How is lead iodide (PbI₂) transformed into methylammonium lead iodide (CH₃NH₃PbI₃)? The question is very relevant to assess the possibility of dynamic “self-healing” at room temperature (via topotactic reaction) in CH₃NH₃PbI₃ (a promising material for future photovoltaics). We study the room temperature transformation of PbI₂ single crystals, which are exposed to isopropanol solution of methylammonium iodide (CH₃NH₃I), to perovskite-structured CH₃NH₃PbI₃, using Scanning Electron Microscopy (SEM) for revealing structural relations and in-situ photoluminescence microscopy (PLM) for dynamics.

**Conclusions**

- The observed geometrical relations between PbI₂ hexagons and highly oriented CH₃NH₃PbI₃ crystals can be explained by the structural ease to keep [PbI₆] 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 PbI₂ sheets indicates towards intercalation between PbI₂ 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 luminous structure in IPA solution is found to be only ~3kT @ RT!

**Results**

Dipping in 0.1M CH₃NH₃I in IPA for 55 hours (@RT)

**Morphological changes**

**Reaction dynamics**

Photoluminescence Microscope

- Only λ=700-770 nm is collected

**Thermodynamics:**

- No reaction was observed at 0.025M
- MAI(IPA)+PbI₂(s) ⇌ MAPbI₃(s) 
  \[ K_{eq} = 20 \text{M}^{-1} \Rightarrow \Delta G_{(300K)} = -75 \text{meV} \]

**Before the reaction**

- Separated PbI₂ sheets

**Side view**

**Reversibility:** after washing with IPA exposed PbI₂ crystals to CH₃NH₃I solution (at given concentration)

**Low kinetic barrier**

Transformation starts at once

**Definition**

Topotactic vs dissolution+reconstruction

**Structural relation**

- Repeating unit PbI₆ octahedrons

Image from:
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