Room-temperature transformation dynamics and structural relationship between PbI_2 and $CH_3NH_3PbI_3$

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How is lead iodide (PbI_2) transformed into methylammonium lead iodide ($CH_3NH_3PbI_3$)? The question is very relevant to assess the possibility of dynamic "self-healing" at room temperature (via topotactic reaction) in $CH_3NH_3PbI_3$ (a promising material for future photovoltaics). We study the room temperature transformation of PbI_2 single crystals, which are exposed to isopropanol solution of methylamonium iodide (CH_3NH_3I), to perovskite-structured $CH_3NH_3PbI_3$, using Scanning Electron Microscopy (SEM) for revealing structural relations and in-situ photoluminescence microscopy (PLM) for dynamics.

Background

Definition

Topotactic vs dissolution+reconstruction

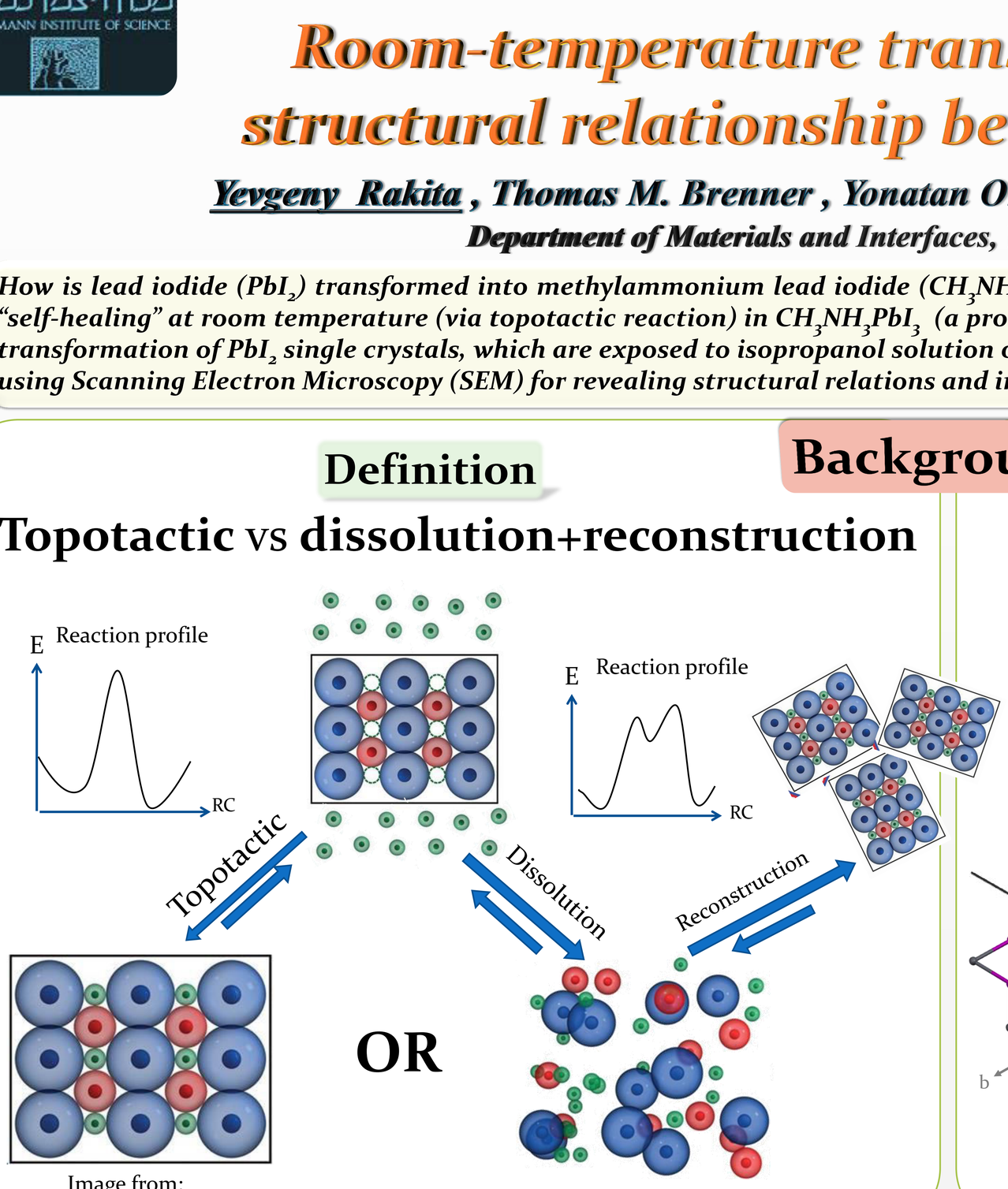
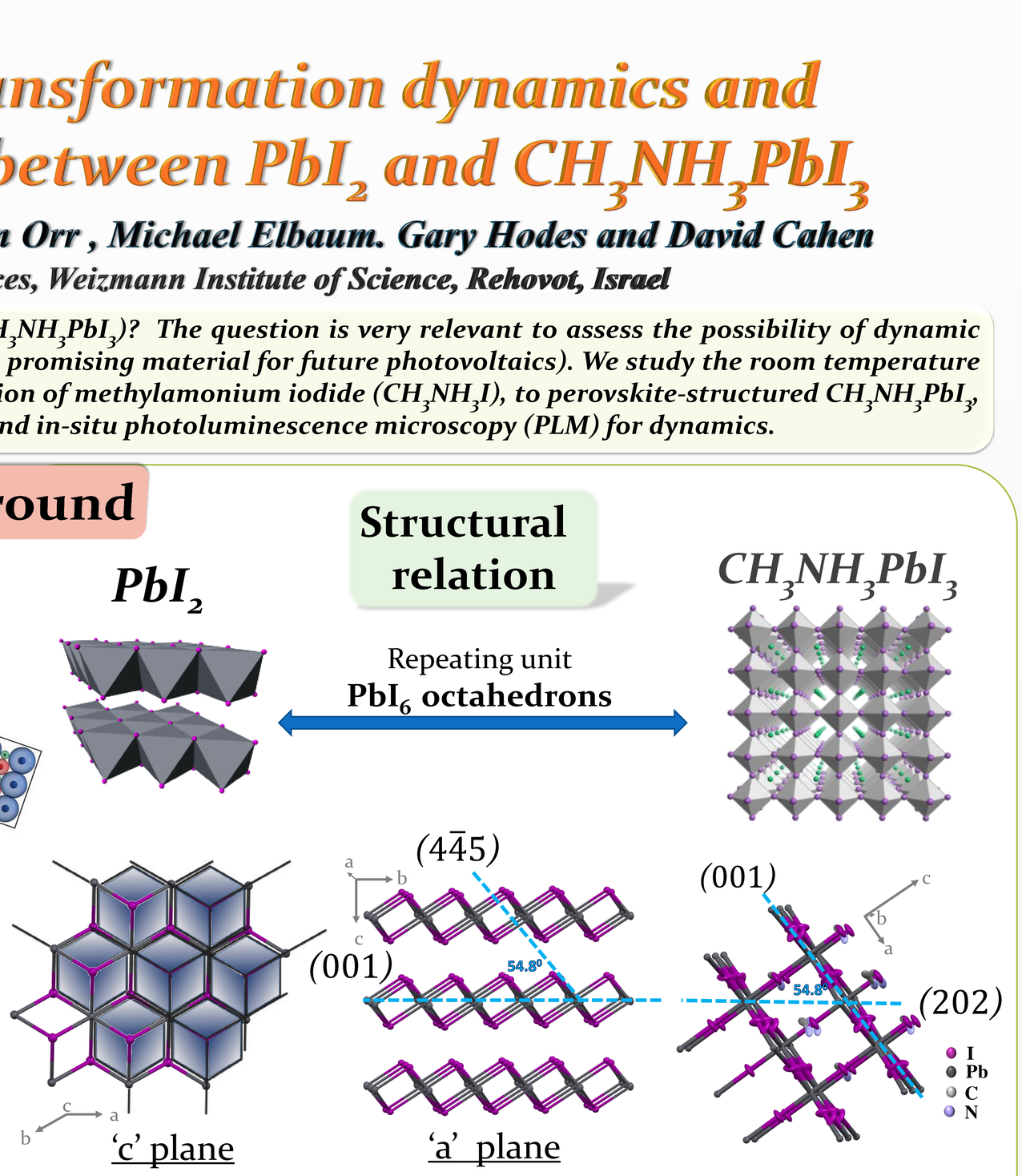


Image from:
Science 341, 1222 (2013)

Structural relation

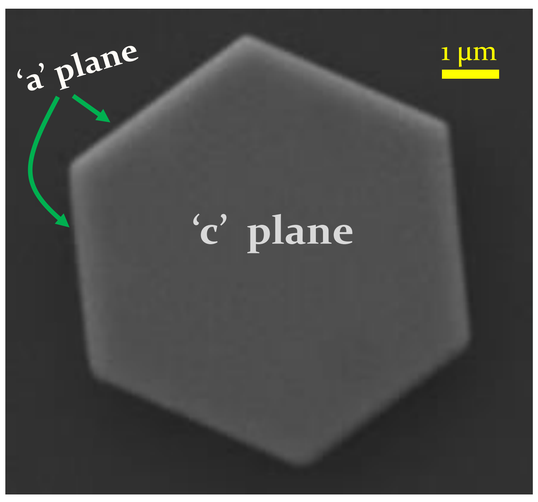


Structural relation will be reflected in morphology

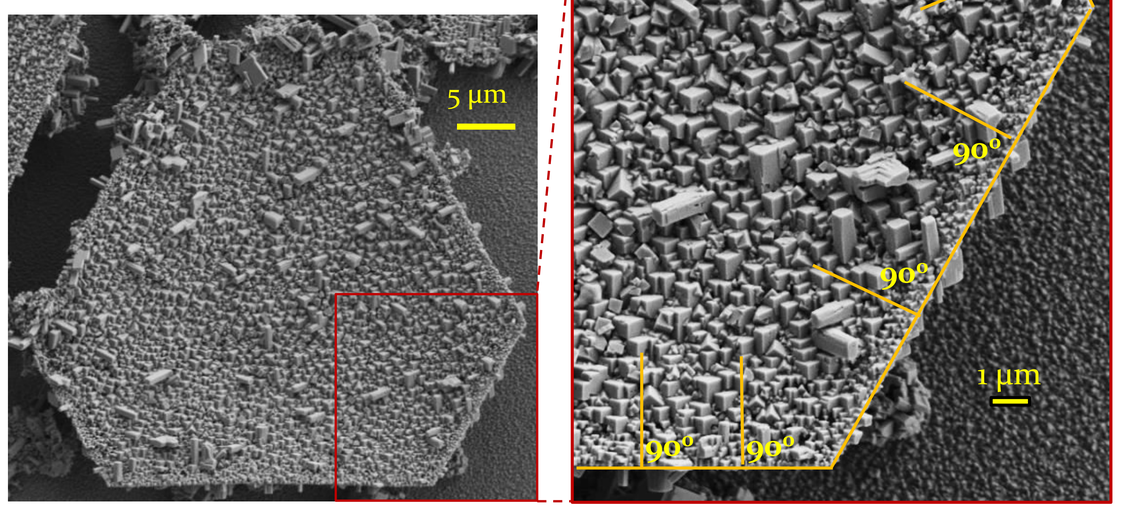
Results

Morphological changes

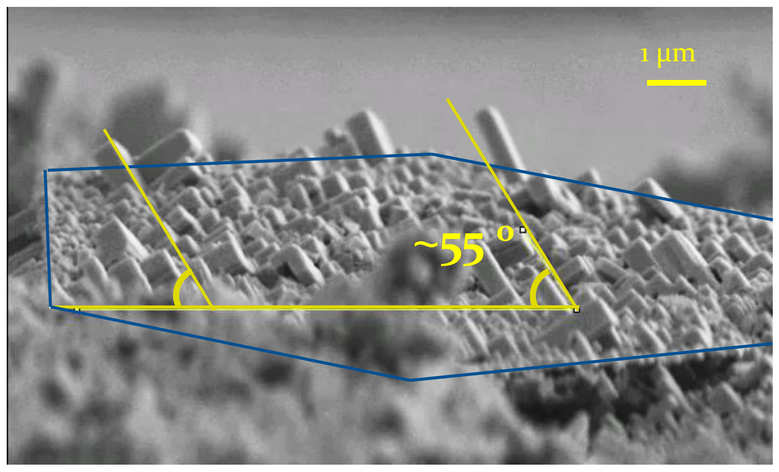
Before the reaction



Dipping in 0.1M CH_3NH_3I in IPA for 55 hours (@RT)

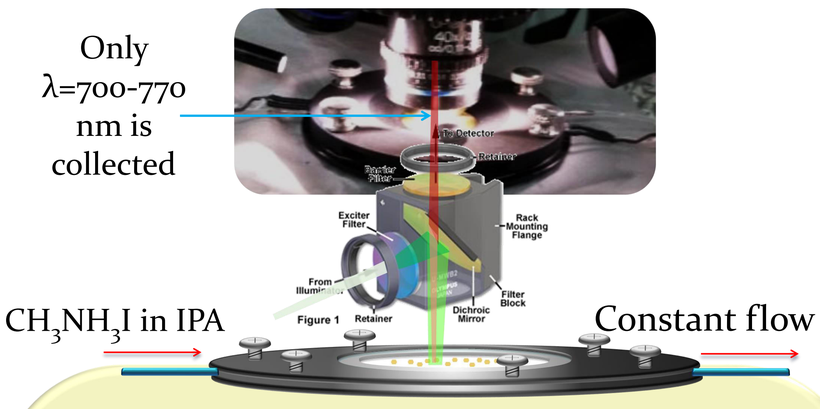


Side view



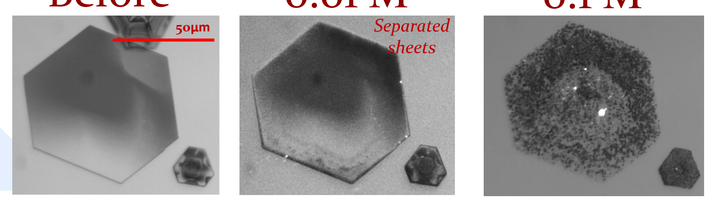
Reaction dynamics

Photoluminescence Microscope

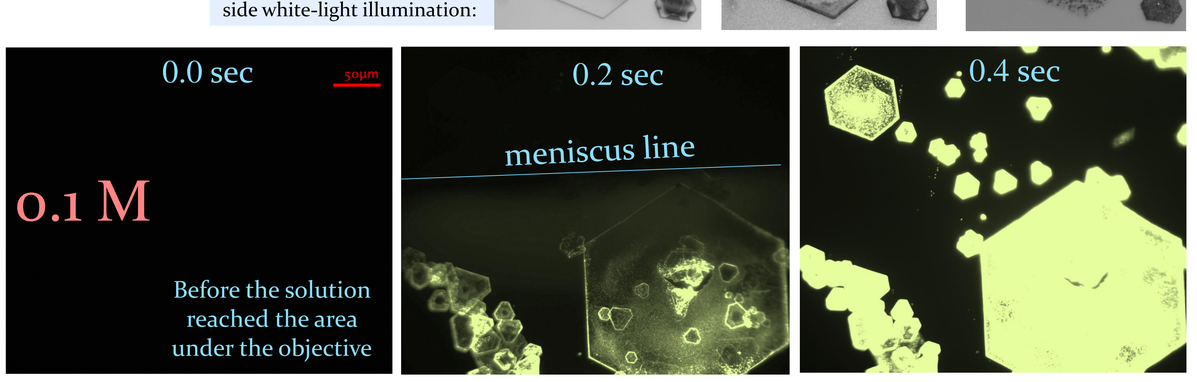


***Reversibility**: after washing with IPA exposed PbI_2 crystals to CH_3NH_3I solution (at given concentration)*

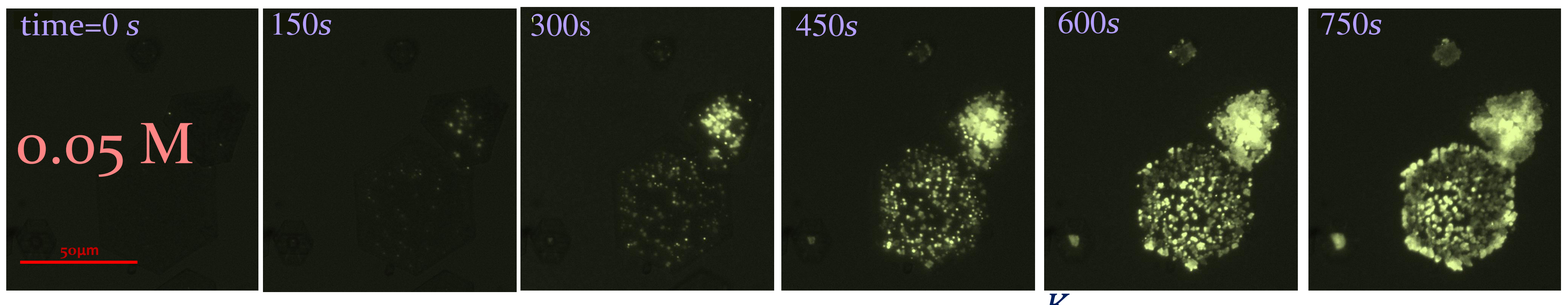
PL microscope images with side white-light illumination:



Low kinetic barrier
Transformation starts at once



Thermodynamics:



No reaction was observed at 0.025M

$MAI_{(IPA)} + PbI_{2(s)} \overset{K_{eq}}{\Leftrightarrow} MAPbI_{3(s)}$

K_{eq}=~20M^{-1} → $\Delta G_{(300K)}$=-75meV

Conclusions

- The observed geometrical relations between PbI_2 hexagons and highly oriented $CH_3NH_3PbI_3$ crystals can be explained buy the structural ease to keep [PbI_6] octahedrons in the same orientation, which indicates towards possible fast topotactic nucleation at the micro-scale followed by dissolution and regrowth.
- Reversibility of the reaction and what appears as separated PbI_2 sheets indicates towards intercalation between PbI_2 sheets, where only at threshold concentration a complete conversion occurs. Converted sites act as nucleation centers.
- Negligible kinetic barrier was observed
- Free energy for forming a luminescent structure in IPA solution is found to be only ~3 kT @ RT!