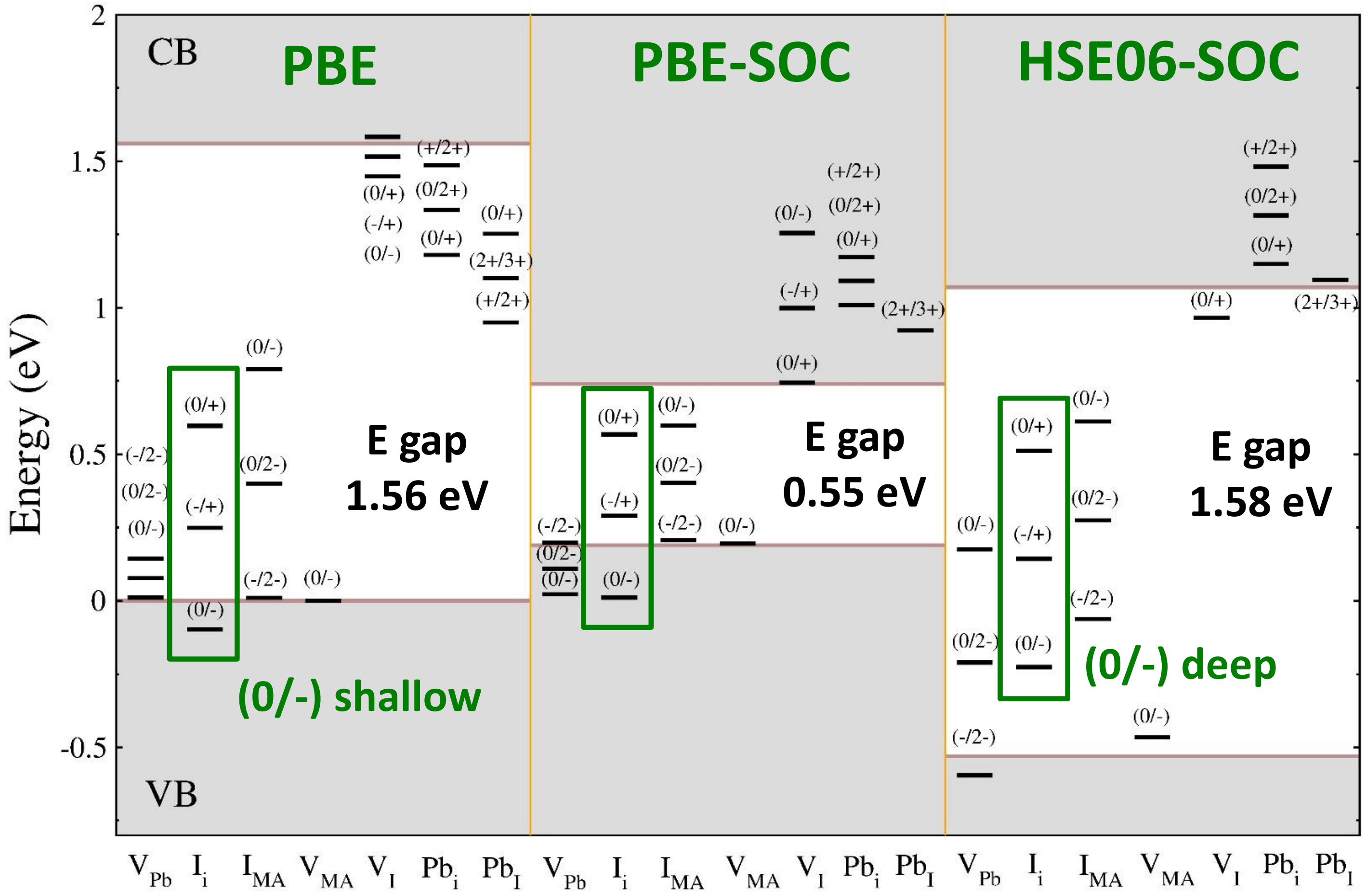
- **Deep ionization levels: charge trapping**

Van de Walle et al. J. Appl. Phys. ***2004****, 95, 3851-3879*

Defects – Band gap problem

$$DFE(X_q) = E^{def}(X_q) - E^{prist} + \sum_i n_i \mu_i + \boxed{q(E_F + E_{VB} + \Delta V)} + E^q$$

MAPbI$_3$ - Thermodynamic ionization levels



Meggiolaro et al. ACS Energy Lett. ***2018****, 3, 2206*

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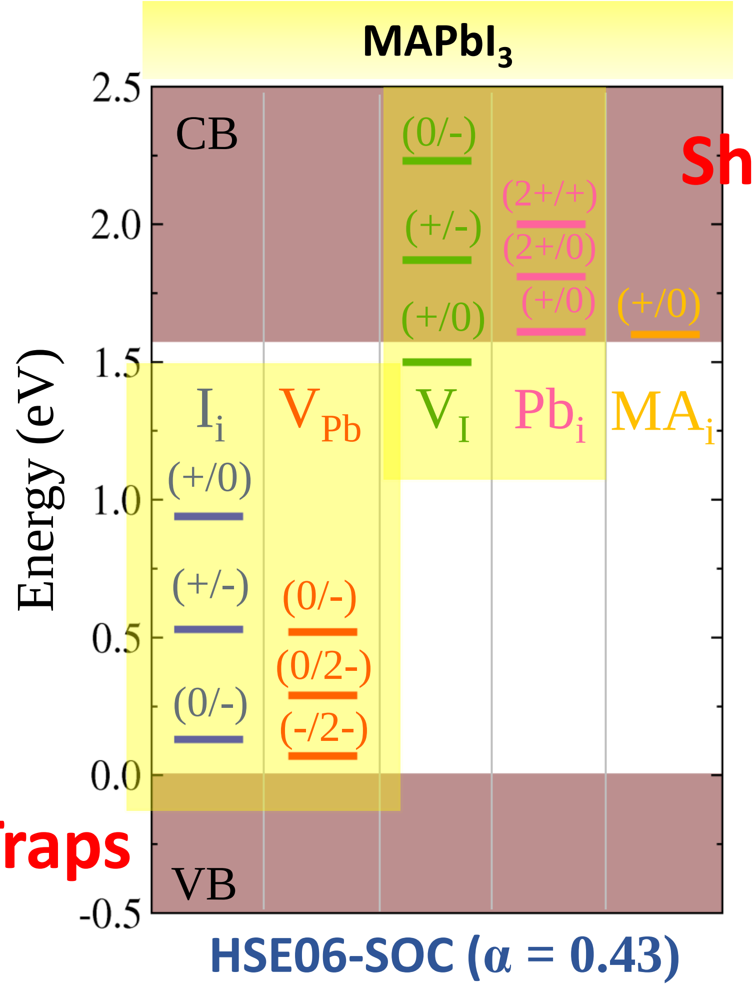
- **Defects chemistry** and **Defects Tolerance** of Lead-Halide Perovskites *(Energy Environ. Sci. **2018**, 11, 702-713)*

- **Role of surfaces** and defects reactivity *(ACS Energy Lett. **2017**, 2794-2798)*

Trapping properties - Thermodynamic ionization levels

- **I_i and V_{Pb} are deep traps**. They can trap both electrons or holes depending on their oxidation states
- I_i and V_{Pb} are associated to **undercoordinated iodines** (I-rich environment)
- **Iodine chemistry dominates the charge trapping activity in $MAPbI_3$**



- **V_I and Pb_i show shallow levels.**
- **Inert** in charge trapping processes
- V_I and Pb_i are associated to **under-coordinated Pb** (Pb-rich environment)
- MA defects do not couple with band edges (shallow)

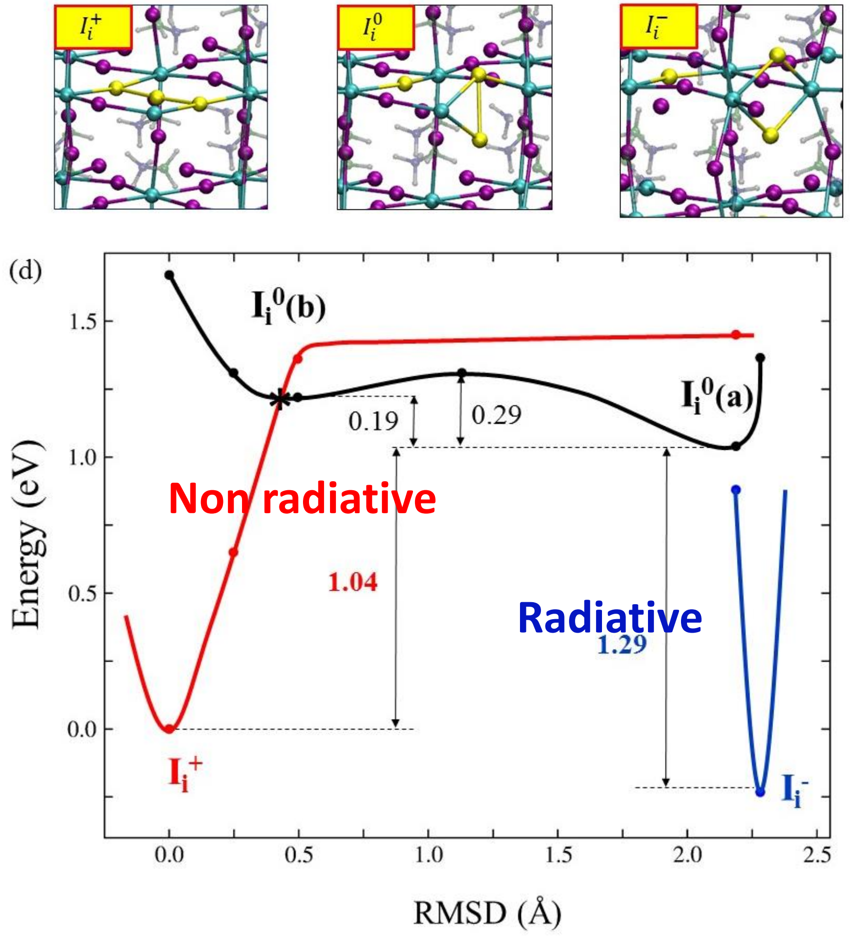
Iodine Chemistry determines the charge traps activity in LHP

Meggiolaro et al. Energy Environ. Sci. ***2018****, 11, 702-713*

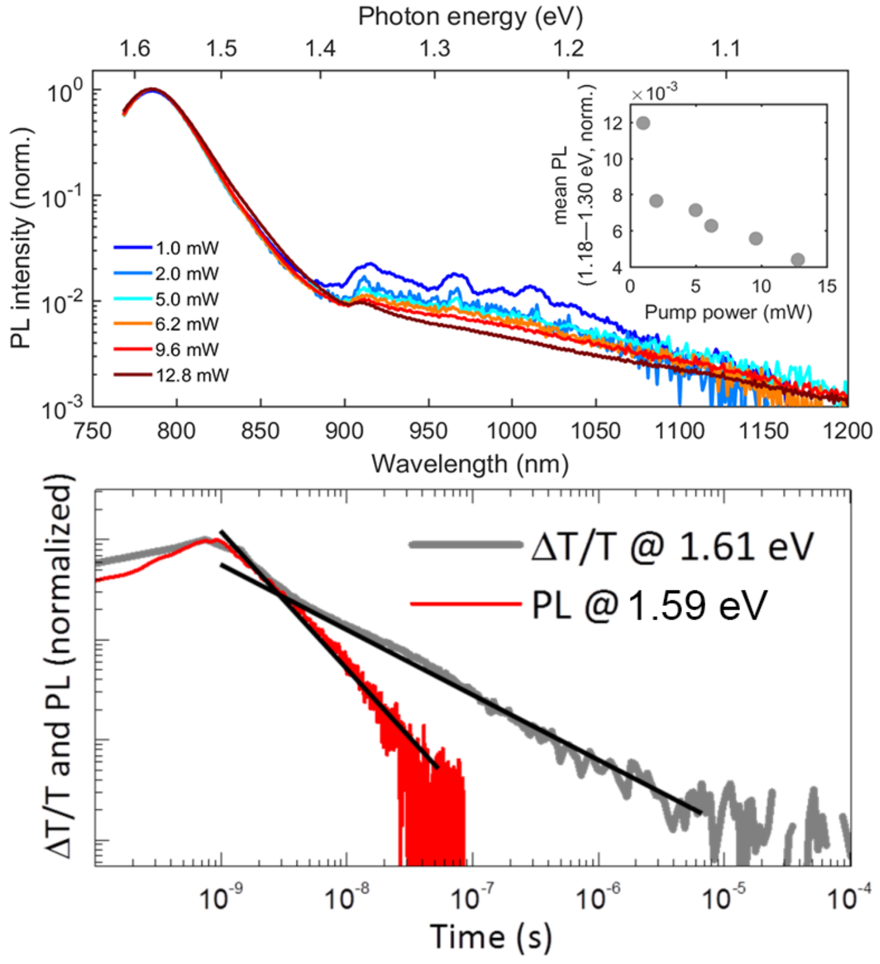
Metastable and emissive traps in MAPI

Theory

- **Long-lived electrons traps (μs), non-radiative decay: I_i^+**
  - **Short-lived holes traps, radiative decay: I_i^-**



MAPbI$_3$ - Experiments



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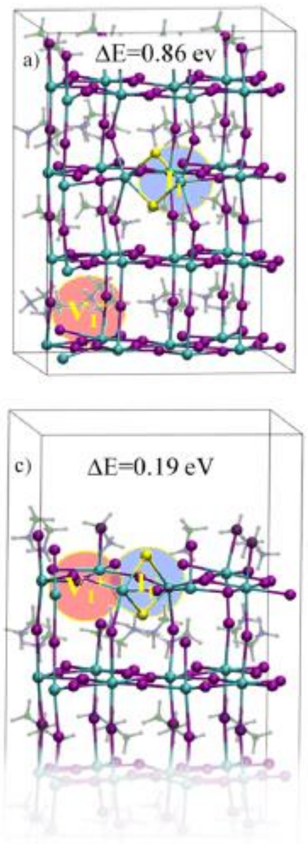
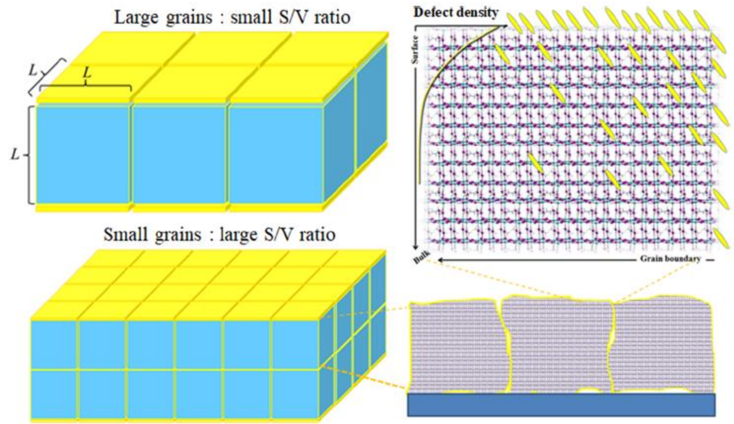
Surface defects activity

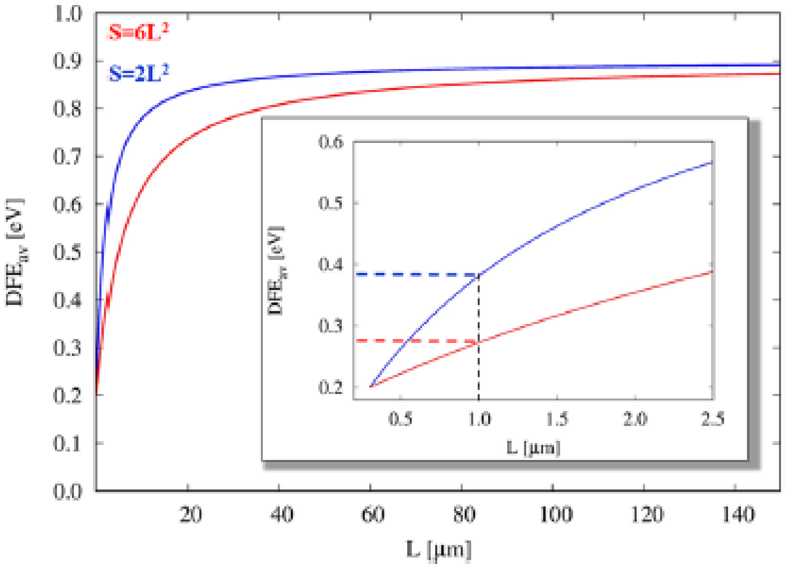
- **Defects are stabilized at surfaces**
- **Enhanced migration and trapping activity**

Model: Dimensions of NCs and surface availability strongly affect DFEs and diffusion of defects

$$\mathrm{DFE_{av}} = (d_{\mathrm{surf}} 6L^2 \mathrm{DFE_{surf}} + d_{\mathrm{bulk}} L^3 \mathrm{DFE_{bulk}}) / (d_{\mathrm{surf}} 6L^2 + d_{\mathrm{bulk}} L^3)$$







$$\sigma = T^m e^2 D_0 / kT \ \exp(-\Delta H^{\neq}/kT) \ \exp(-\mathrm{DFE}/kT)$$

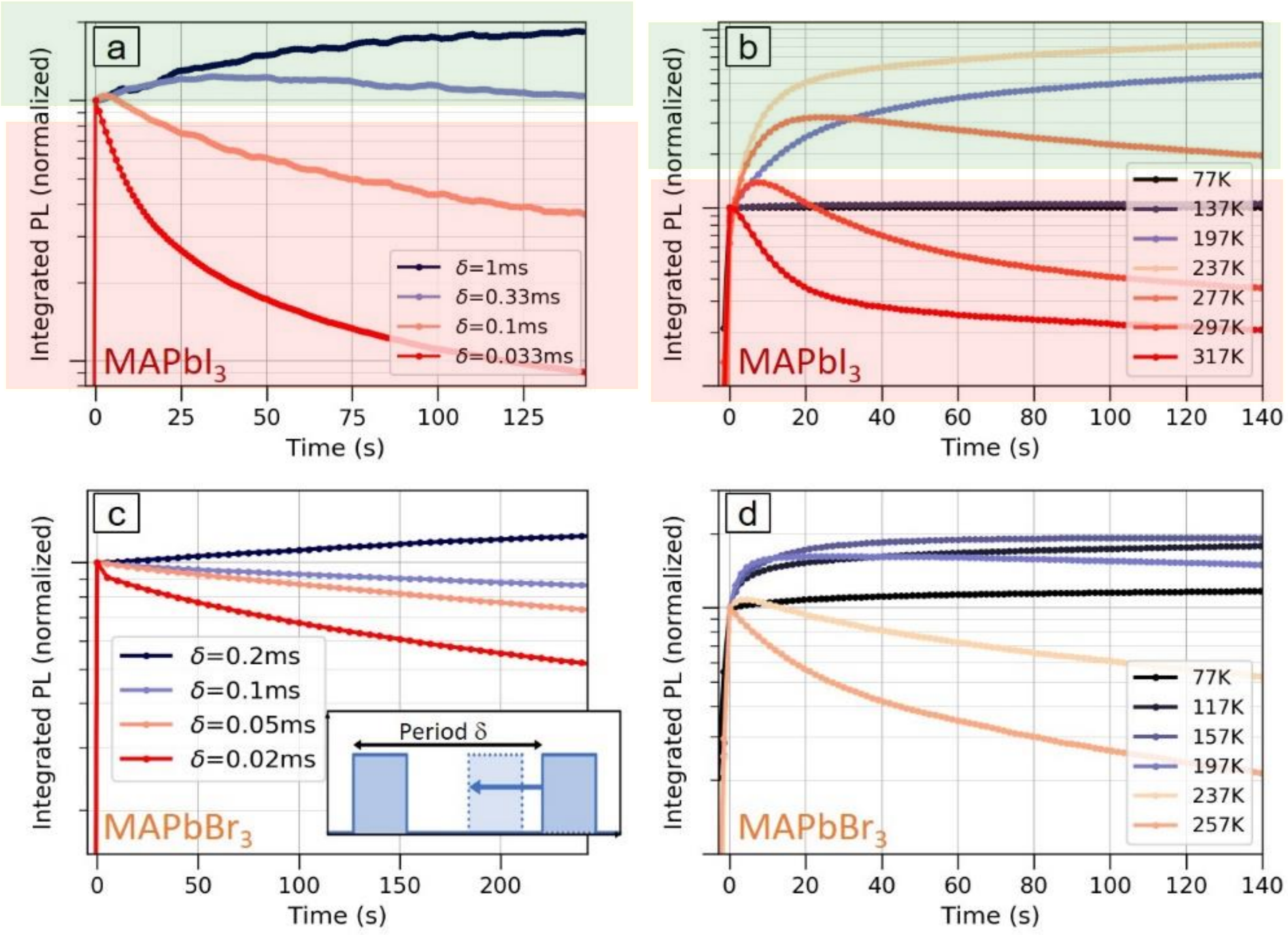
Passivation of surface sites limits defects formation and migration

Meggiolaro et al. *ACS Energy Lett.* **2019**, 4, 779-785

Photostability of LHP

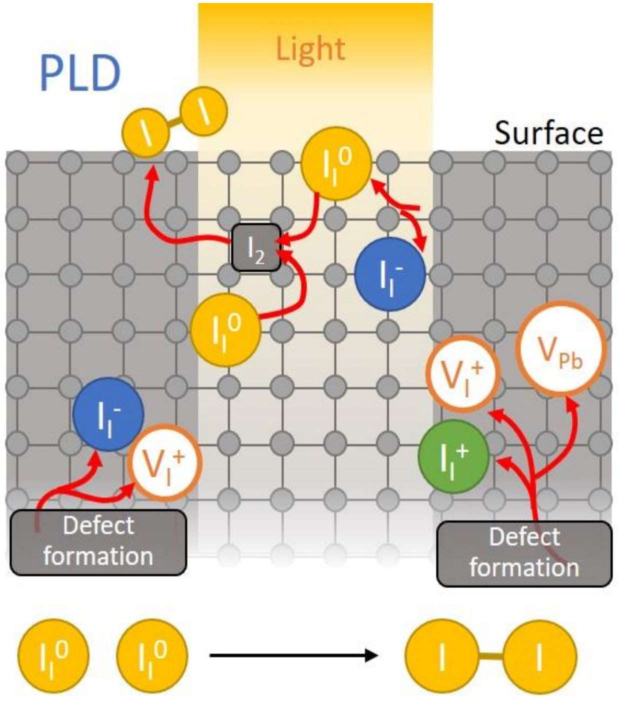
Photostability and PCEs of LHP are influenced by temperature and light exposure

Light repetition rate | **Temperature**



PLE

PLD



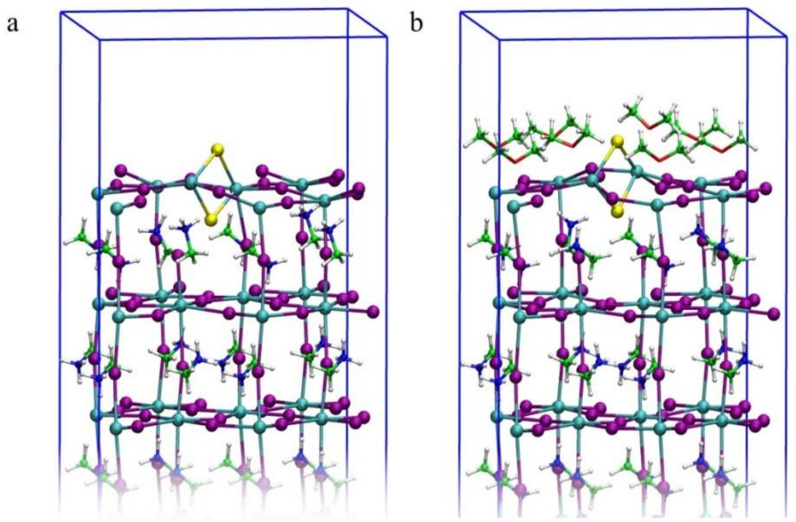
Motti, S. G.; Meggiolaro, D. et al. *Nat. Photon.* **2019**, 13, 532-539

Surface passivation to stabilize PVK thin films

Passivation of surfaces with oxygen-containing agents / polymers, such as PEO or TOPO

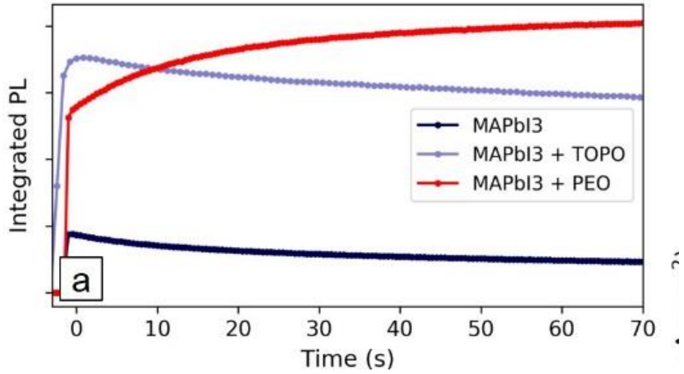
Theory

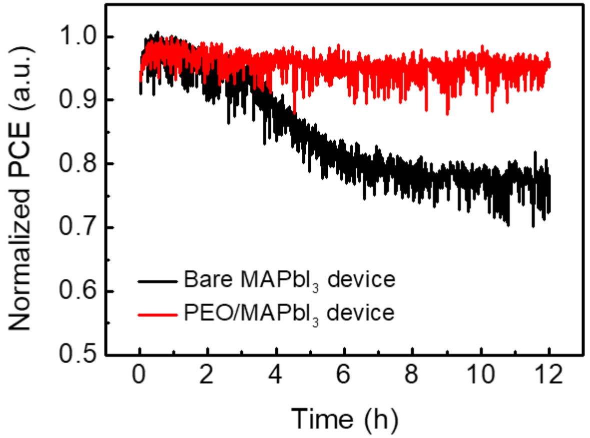
Iodine interstitial
DFE increase by 0.1 eV



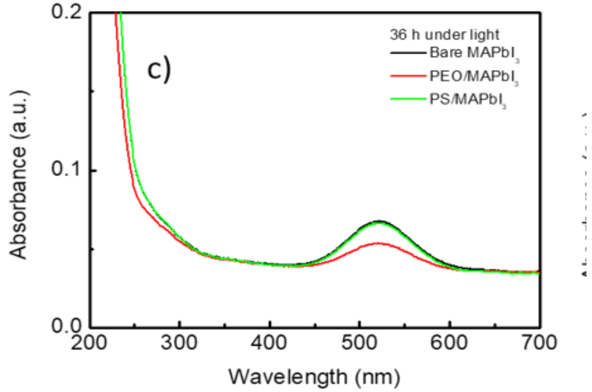
Experiments

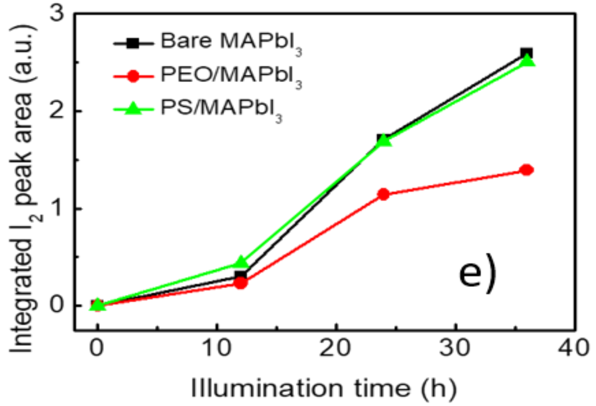
Increased Photostability and PCE





Limited I_2 release





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Thank you!