Organic-inorganic perovskites - chemical mapping and spectroscopy at the nanoscale with AFM-IR

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Introduction

01

In this work the combination of scanning probe microscopy & mid-IR spectroscopy is utilized to achieve nanoscale resolution and chemical identification (AFM-IR). Using AFM-IR, we can discern chemical variations within an individual organic-inorganic perovskite crystallite. Furthermore, the incorporation of hyperspectral nanoscale chemical imaging enables us to capture images depicting the distribution of perovskites and stabilizers. This then helps with further development of new recipes.

Organic-inorganic perovskites

02

Hybrid organic-inorganic perovskites are a class of materials with a crystal structure resembling the octahedral natural perovskite. The chemical formula of halide-based hybrid perovskites is ABX_3, where:

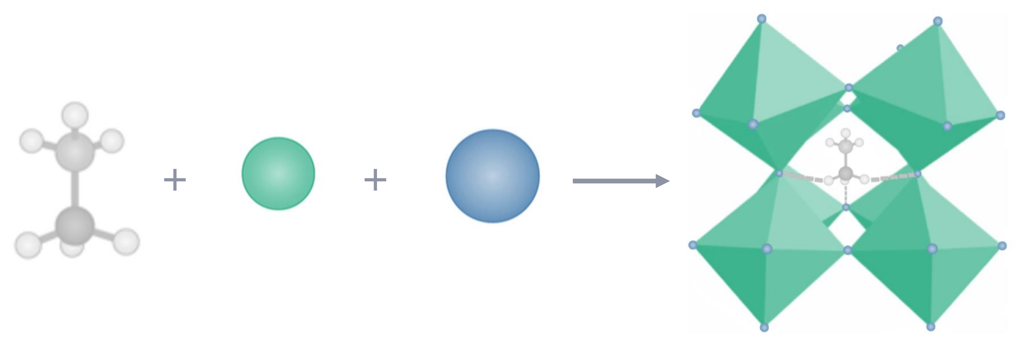
- **A** is an organic cation
- **B** is a divalent metal
- **X** is a halogen/ pseudo-halogen

By changing the constituents **A, B** and **X** it is possible to **alter properties** like:

- absorption coefficient
- bandgap tunability

In recent years additives and stabilizers play a big role to benefit either **film formation** or **stabilization** e.g., starch for viscosity in printable ink, polymers or ionic additives for retarding thermal degradation.

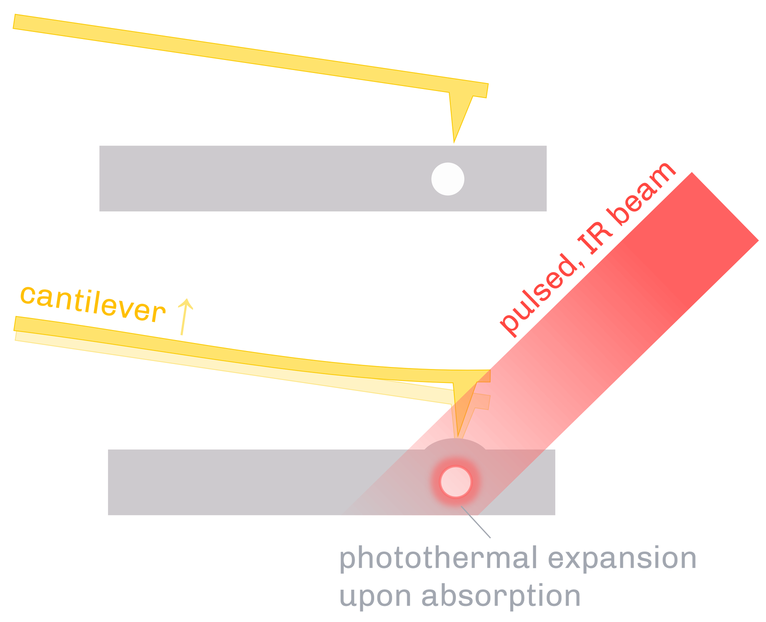
Example of a hybrid organic-inorganic perovskite with an organic cation [1]:



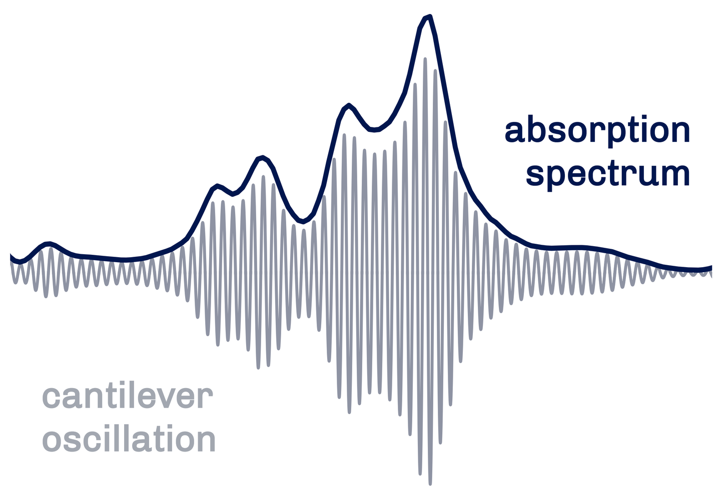
AFM-IR, a photo-thermal technique

03

Infrared spectroscopy (IR) is a powerful technique enabling identification of functional groups and chemical bonds. However, traditional mid-IR spectroscopy is limited by the Rayleigh criterion due to the long wavelength of mid-IR constraining the spatial resolution. Photo-thermal scanning probe microscopy **(AFM-IR)** can overcome this issue by combining atomic force microscopy with mid-IR spectroscopy.



A local, **short-lived thermal absorption** of IR-light induced by a pulsed, tunable EC-QCL source, is measured by the sharp tip of a cantilever. The oscillation amplitude of the cantilever is proportional to the optical absorption coefficient [2].



Thus, by tuning the wavelength of the infrared laser, absorption spectra - or by keeping the wavelength fixed and scanning the AFM tip, absorption images can be recorded.

Perspectives & Challenges

04

Hybrid perovskites are seen as **promising materials** for high-efficiency devices:

- photovoltaic devices (PVs)
- light-emitting diodes (LEDs)
- light fidelity (LiFi)

Advantages over conventional semiconductors:

+ easily processible
  e.g., solution processing
+ cheaper production
  less energy consuming
+ easily scaleable

However, state of the art perovskite devices bring several **challenges**:

- water
  irreversible degradation of the perovskite
- heat
  thermal stress can decompose structure
- oxygen & light
  scavenger effects in structure

Research into these hybrid perovskites has been going on for two decades [3], however the challenges regarding stability and longevity remain the same.

To understand failure modes, macroscale characterization is insufficient!

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nanoscale characterization is required to understand failures & optimize devices

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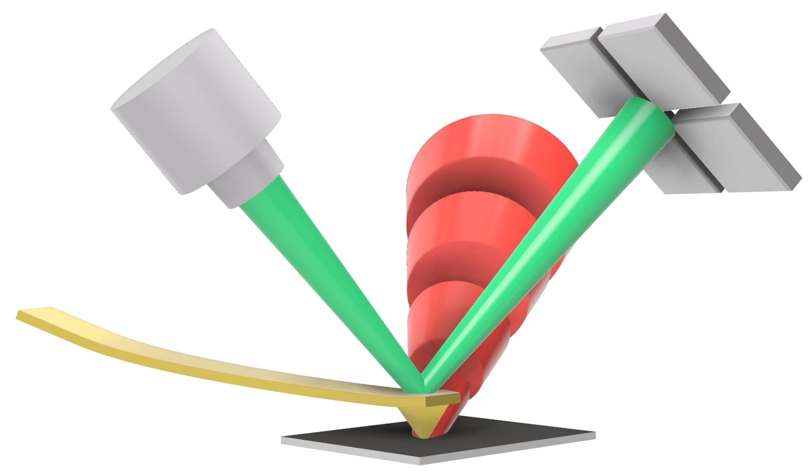
AFM-IR offers both, nanoscale spatial resolution & chemical information & is thus suitable.



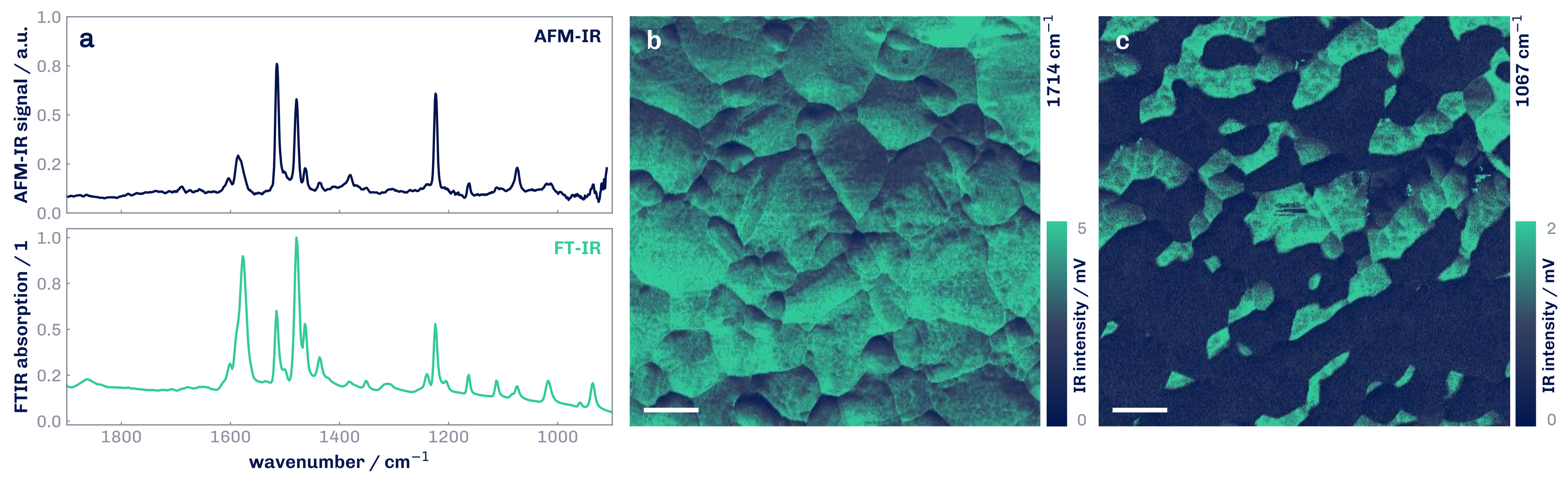
Schematic of a top-illuminated AFM-IR setup using a pulsed, mid-IR laser.

Results

05

We are able to study organic-inorganic perovksites topographically with **nanoscale resolution** to collect information about e.g., crystallization in solution processed perovskites even down to a single crystallite.

Furthermore, we were able to show the distribution of additives and stabilizers in perovskites thanks to AFM-IR - allowing us to collect **chemical-** and **topographical information** simultaneously.



a) AFM-IR measurement of a single perovskite crystallite with ~20 nm spatial resolution, compared to a bulk measurement with diffraction limited FT-IR; b) chemical imaging of a hybrid-perovskite at 1714 cm^{-1} corresponding to C=N stretch of the cation Formamidinium; and c) IR imaging at 1067 cm^{-1} corresponding to C-O stretch of stabilizer starch. Scalebars are 200 nm.

Conclusions

06

We were able to demonstrate the feasibility of AFM-IR for the nanoscale characterization of hybrid perovskite materials.

Quick takes

✓ organic-inorganic perovskites, bear huge potential for photovoltaic- & light emitting devices.

✓ AFM-IR enables high-resolution chemical imaging, thus can help optimizing future developments.

[1] Li, W., Wang, Z., Deschler, F. et al. Chemically diverse and multifunctional hybrid organic–inorganic perovskites. Nat Rev Mater 2, 16099 (2017) DOI: 10.1038/natrevmats.2016.99

[2] A. Dazzi, F. Glotin, and R. Carminati, Theory of infrared nanospectroscopy by photothermal induced resonance, Applied Physics 107, 124519 (2010) DOI: 10.1063/1.3429214

[3] Brenner, T., Egger, D., Kronik, L. et al. Hybrid organic-inorganic perovskites: low-cost semiconductors with intriguing charge-transport properties. Nat Rev Mater 1, 15007 (2016). DOI: 10.1038/natrevmats.2015.7

This work has received funding from the European Union's Horizon 2020 research and innovation programme within the PeroCUBE project under the grant agreement no.: 861985.

European Commission | Horizon 2020 European Union funding for Research & Innovation