Lehrstuhl für Elektronische Bauelemente

The Impact of Additives on Halide Perovskite Grain Growth

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Motivation and Methods

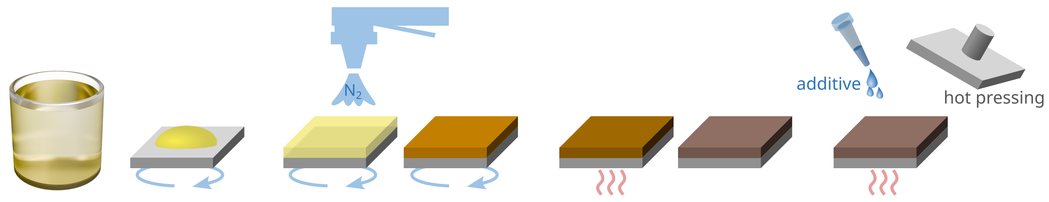
additive engineering on perovskite crystallization:
grain size increase → e. g. improve solar cell performance

nucleation phase ⟵ **additive impact** ⟶ **grain growth**

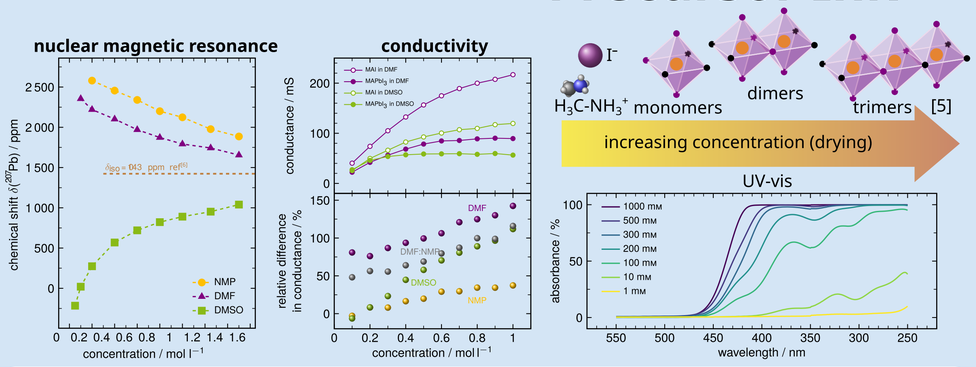
- NMR spectroscopy
- electric conductance
- UV-vis spectroscopy

- X-ray diffraction
- topography
- solar cell devices
- post processes

liquid Pb NMR | in-situ X-ray scattering | solid state NMR | X-ray diffraction
absorbance | el. conductivity | phase field simulations | solar cells | microscopy

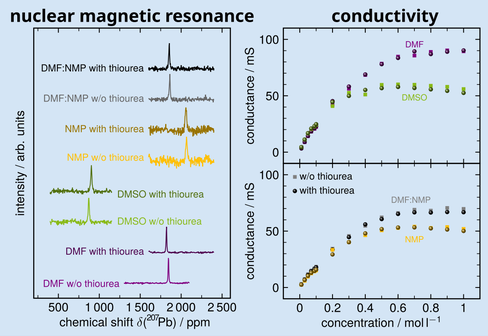


Precursor Ink



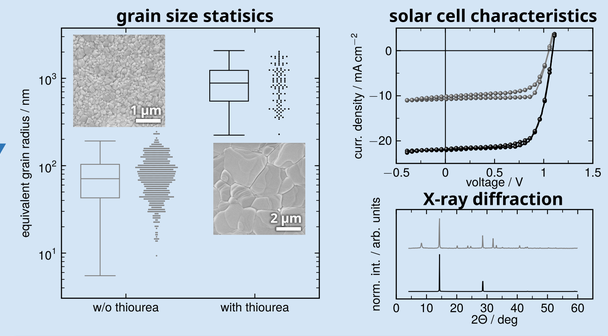
- perovskite ink: a lead-complex **colloidal ink** → literature[2]
- **colloids grow** in size during **drying process**

addition of thiourea



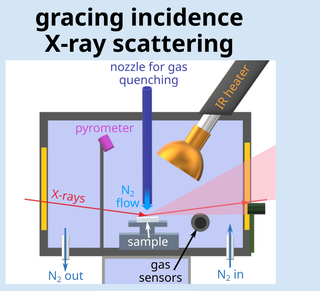
- **no detectable impact** of additive on:
  Pb-complexes, colloidal nature, nor drying

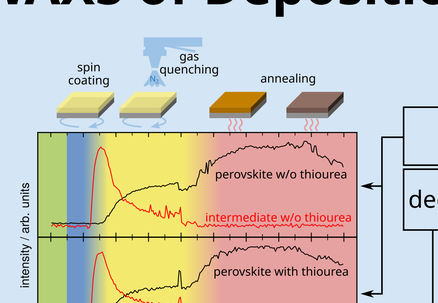
Perovskite Layer



- thiourea: **increased grain size**
- **improved** solar cell **performance**[3]

In-Situ GIWAXS of Deposition Process

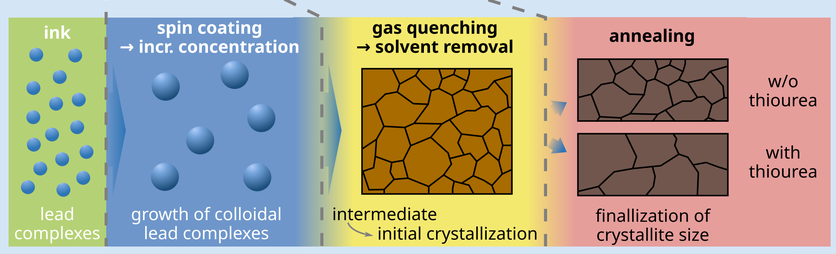




GIWAXS Evaluation:

peak intensity: perovskite vs. intermediate

deg. of orientation = intensity(45°) / intensity(90°)



- **crystallite formation identical** with vs. w/o thiourea additive
- grain **growth during annealing** step

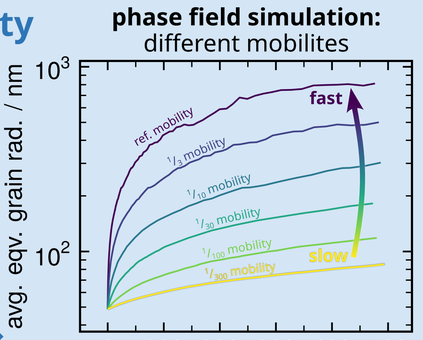
→ **nucleation** dynamic **not impacted** by additive

Mechanism of Grain Growth

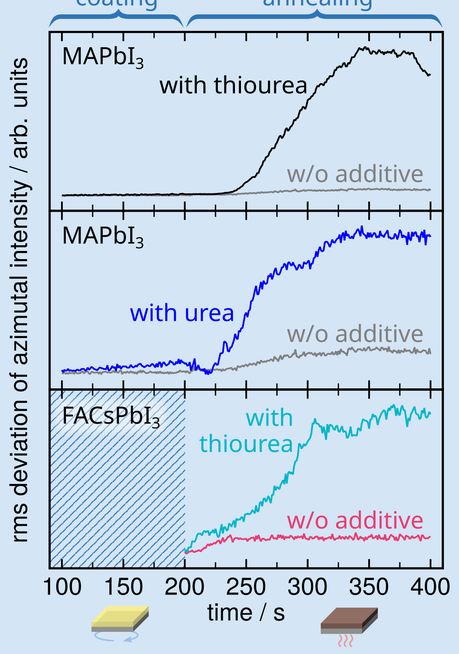
boundary mobility = grain growth:

additive engineering facilitates **ion mobility** → grain coarsening

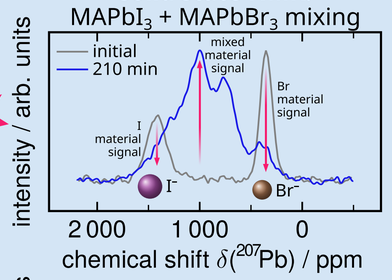
phase field simulation: different mobilites



composition/additve variation

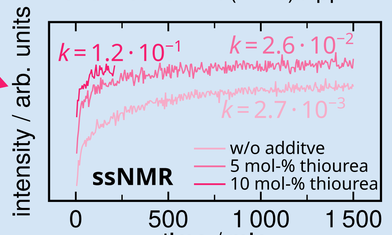


solid state NMR: $MAPbI_3$ + $MAPbBr_3$ mixing

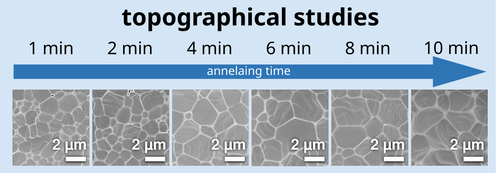


ion mixing speed ↕ **ion mobility**

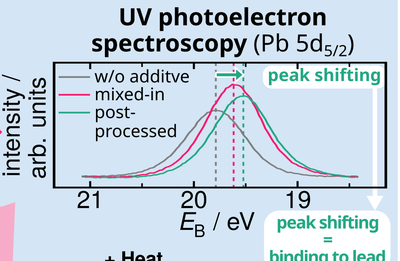
$y = 1 - A \cdot \exp(-k \cdot t^n)$



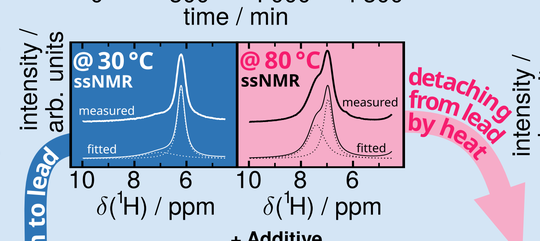
topographical studies

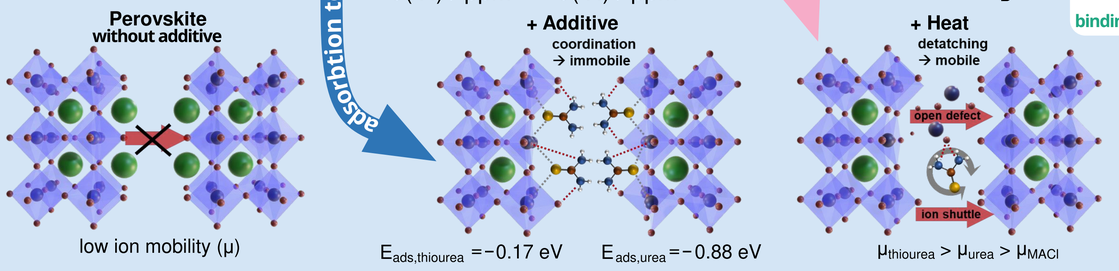


UV photoelectron spectroscopy ($Pb\ 5d_{5/2}$)



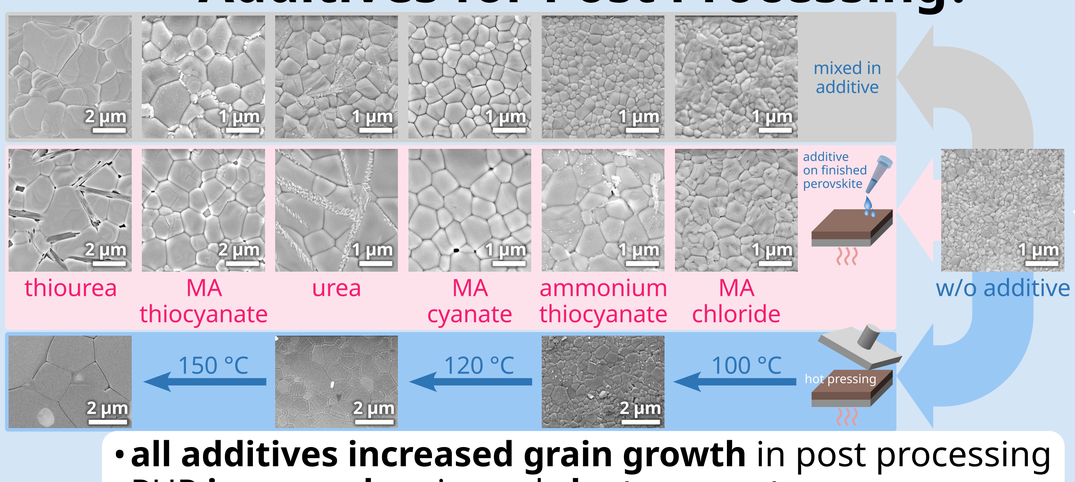
additive: adsorption and detachement





- **speed** of coarsening/grain growth → dependant on **ion mobility**
- ion **mobility** dependant on **binding energy** (from DFT)

Additives for Post Processing?



- **all additives increased grain growth** in post processing
- PHP **increased** grains only **by temperature**

Conclusion

- Thiourea crystallization additive **does not impact the nucleation** step, but **ion mobility across grain boundaries**. → grain coarsening
- Concept transferable to **different additives, perovskite compositions** and provides a **link to post-processing**.
- DFT calculations explain **mobility increase upon annealing**. → loose bonding to MA^+ vacancies

References:

[1] T. Maschwitz, et al. How Crystallization Additives Govern Halide Perovskite Grain Growth Nat. Comm. 2025 in production
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[5] A. M. Valencia, et al. Optical Fingerprints of Polynuclear Complexes in Lead Halide Perovskite Precursor Solutions J. Phys. Chem. Lett. 2021, 12, 2299–2305
[6] C. Roiland, et al. *Multinuclear NMR as a tool for studying local order and dynamics in $CH_3NH_3PbX_3$ (X = Cl, Br, I) hybrid perovskites* Phys. Chem. Chem. Phys., **2016**, 18, 27133

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