Structure-property relationships of functional materials

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BERKELEY LAB

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Combining characterization and synthesis facilities

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Berkeley Lab's synchrotron light source

- In situ XRD during thin-film synthesis (BL 12.3.2)
- In situ, high-temperature pXRD (BL 12.2.2)

Berkeley Lab's NanoScale Research Center

- Glove boxes for synthesis in inert atm
- (Robotic) Thin film deposition tools
  Sol-gel powder synthesis
- In situ optoelectronic characterization; high-throughput XRD
  (all: Inorganic Nanostructures Facility)
- National Center for Electron Microscopy

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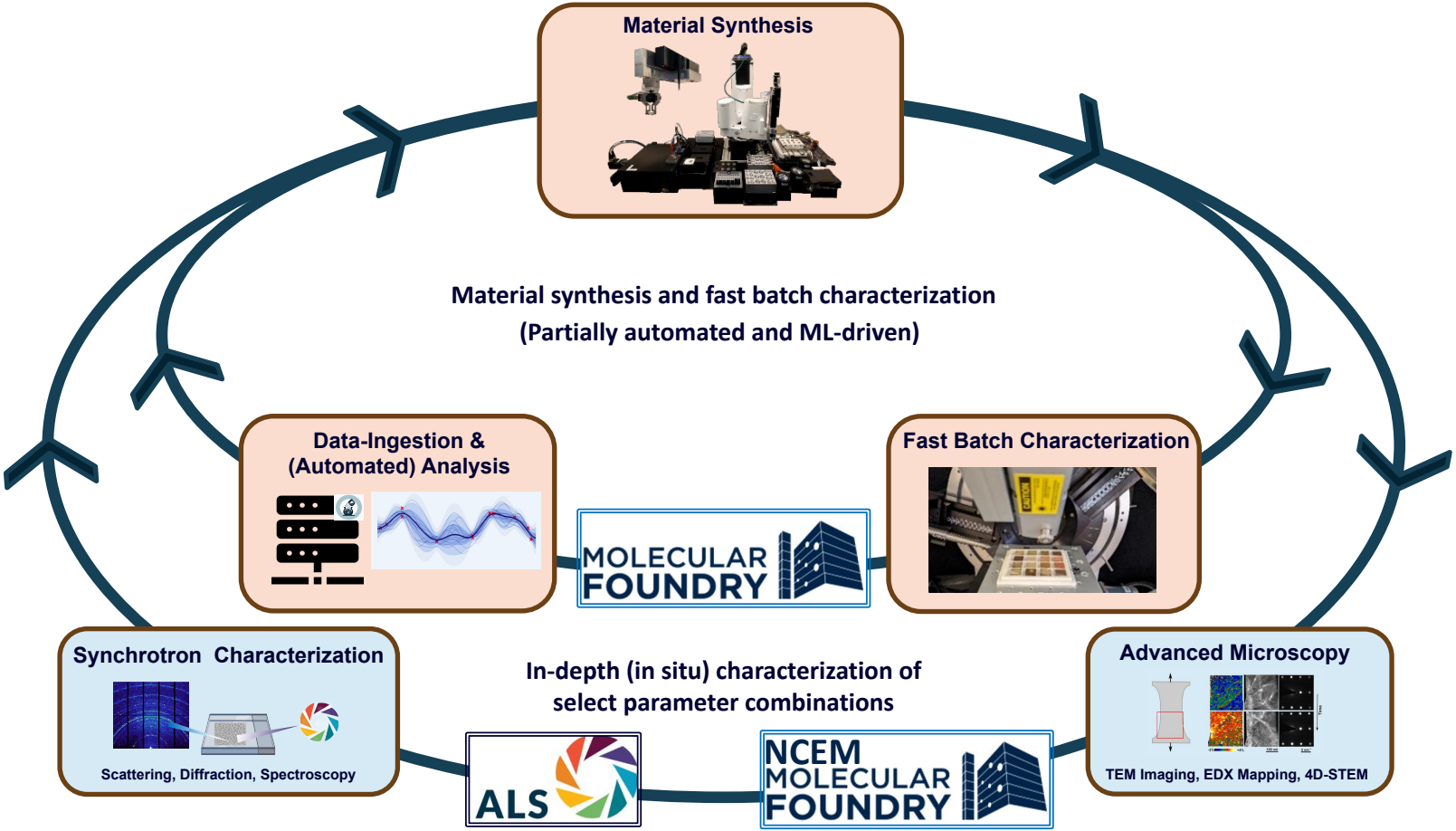
Leveraging MF and ALS capabilities



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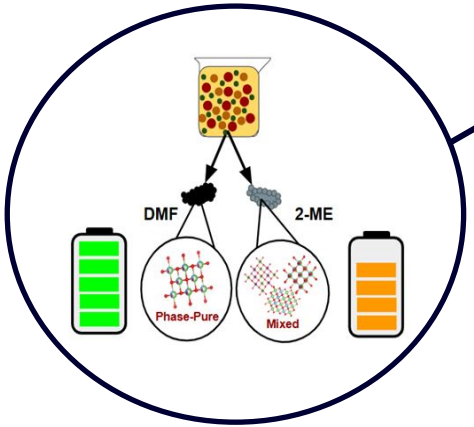
Materials discovery and characterization



Structure-property relationships in cathode materials

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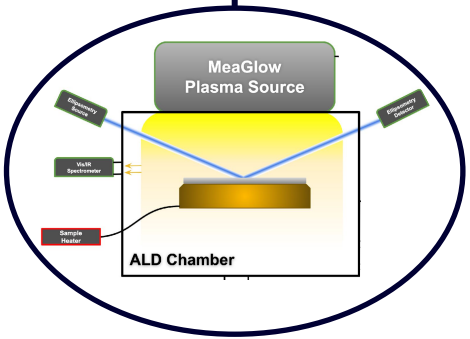
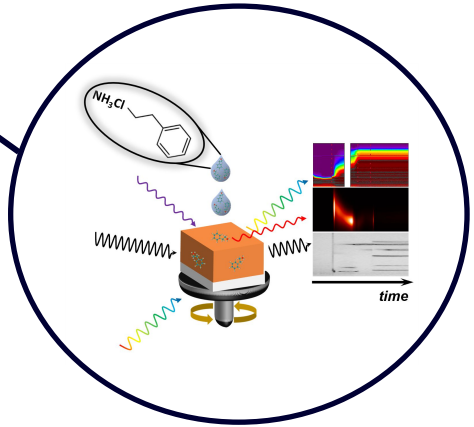


Closed loop, ML-driven, robotic ALD



Structure-property relationships of PV materials

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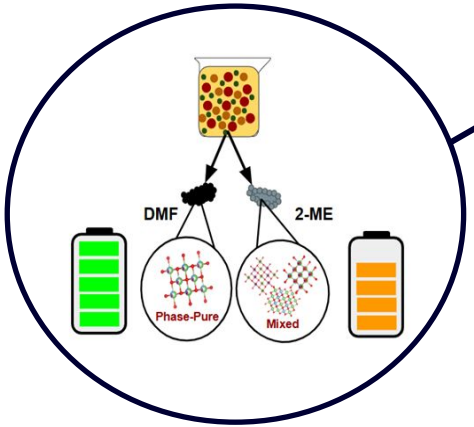
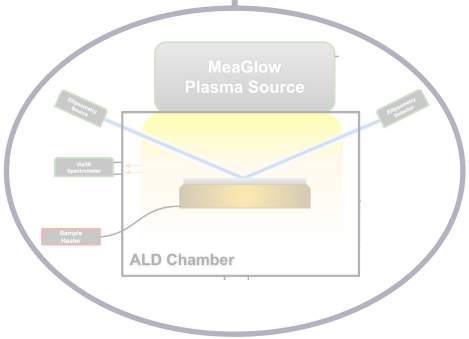
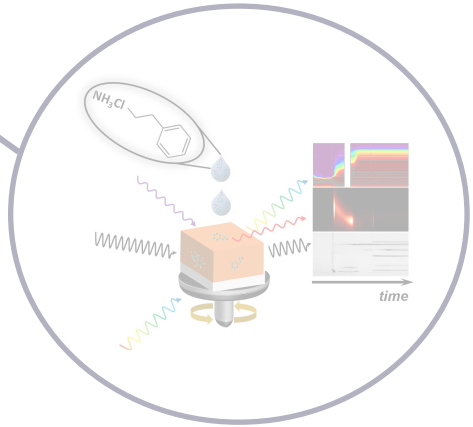
Materials discovery and characterization



Structure-property relationships in cathode materials



Closed loop, ML-driven, robotic ALD



Structure-property relationships of PV materials

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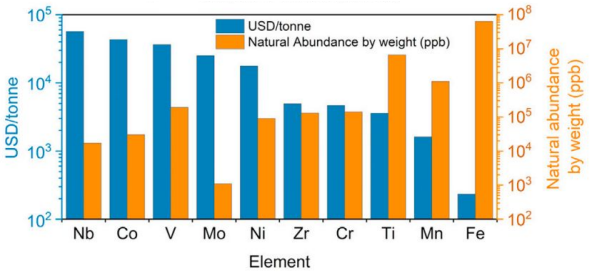
Disordered rock salt enables replacement of Co and Ni in cathodes for Li-ion batteries

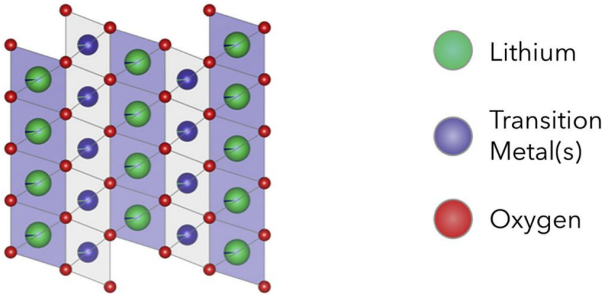
State-of-the-art layered cathodes for Li-ion batteries typically contain Co and/or Ni

 expensive and non-abundant



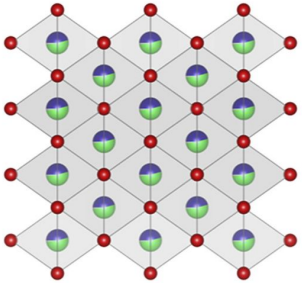
H. Li et al. Joule 6, 53-91 (2022)

Replacing Co/Ni with other TMs in layered structures leads to poor Li-diffusion due to layer-contraction



Adapted from: S. W. D. Gourley et al. iScience 23 (9), 101505 (2020)

Disordered rock salt cathodes can tolerate other TMs



For efficient Li-diffusion, $Li_xTM_{2-x}O_2$ with x > 1.1 needed, here $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$

Major challenges for solid state synthesis of $Li_{1.2}Mn_{0.4}Ti_{0.4}O_2$ (DRX):

- Poor control over particle morphology and size
- High annealing temperatures and intense mechanical mixing/milling needed to achieve DRX-phase

T. N. L. Doan, et al., Front. Energy Res. 2 (2014)

 Sol gel synthesis can potentially overcome these challenges

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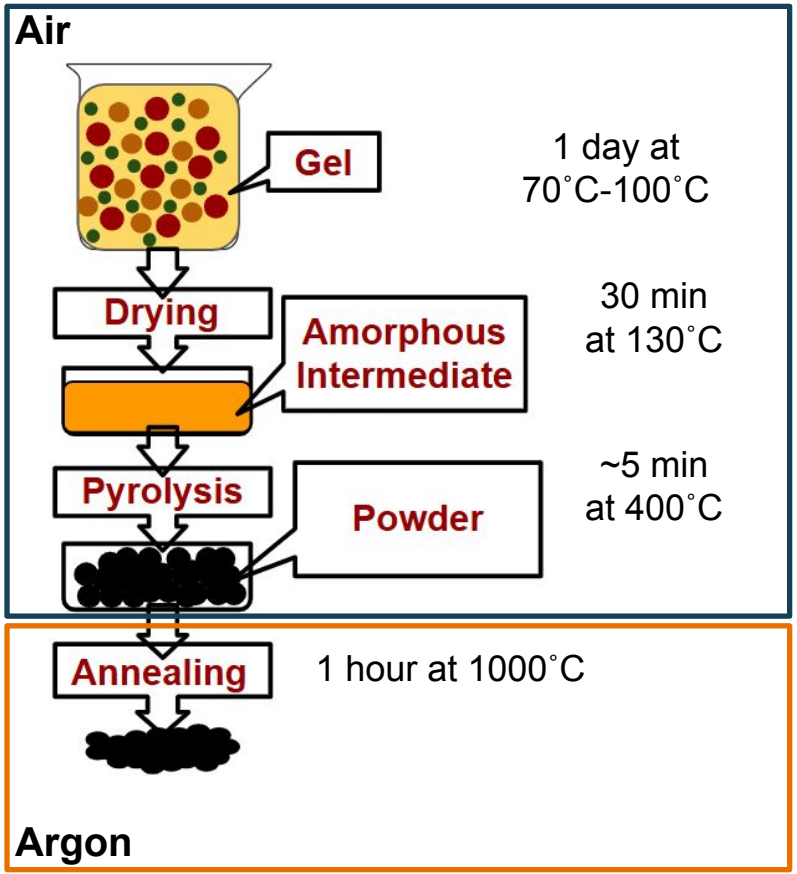
Sol-Gel Synthesis of LMTO-DRX



Goal:

Obtain phase pure & small-grained DRX-material

Solution engineering

Solvents:
Water & 2-Methoxyethanol
DMF (+ Water)
Ethanol (+ Water)
Water & Ethylene Glycol
Methanol (+Water

Metal-Precursors:
Lithium Acetate / Li Hydroxide / Li Nitrate / …
Manganese(II) Acetate / Manganese(III) Acetate / …
Titanium Isopropoxide

Acidic Agents:
Citric Acid
Nitric Acid
Acetic Acid

Composition:
Li-to-TM ratio
Mn/Ti-ratio

T. Kodalle et al., Nano Letters 25(30), 2025.

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High throughput parameter screening via automated synthesis & XRD

Spinbot One

Automatic solution engineering & thin film deposition:

- Precursor solution mixing
- Spin-coating
- Annealing
- Optoelectronic in-line characterization

High-Throughput XRD

Batch characterization:

- 16 samples per batch
- Automated alignment & measurement
- Automated data integration and visualization

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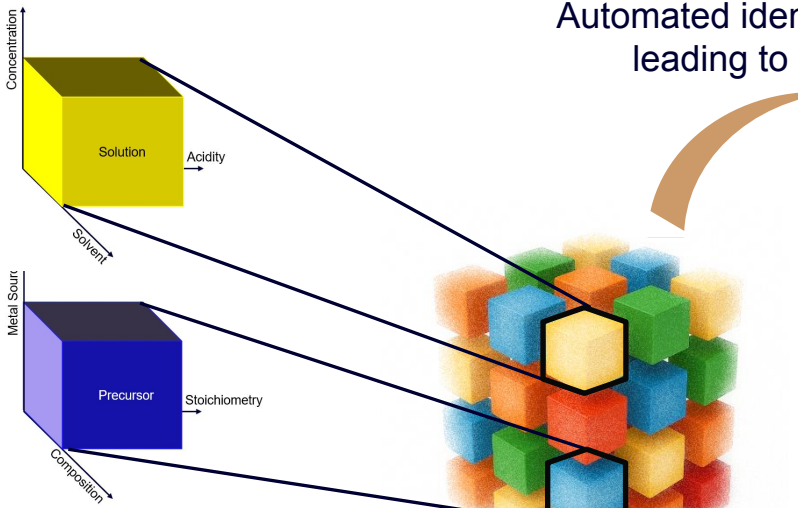
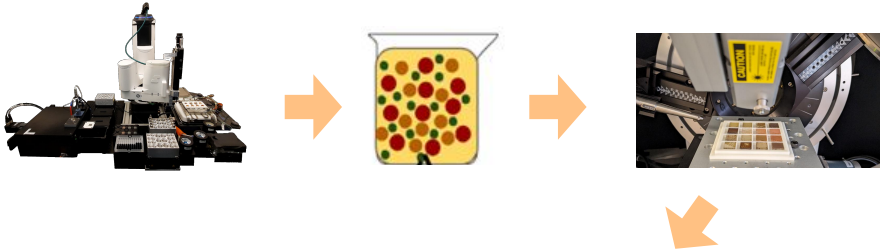
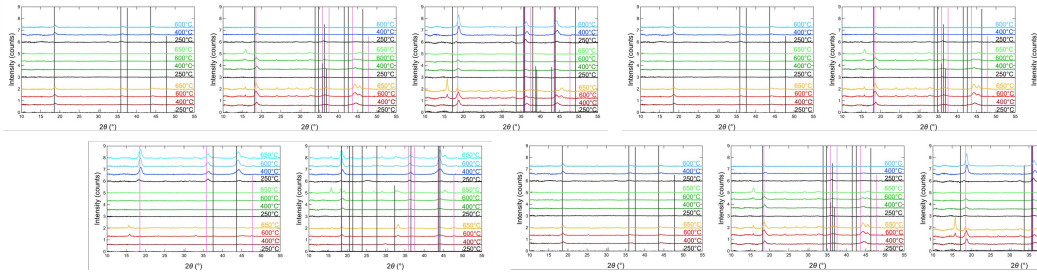
High throughput parameter screening via automated synthesis & XRD



Automated identification of parameters leading to high sol-gel quality





Large multi-dimensional parameter space for sol-gel derived LMTO-DRX:

- Solution
- Precursor chemistry
- Hydrolysis
- Gelification
- Pyrolysis
- …

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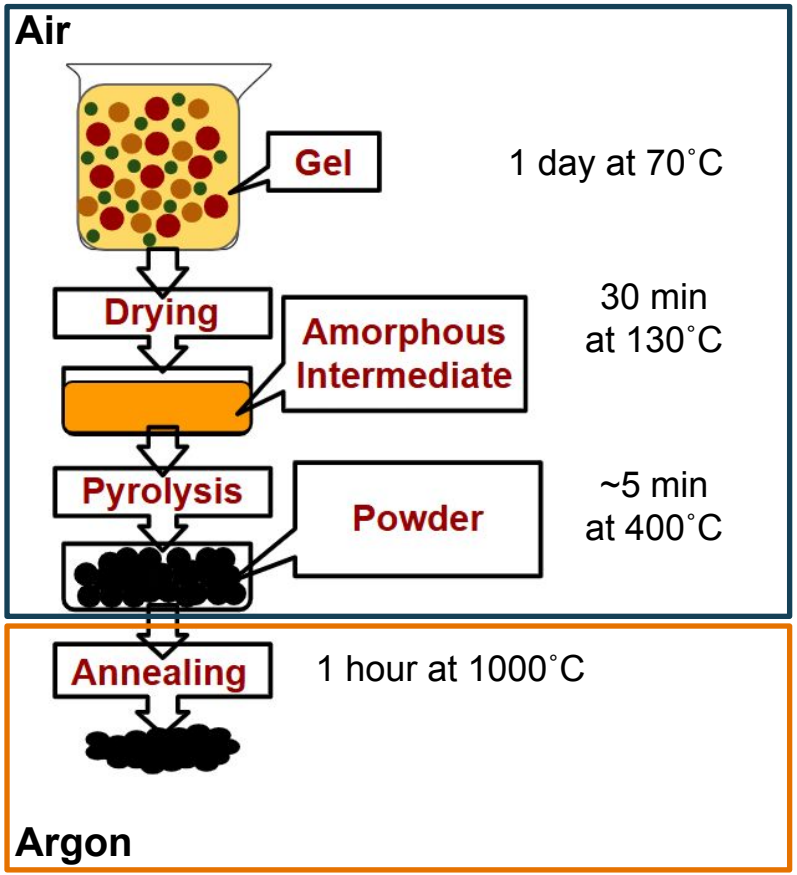
Choice of solvent is the most influential parameter for DRX-phase purity



Engineering approaches

Solvents:
Water & 2-Methoxyethanol
DMF (+ Water)
Ethanol (+ Water)
Water & Ethylene Glycol

Metal-Precursors:
Lithium Acetate / Li Hydroxide / Li Nitrate
Manganese(II) Acetate / Manganese(III) Acetate
Titanium Isopropoxide

Acidic Agents:
Citric Acid
Nitric Acid
Acetic Acid

Compositional Engineering:
Li-to-TM ratio
Mn/Ti-ratio
pH-control

T. Kodalle et al., Nano Letters 25(30), 2025.

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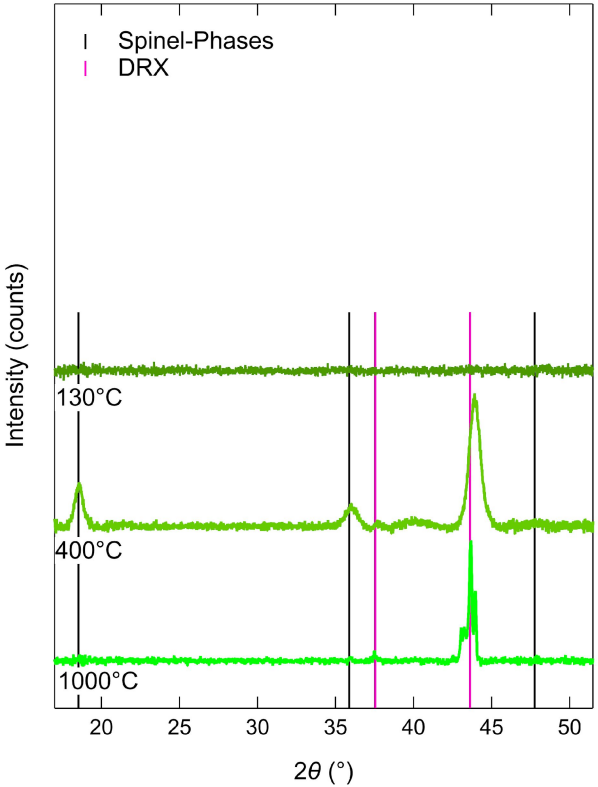
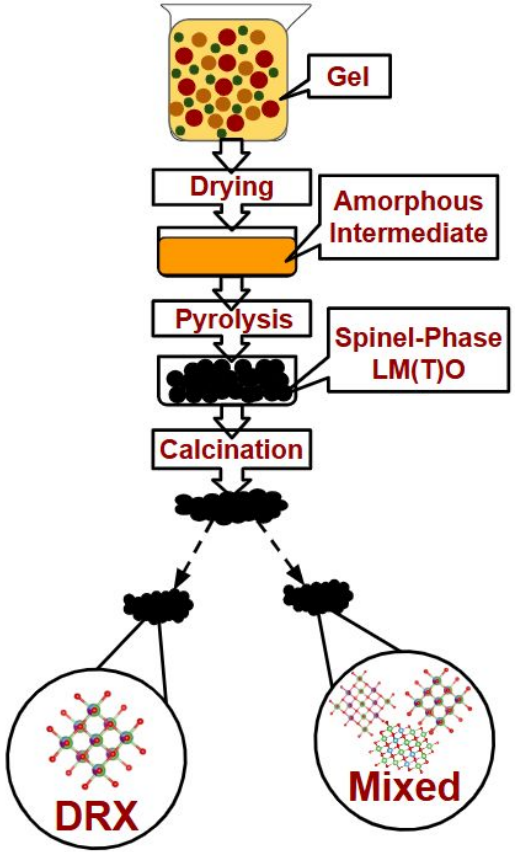
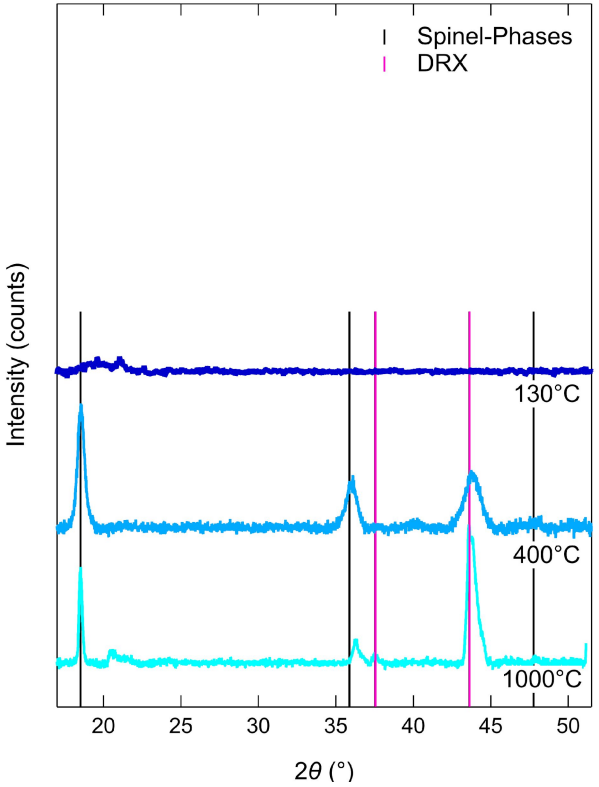
Choice of solvent is the most influential parameter for DRX-phase purity

DMF





2-ME



T. Kodalle et al., Nano Letters 25(30), 2025.

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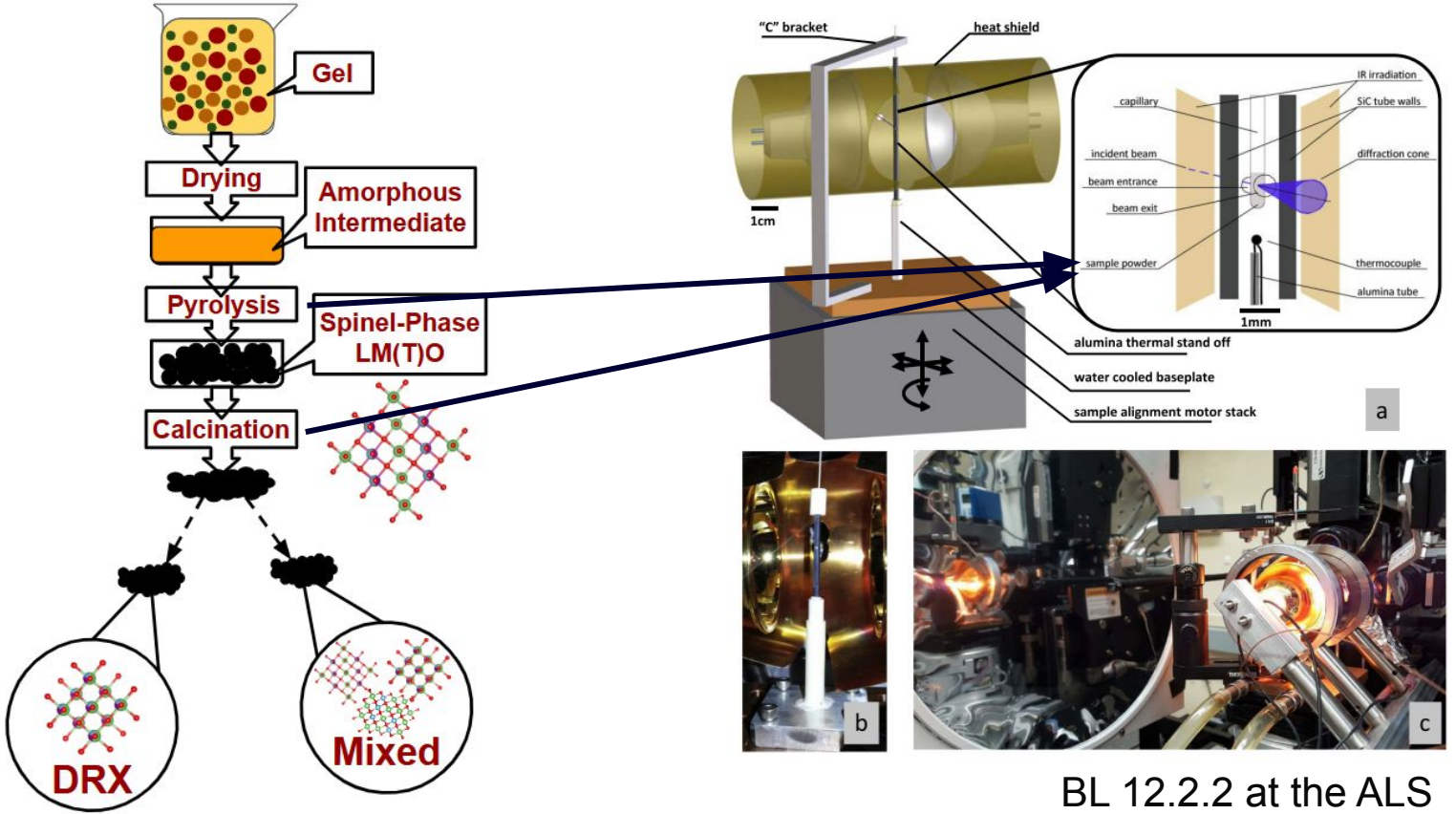
In situ pXRD during pyrolysis and calcination reveals driving force for impurity-formation



BL 12.2.2 at the ALS

T. Kodalle et al., Nano Letters 25(30), 2025.

A. Doran et al., Rev. Sci. Instrum. 88, 013903 (2017)

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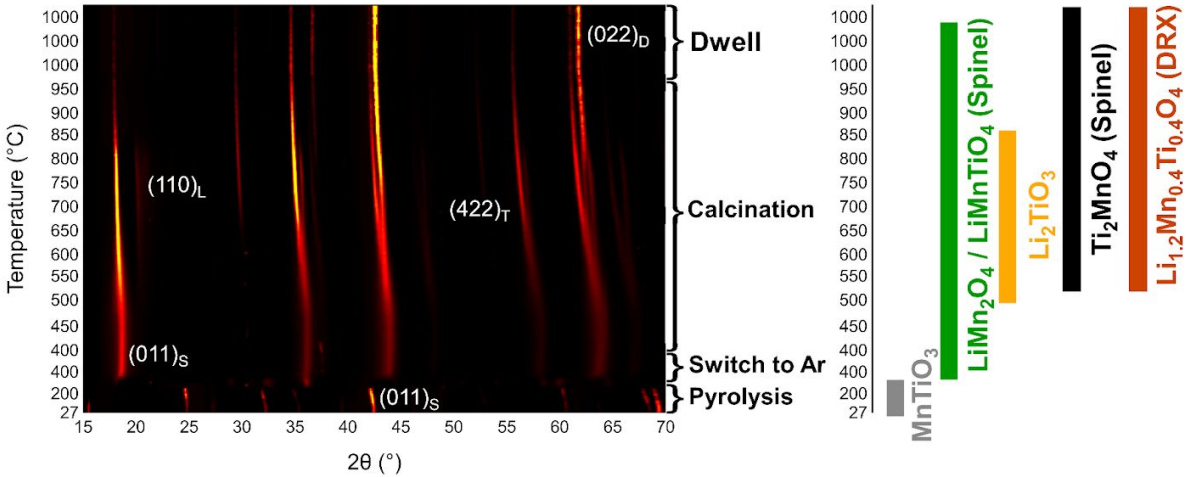
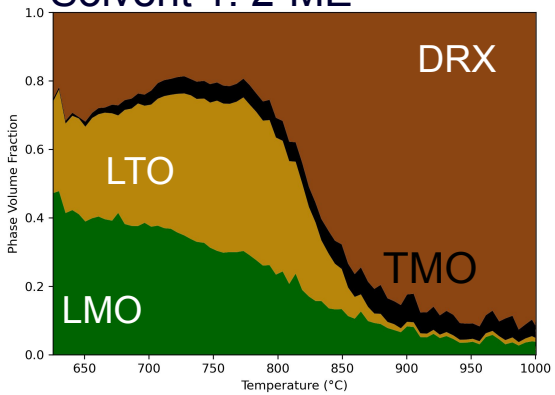
In situ pXRD during pyrolysis and calcination reveals driving force for impurity-formation



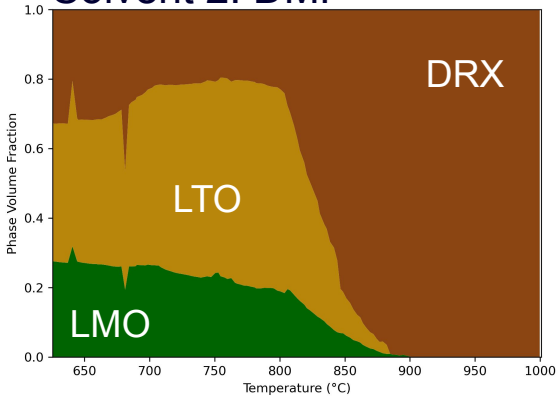
2-ME + Water as solvent:

- Main DRX-formation window between 775°C and 860°C
- Intermediate phase formation around 400°C to 500°C:
  - $LiMnO_2$ (Mn-rich)
  - Li_2TiO_3 (Ti-rich)
  - Ti_2MnO_4 (Ti-rich)

Solvent 1: 2-ME



Solvent 2: DMF



DMF + Water as solvent:

- Main DRX-formation window between 775°C and 860°C
- No Ti_2MnO_4 formation

  → phase purity at 900°C

T. Kodalle et al., Nano Letters 25(30), 2025.

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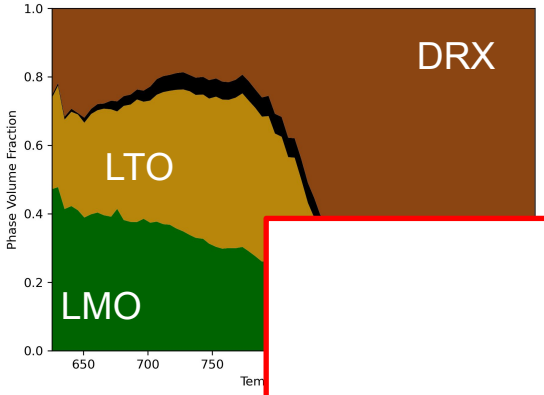
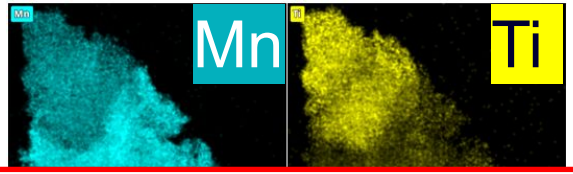
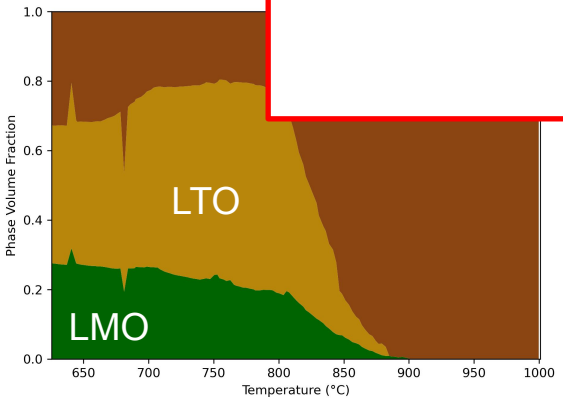
Choice of solvent determines phase purity & cell performance

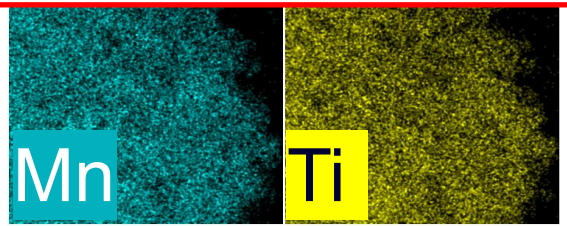
Solvent 1: 2-ME



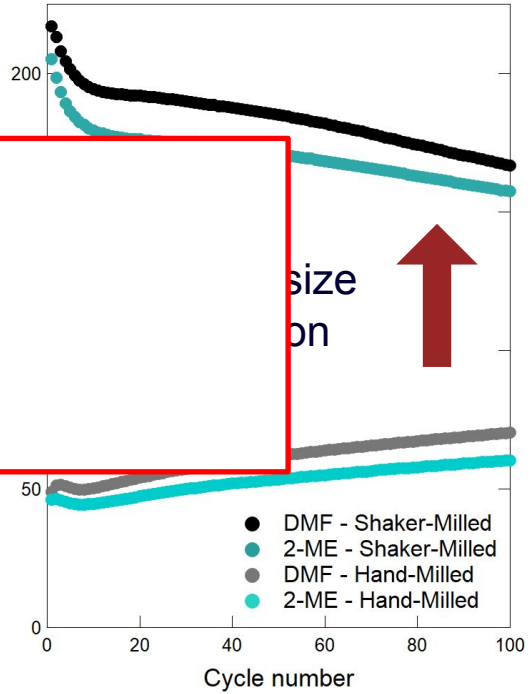


Solvent 2: DMF





Next Step:
Limit particle growth via solution and process engineering



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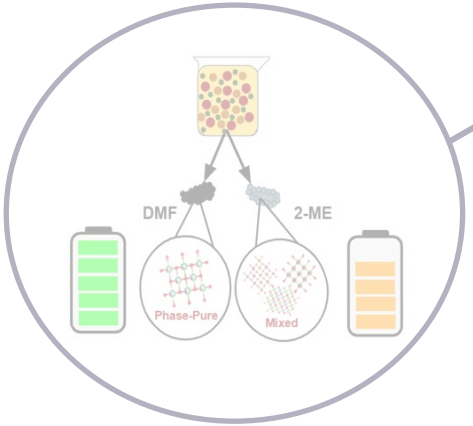
Materials discovery and characterization



Structure-property relationships in cathode materials

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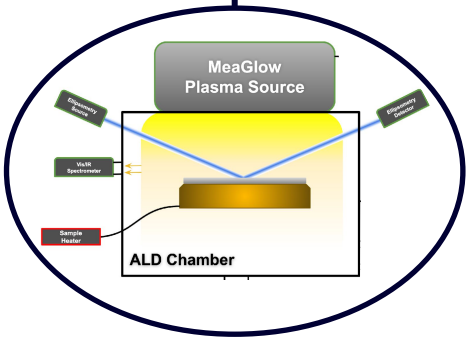
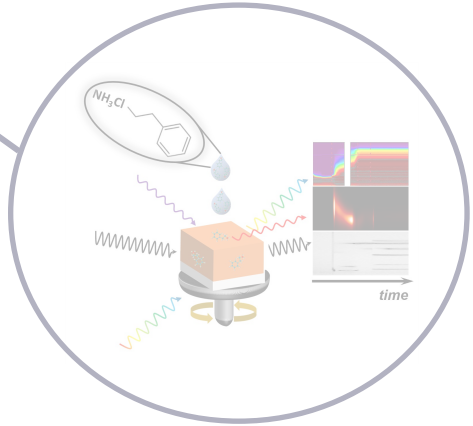


Closed loop, ML-driven, robotic ALD



Structure-property relationships of PV materials

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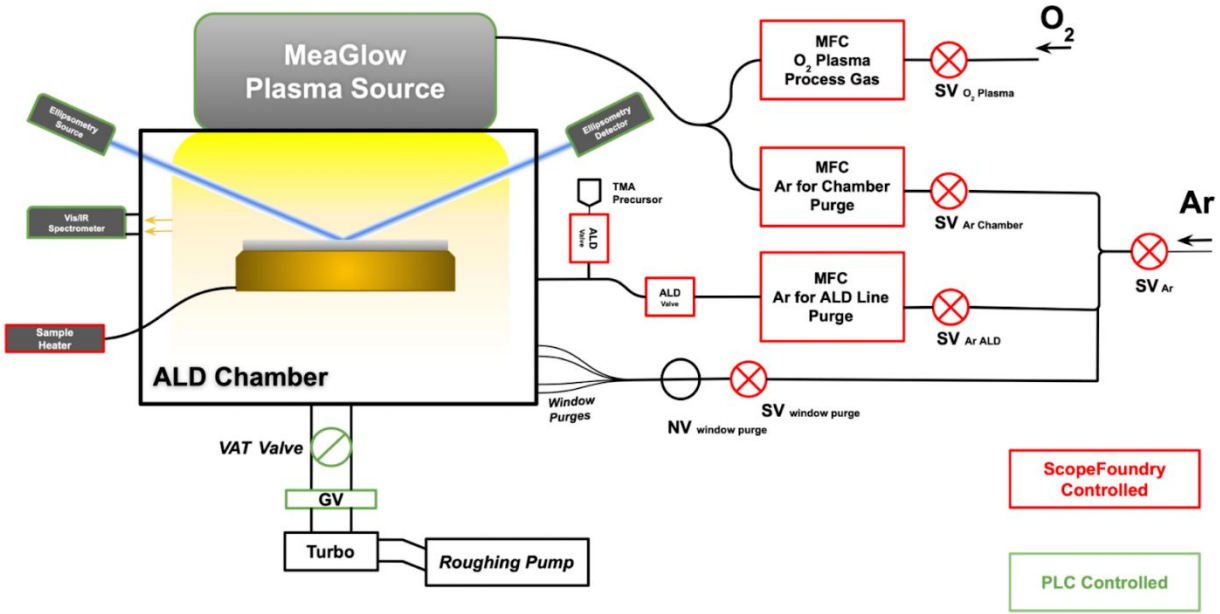
Robotic PE-ALD tool for fast process optimization



- In-house constructed ALD-Tool with integrated software control system: “ALDBot”
- Test system: ALD-TiO_2 for microelectronics/catalysis
- **Main goal: Closed loop parameter space exploration and optimization**

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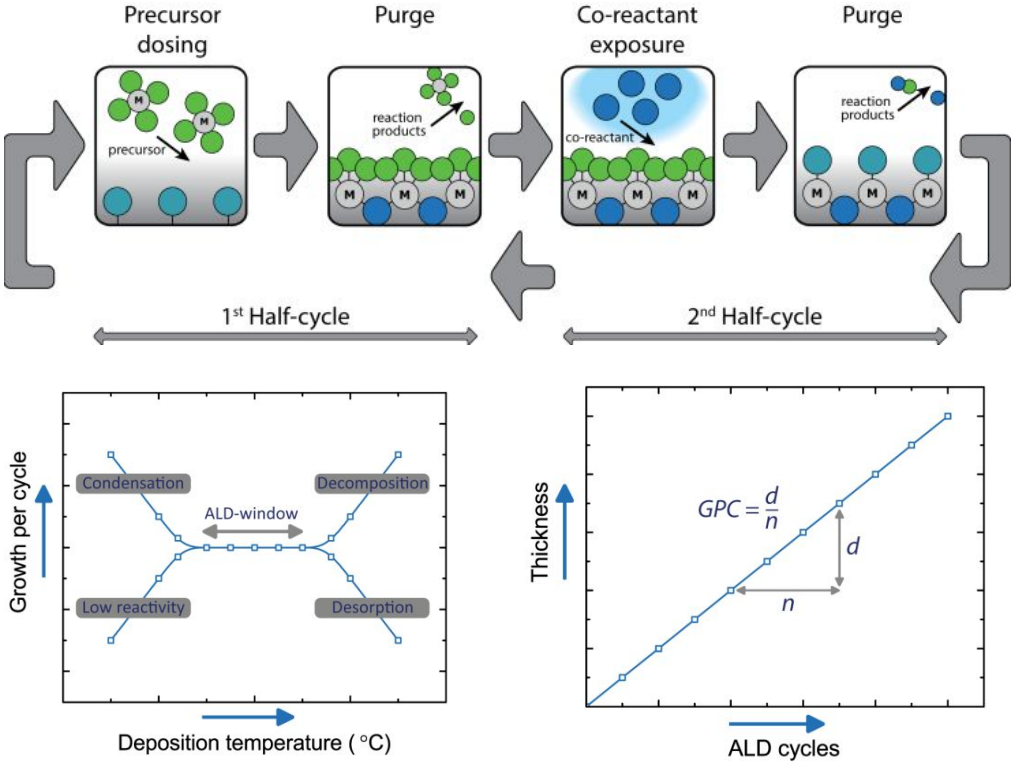
ML-assisted exploration of the ALD parameter space using Gaussian Processing



20-dimensional parameter space for ALD and plasma conditions:

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    "Number_of_ALD_cycles": 25
},
```

+ Substrate and precursor temperature

*M.F.J. Vos, et al. Atomic Limits 3, **2019**.*

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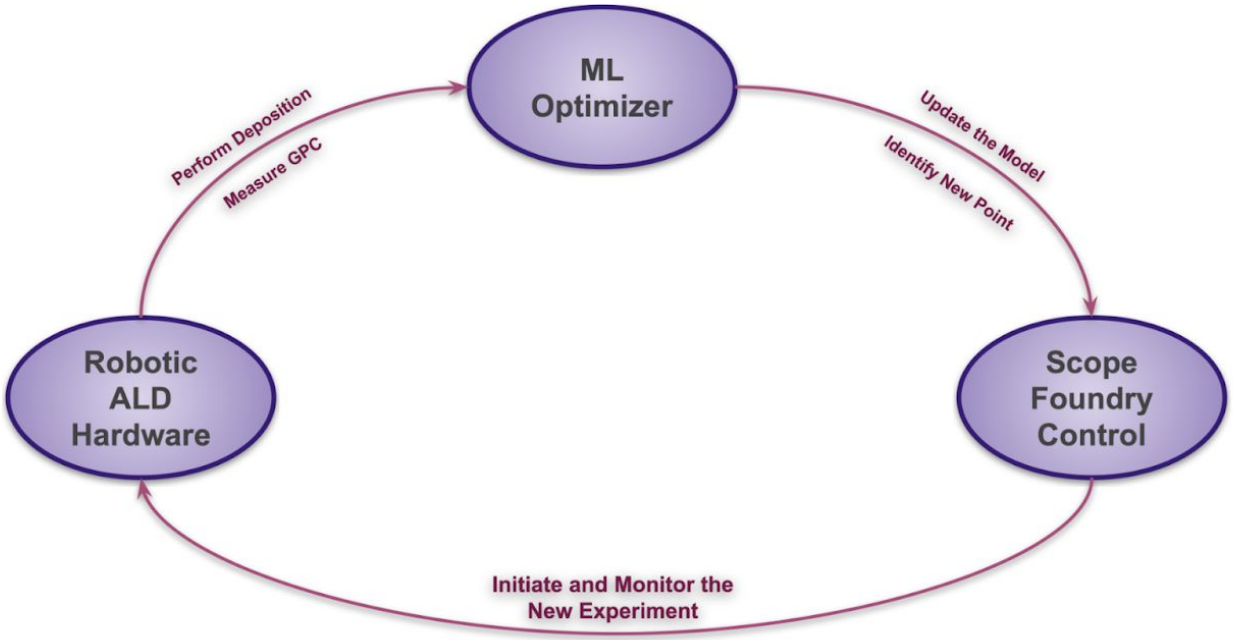
Robotic PE-ALD tool for fast process optimization



- In-house constructed ALD-Tool with integrated software control system: "ALDBot"
- Test system: ALD-TiO_2 for microelectronics
- **Main goal: Closed loop parameter space exploration and optimization**
- **Secondary Goal: Finding the "ALD-Window" for TiO_2**

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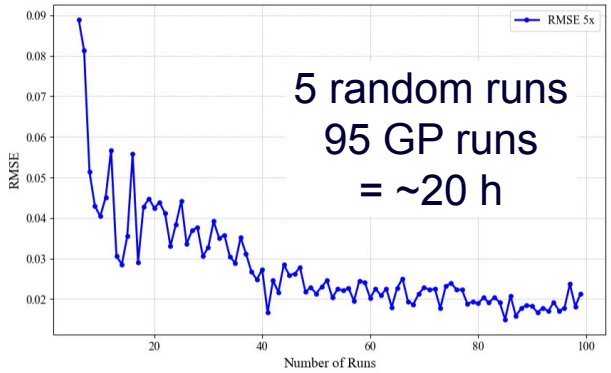
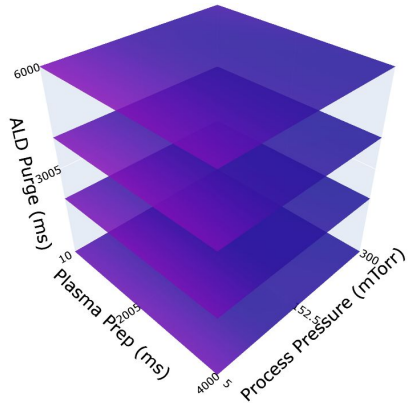
ML-assisted exploration of the ALD parameter space using Gaussian Processing

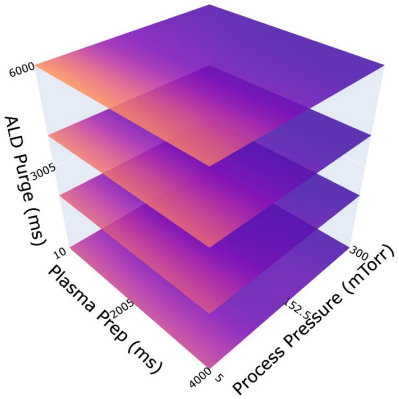
Demonstration: Explore 4D parameter space
- Precursor Dose Time
- ALD Purge Time
- Plasma Preparation Time
- Process Pressure



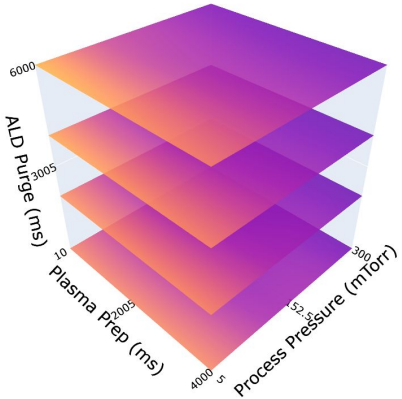
Dose Time = 1 s

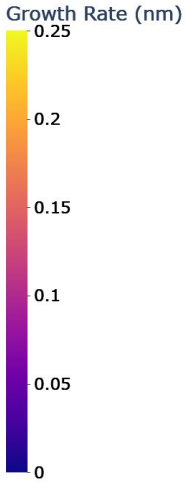


Dose Time = 3 s



Dose Time = 5 s





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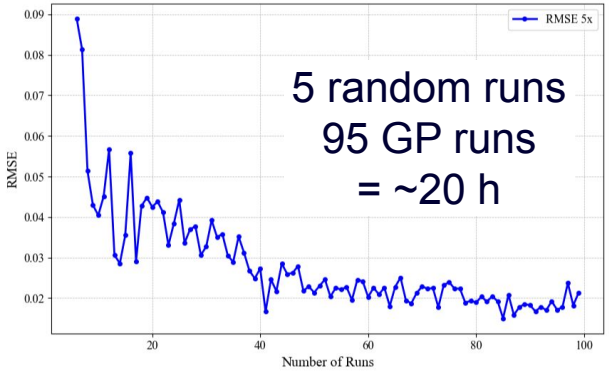
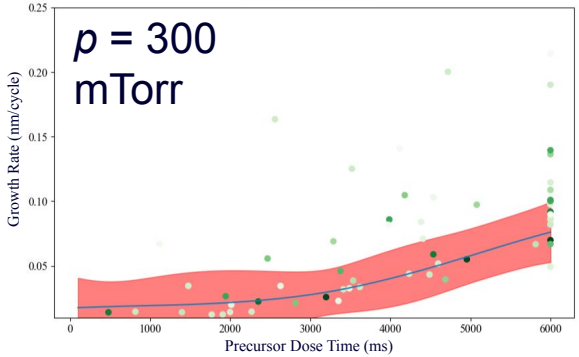
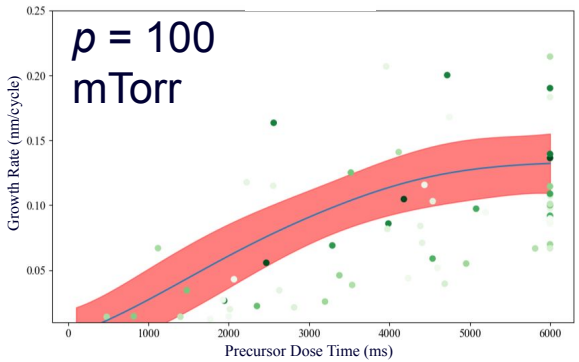
ML-assisted exploration of the ALD parameter space using Gaussian Processing

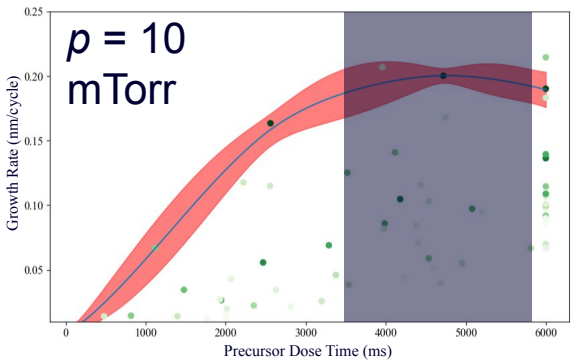
Demonstration: Explore 4D parameter space
- Precursor Dose Time
- ALD Purge Time
- Plasma Preparation Time
- Process Pressure



"ALD Window"







- Working conditions for TiO_2 found within 1 day of experiments

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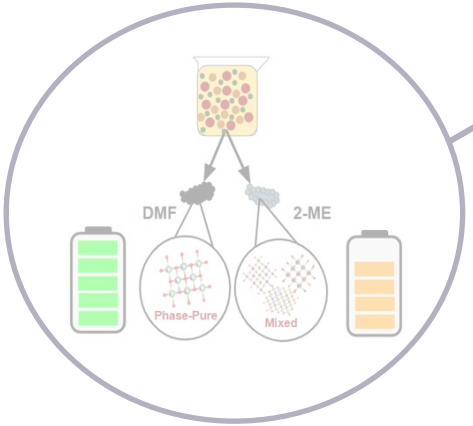
Materials discovery and characterization



Structure-property relationships in cathode materials

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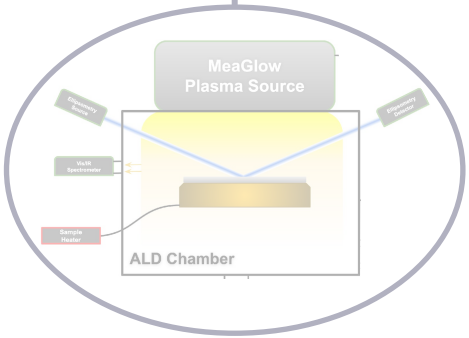
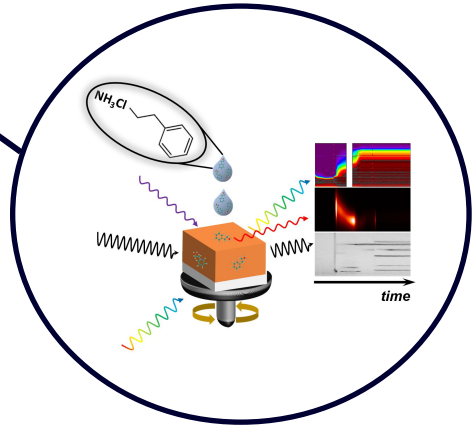


Closed loop, ML-driven, robotic ALD



Structure-property relationships of PV materials

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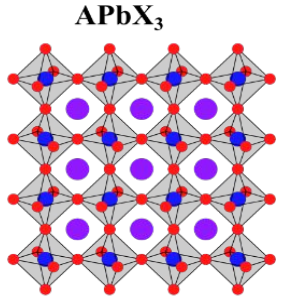
Metal halide perovskites for photovoltaics

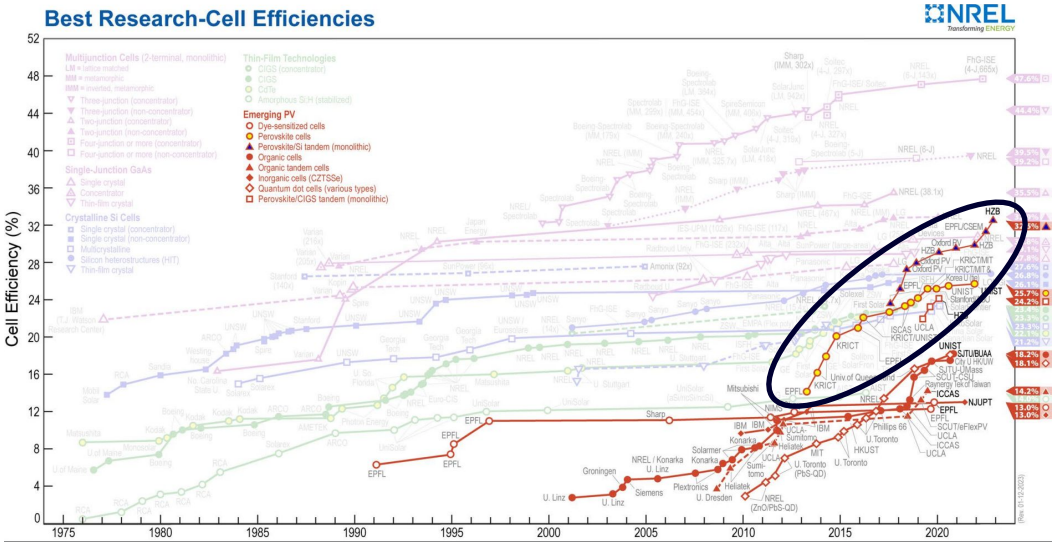


● = Pb^{2+}

● = X-Site (Br/I)

● = A-site (Cs^+, FA^+, MA^+)

T. Kodalle et al., Adv. Ener. Mat. 13(33), 2201490, 2023



NREL Efficiency Chart: https://www.nrel.gov/pv/cell-efficiency.html

Main Issues:

- Toxicity
- Stability in ambient/humid environment

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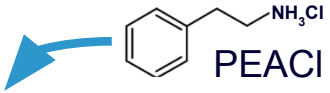
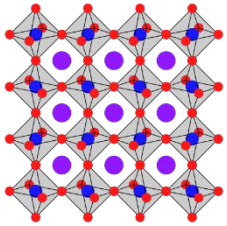
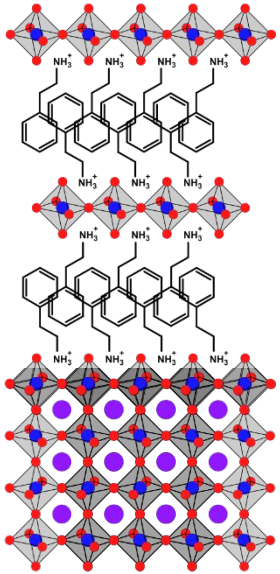
2D structures in halide perovskites for improved stability



$APbX_3$ 3D





- = Pb^{2+}
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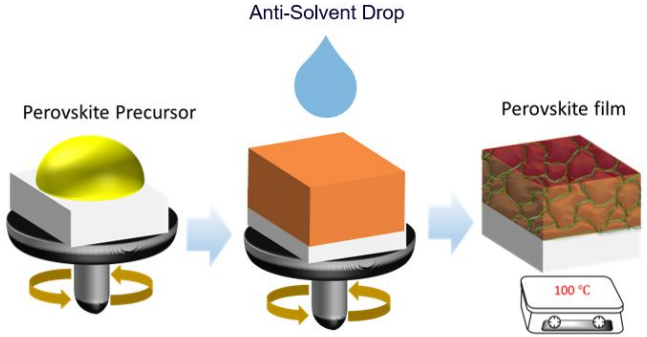
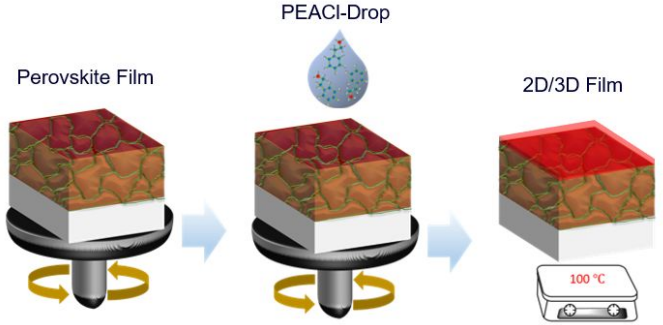
1. 3D Perovskite Deposition



2. 2D Perovskite Formation



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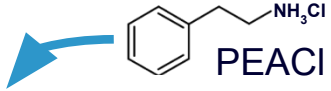
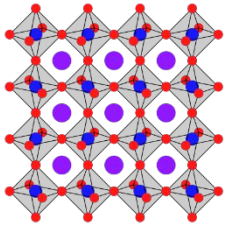
2D structures in halide perovskites for improved stability



$APbX_3$ 3D



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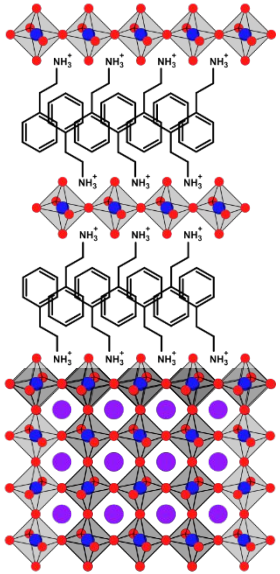
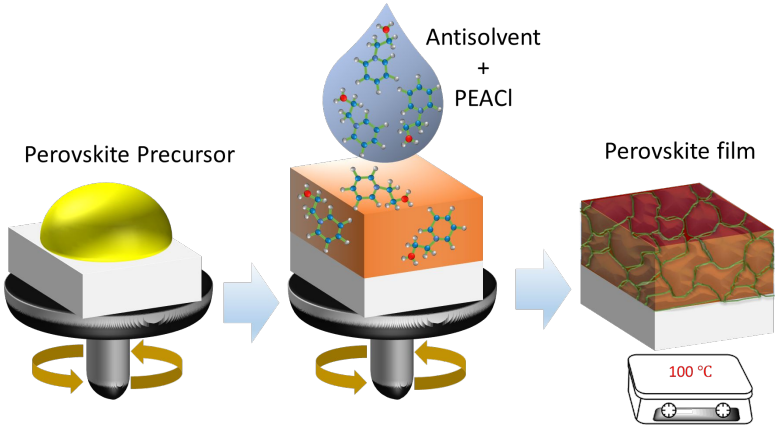


1. Integrated 3D & 2D Perovskite Deposition



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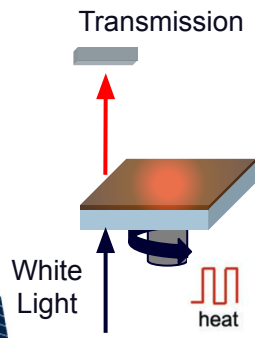
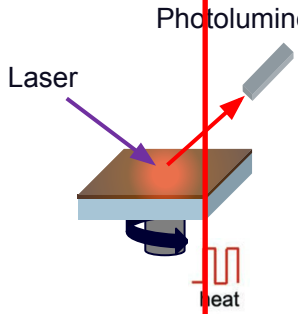
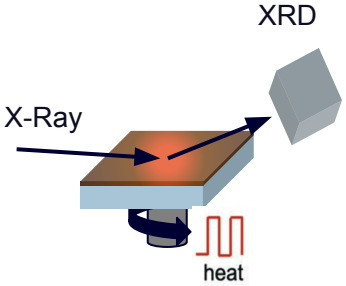
The MMSC – now a joint user program of the Foundry and ALS







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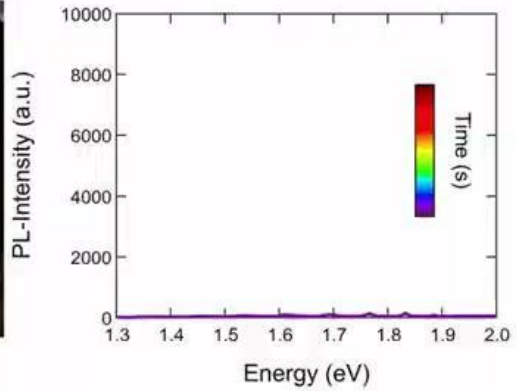
Photoluminescence and transmission setups at the Molecular Foundry

Perovskite Glovebox in the Sutter-Fella Lab

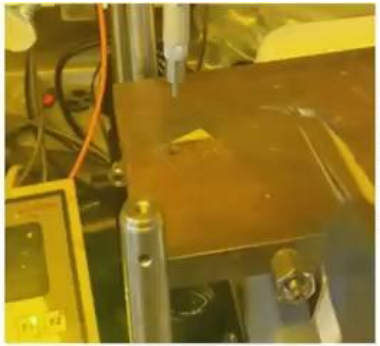
- Inert glove box atmosphere
- Same deposition conditions as in most device-oriented labs
- Time resolution around 0.1s

In Situ Photoluminescence

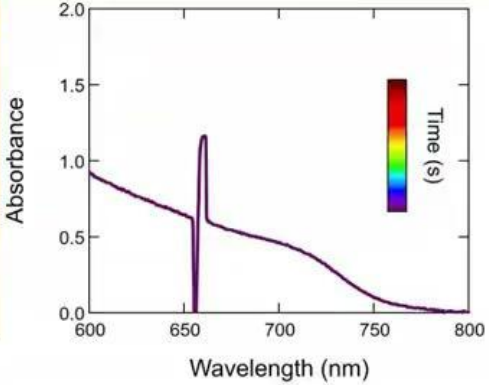
Spin-Coating



In Situ



Annealing



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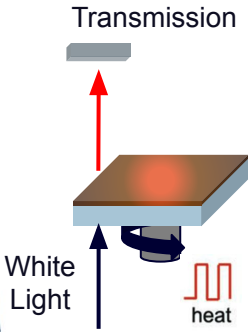
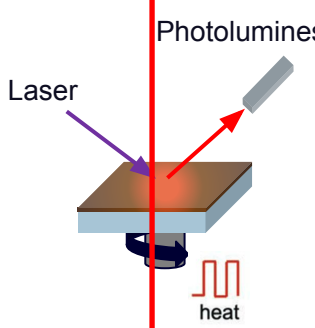
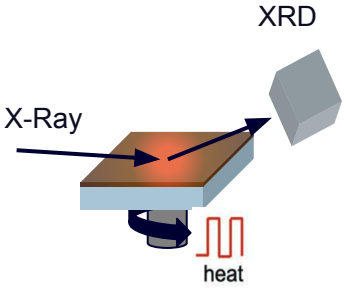
The MMSC-Program – a joint user program of the Foundry and ALS







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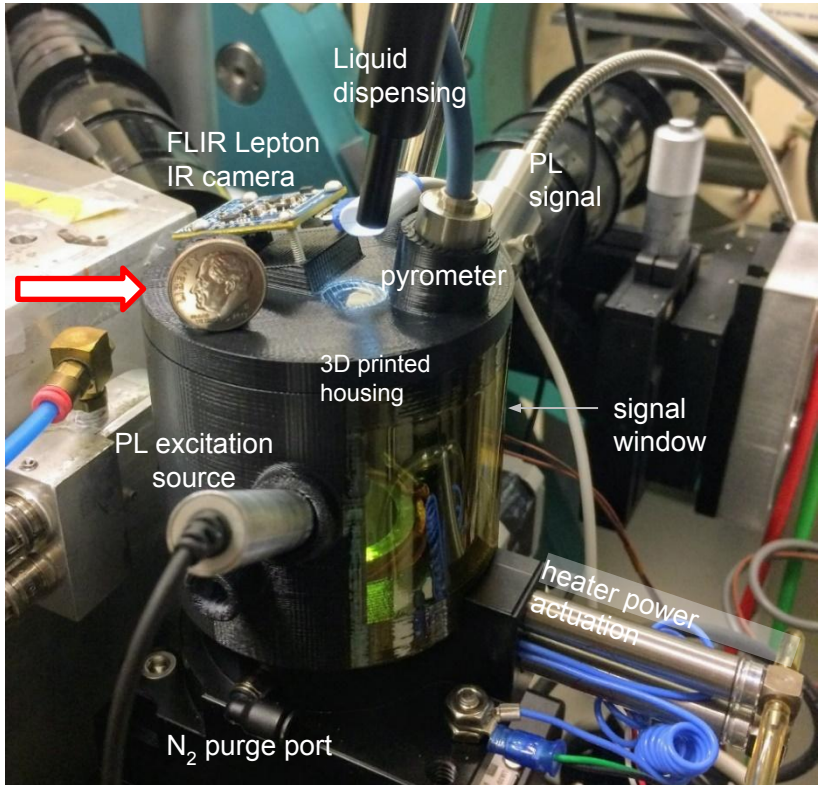
Multimodal in situ spin-coater at Beamline 12.3.2



- Automated sequences of spin-coating, heating, and liquid dispensing in variable atmosphere
- Multimodal in situ photoluminescence and X-ray diffraction measurements
- Real time data acquisition (< 1s time resolution)
- Assembly at microdiffraction beamline allows for precise control of beam spot and incidence angle

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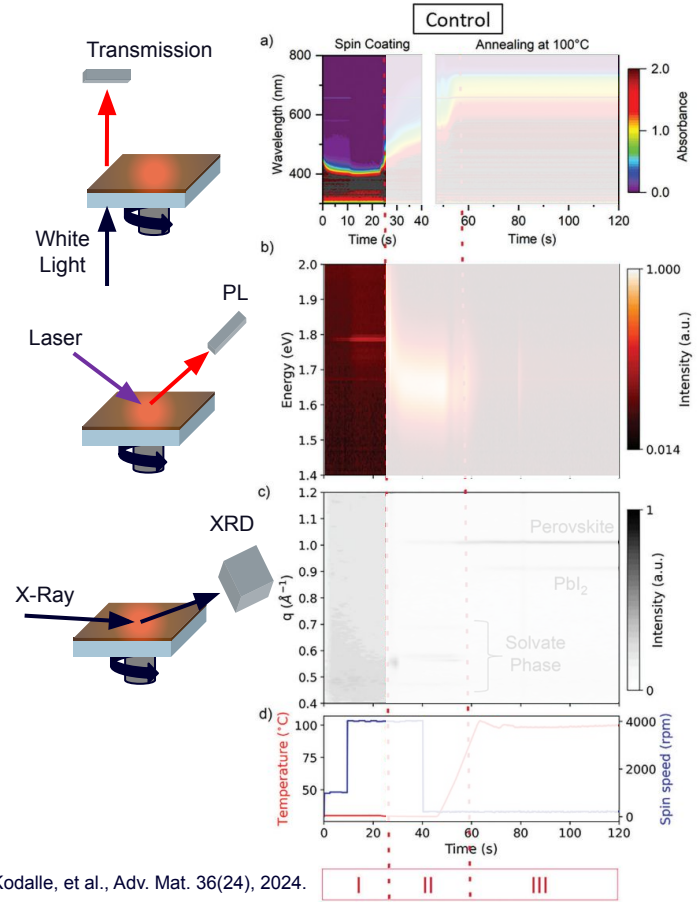
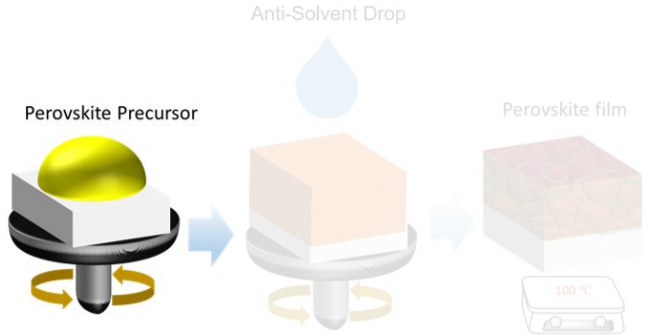
Multimodal analysis of the perovskite growth: Reference case





- Phase I (Spin-Coating): Wet film - No PL or WAXS signal

T. Kodalle, et al., Adv. Mat. 36(24), 2024.

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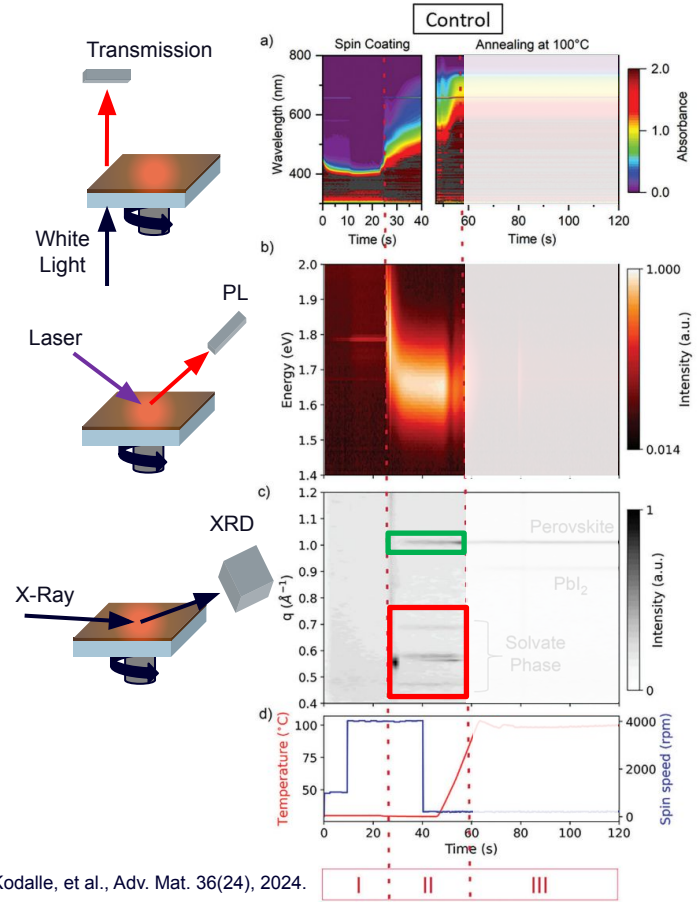
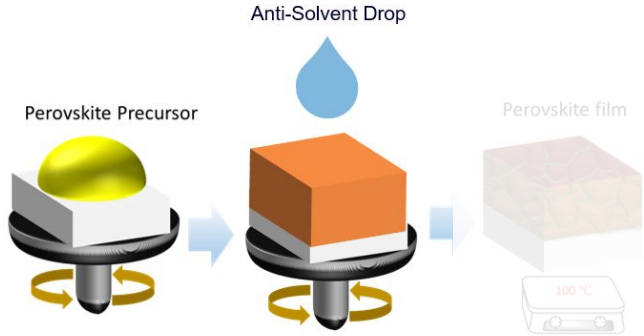
Multimodal analysis of the perovskite growth: Reference case





- Phase I (Spin-Coating): Wet film - No PL or WAXS signal
- Phase II (AS-Drop): Nucleation and growth of intermediate & perovskite phase

T. Kodalle, et al., Adv. Mat. 36(24), 2024.

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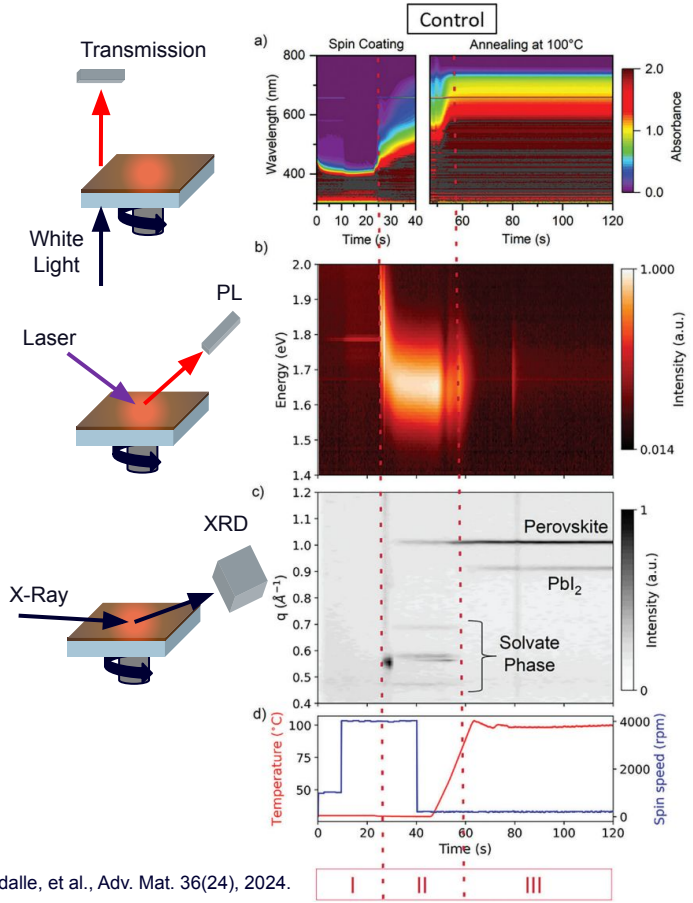
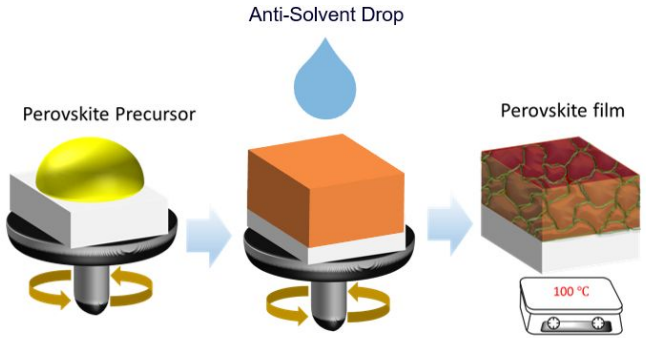
Multimodal analysis of the perovskite growth: Reference case



Kodalle, et al., Adv. Mat. 36(24), 2024.



- Phase I (Spin-Coating): Wet film - No PL or WAXS signal
- Phase II (AS-Drop): Nucleation and growth of intermediate & perovskite phase
- Phase III (Annealing): Solvent-evaporation & crystal growth

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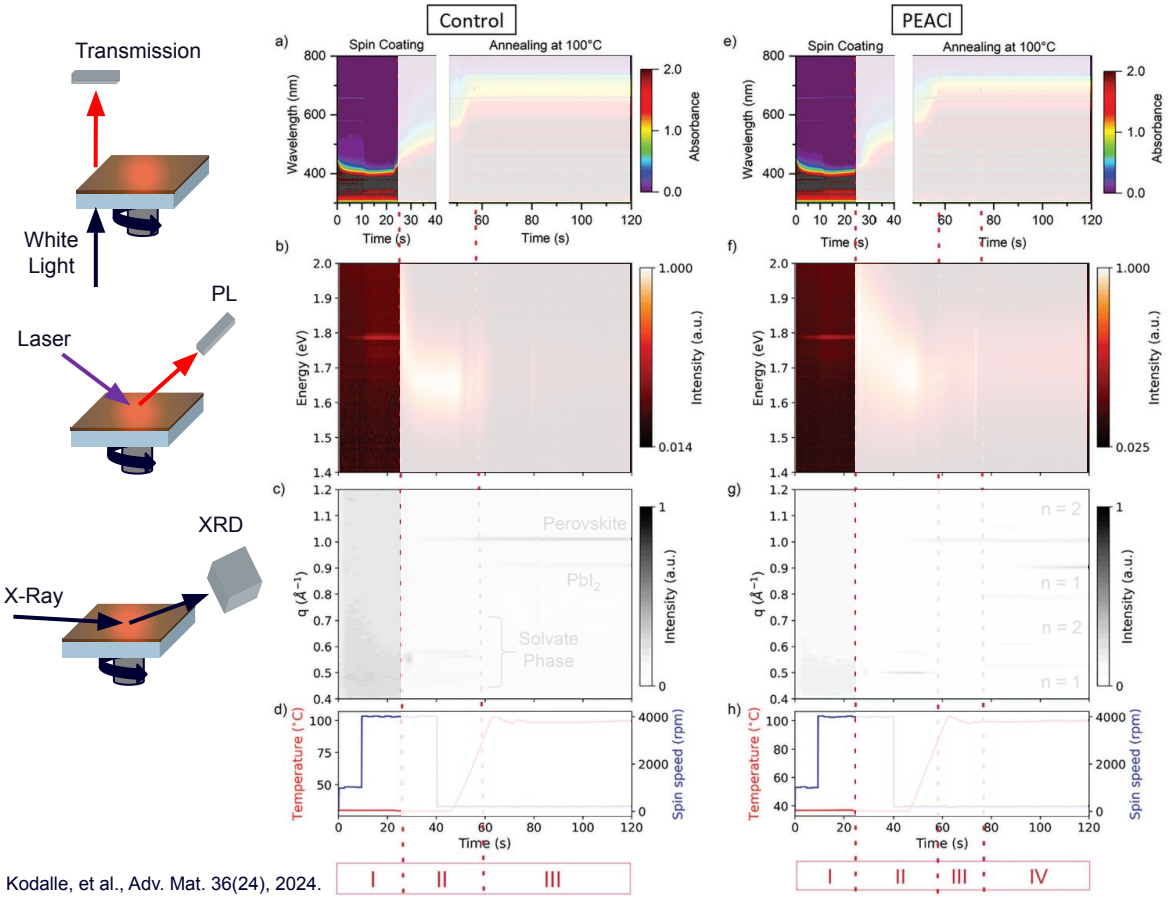
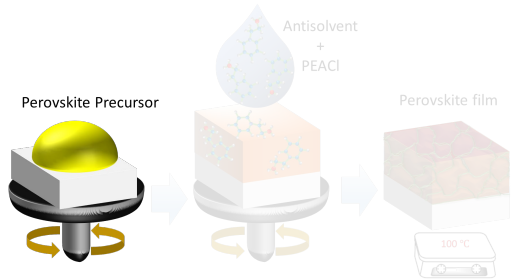
Multimodal analysis of the perovskite growth: PEACl case





- Phase I (Spin-Coating): Wet film

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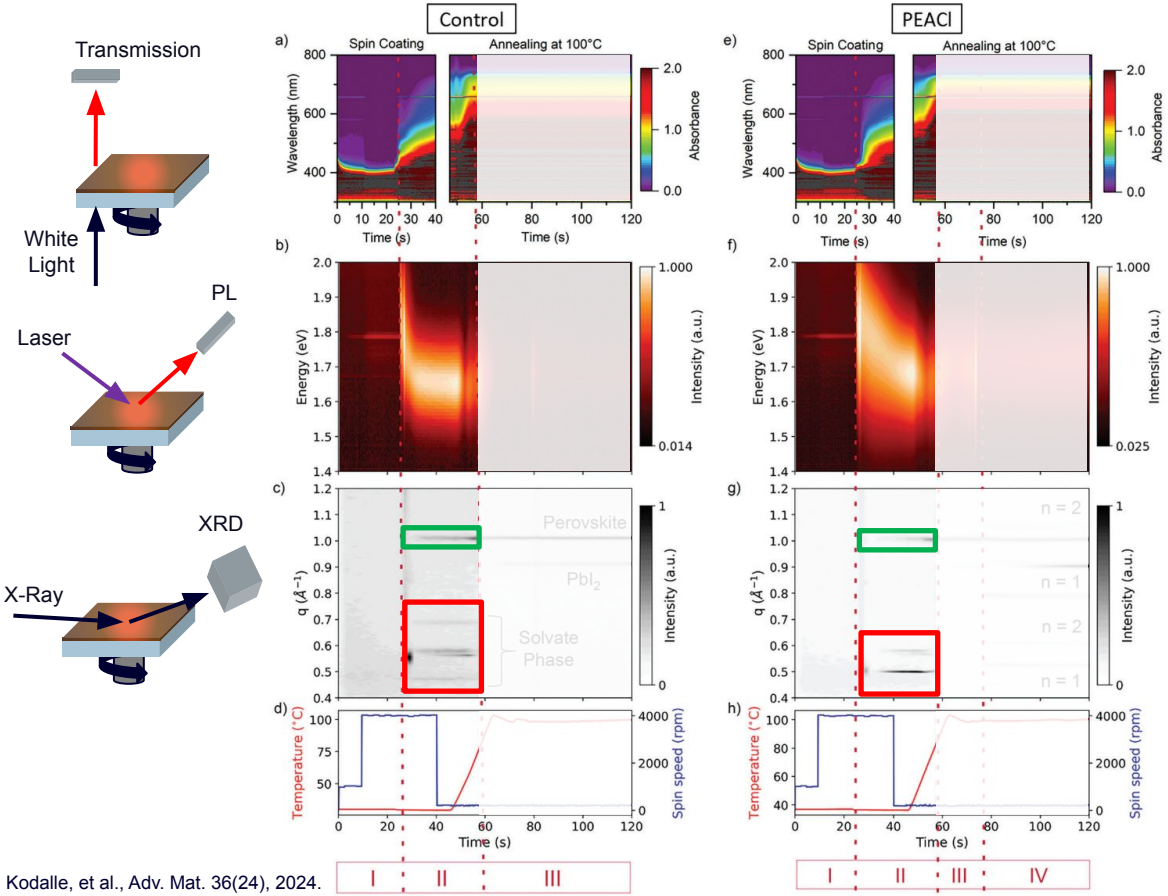
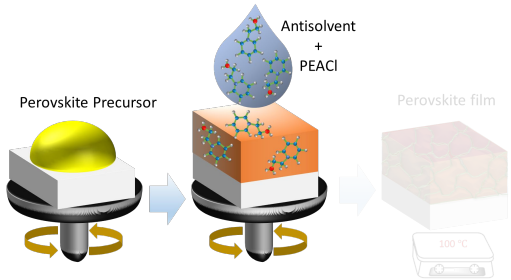
Multimodal analysis of the perovskite growth: PEACl case





- Phase I (Spin-Coating): Wet film
- Phase II (PEACl-Drop): Slower nucleation of pvsk-phase, altered intermediate phase

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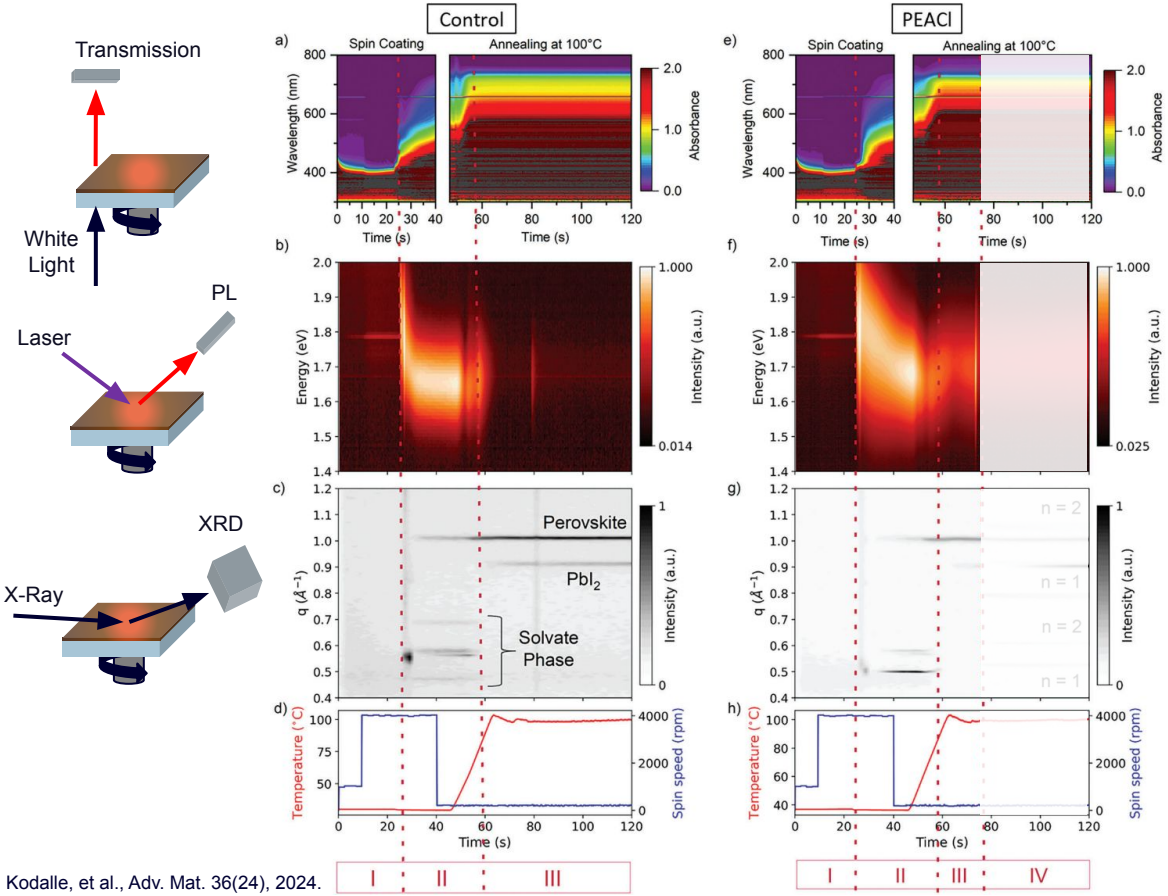
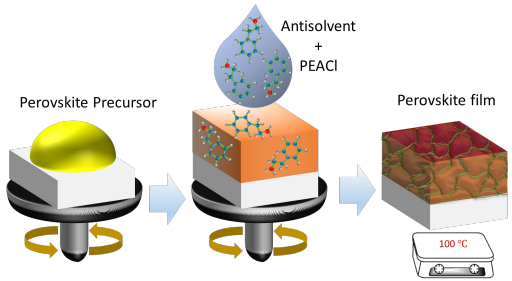
Multimodal analysis of the perovskite growth: PEACl case





- Phase I (Spin-Coating): Wet film
- Phase II (PEACl-Drop): Slower nucleation of pvsk-phase, altered intermediate phase
- Phase III (Annealing): Solvent-evaporation & crystal growth

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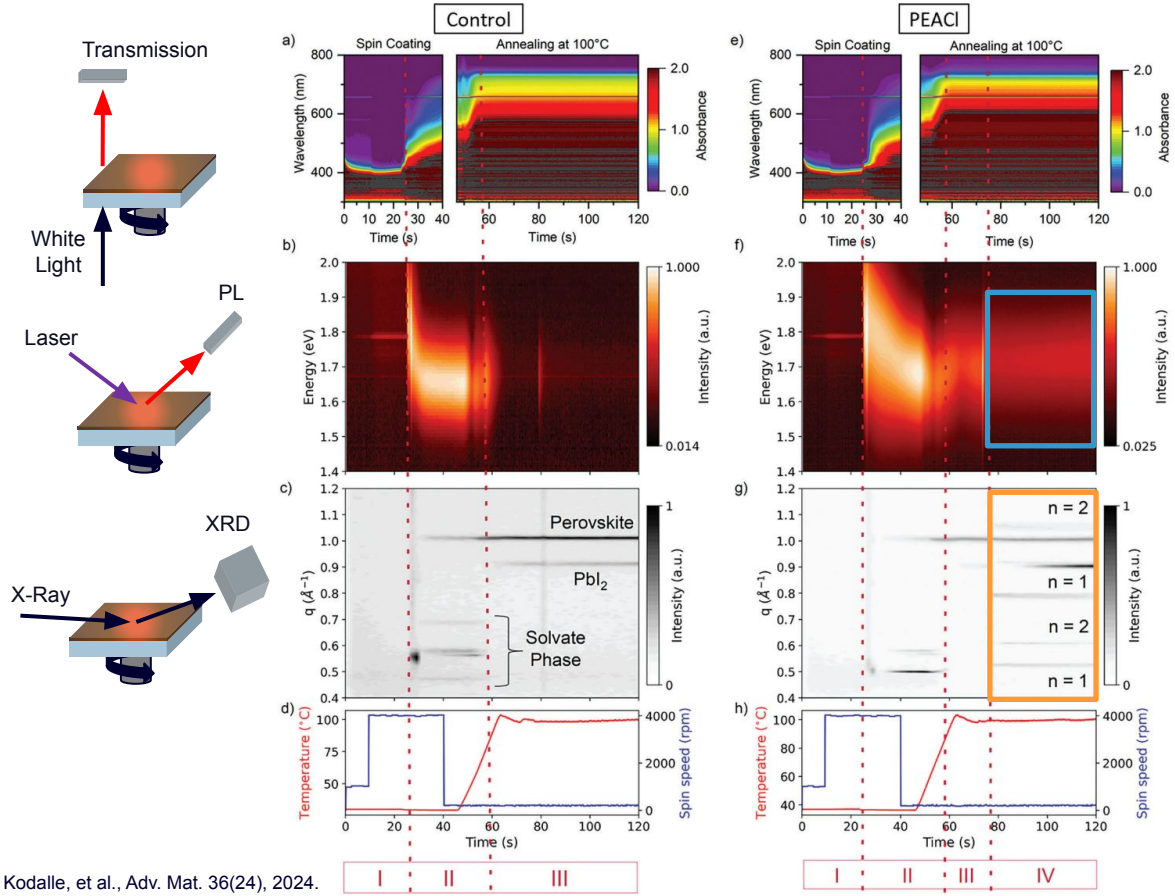
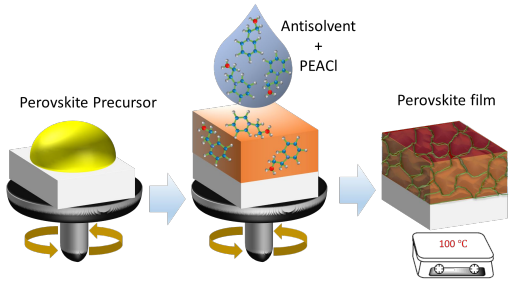
Multimodal analysis of the perovskite growth: PEACl case





- Phase I (Spin-Coating): Wet film
- Phase II (PEACl-Drop): Slower nucleation of pvsk-phase, altered intermediate phase
- Phase III (Annealing): Solvent-evaporation & crystal growth
- Phase IV: Intercalation of PEACl, improved crystal quality

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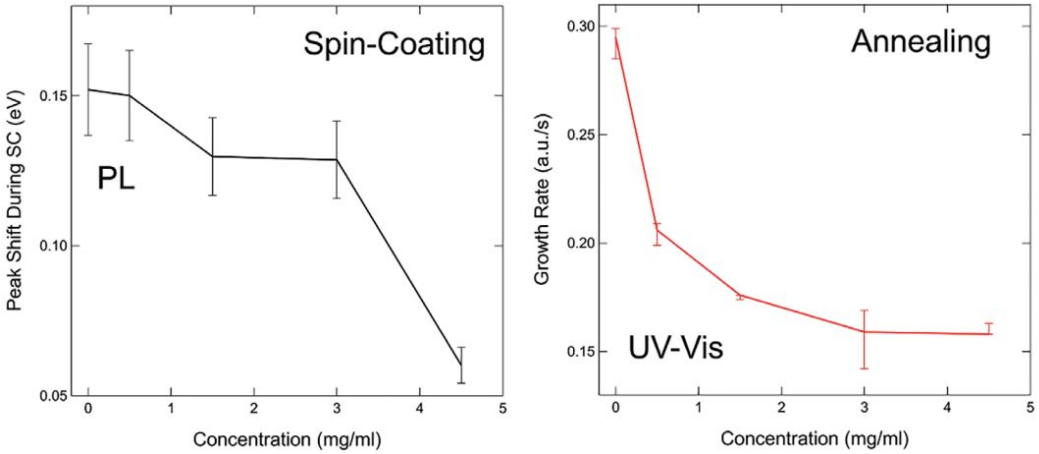
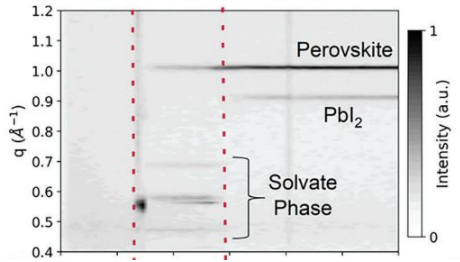
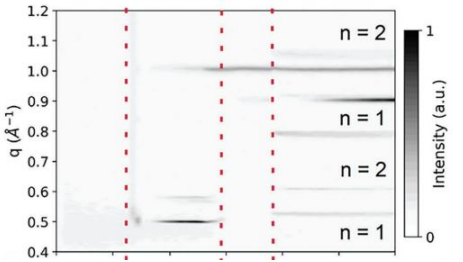
Varying PEACl-Concentration confirms improved growth



- PEACl slows down perovskite nucleation and crystal growth growth (UV-Vis & PL)





- Intermediate solvate phases form in both cases – but incorporates Cl in PEACl case (GIWAXS)

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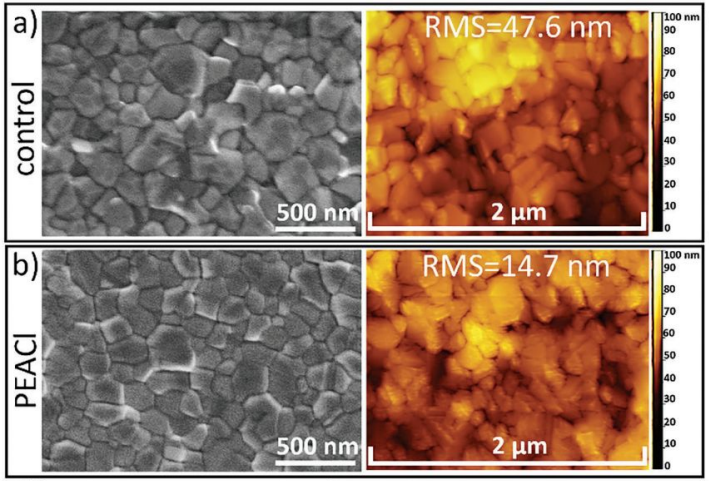
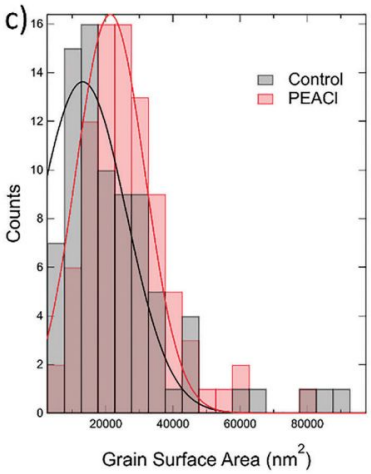
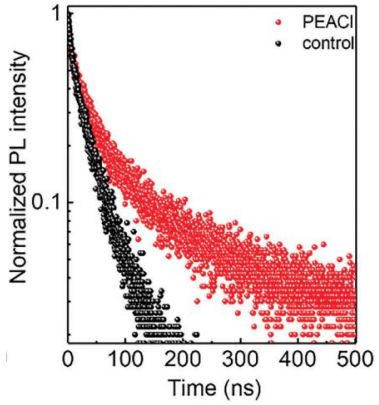
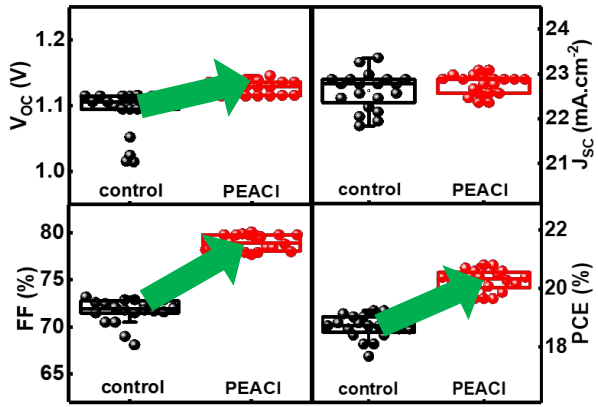
Correlation with ex situ characterization









- SEM & KPFM: Slower nucleation leads to growth of larger grains, smoother surface
- PL & trPL: Lower density of grain boundaries lead to improved carrier lifetime, i.e. reduced non-radiative recombination rate
- *jV*: Reduced non-radiative recombination improves V_{OC} & *FF*

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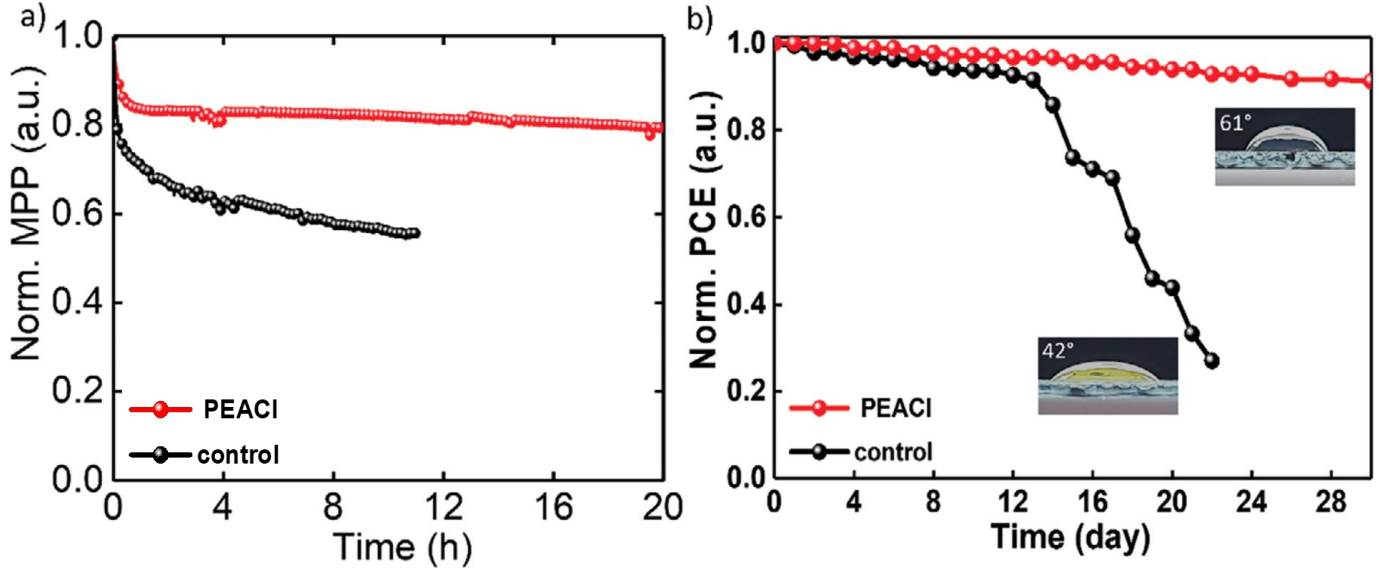
How does the integrated procedure compare to the 2-step deposition?



- Simplified, integrated one-step growth/passivation still stabilizes the perovskite under both continuous operation conditions (left) and under humidity

  - Newly developed PEACl-Antisolvent-Treatment can improve efficiency & stability while reducing the deposition time & effort

T. Kodalle, et al., Adv. Mat. 36(24), 2024.

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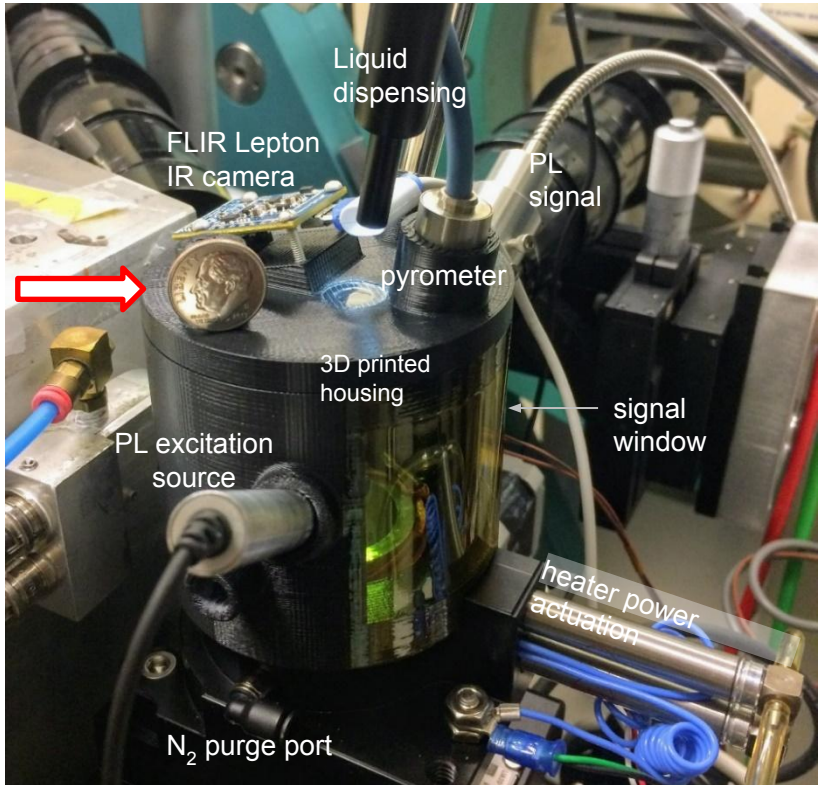
User Program: The multimodal in situ spin-coater at BL12.3.2



- Automated spin-coating, heating, and liquid dispensing in variable atmosphere
- Multimodal in situ photoluminescence and X-ray diffraction measurements
- Real time data acquisition (< 1s time resolution)
- Easy user operation (4 hours training)
- Fairly high throughput (~10 runs/shift)
- Compact and modular design
- Available to users since 2023

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Successful User Program

Collaborations since 2023:

[1] T. Kodalle, et al. **Adv. Ener. Mater.** vol 13, no. 33, p. 2201490, 2023.
[2] M. Ralaiarisoa, et al. **Small Methods**, vol. 7, no. 11, p. 2300458, 2023.
[3] P. Shi et al., **Nature**, vol. 620, pp. 323-327, 2023.
[4] M. Singh, et al., **ACS Chem. Mater.**, vol. 35, no. 18, pp. 7450-7459, 2023.
[5] W. Zuo, et al., **Adv. Mater.**, vol. 35, no. 39, p. 2302889, 2023.
[6] M. G. D. Guita, et al., **Adv. Funct. Mater.**, Early View, p. 2307104, 2023.
[7] K. Park, et al. **Adv. Mater.** vol. 36, no. 14, p. 2307265, 2024.
[8] L. Scalon, et al., **Adv. Optical Mater.**, vol. 12, no. 2, p. 2300776, 2024.
[9] T. Kodalle et al., **Adv. Mater.** vol. 36, no. 24, p. 2309154, 2024.
[10] R. F. Moral, et al., **ACS Energ. Lett.**, vol. 9, no. 6, p. 2703-2716, 2024.
[11] S. Sidhik, et al., **Science**, vol. 384, no. 6701, p. 1227-1235, 2024.
[12] S. Wang, et al., **Small Science**, vol. 4, no. 12, p. 2400292, 2024.
[13] L. Scalon, et al., **ACS Appl. Mat. & Interf.**, vol. 16, no. 38, p. 51727-51737, 2024.
[14] M. G. D. Guita, et al., **Adv. Func. Mat.**, vol. 34, no. 50, p. 2307104, 2024.
[15] P. E. Marchezi, et al., **J. Mat. Chem. A**, vol. 13, no. 22, p. 16671-16680, 2025.
[16] M. G. D. Guita, et al., **Solar RRL**, p. 202500404, 2025.
[17] Y. Zhang, et al., **Science**, vol. 387, no. 6731, p. 284-290, 2025.
[18] K. Datta, et al., **Nature Comm.**, vol. 16, no. 1, p. 1967, 2025.
[19] M.-C. Shih, et al., **Adv. Mat.**, vol. 37, no. 17, p. 2416672, 2025.
[20] S. Liu, et al., **J. Amer. Chem. Society**, vol. 147, no. 19, p. 16681-16693, 2025.
[21] S. Tan, et al., **Science**, vol. 388, no 6747, p. 639-645, 2025

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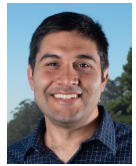
Office of Science

PIs and Main Collaborators

Universität Stuttgart







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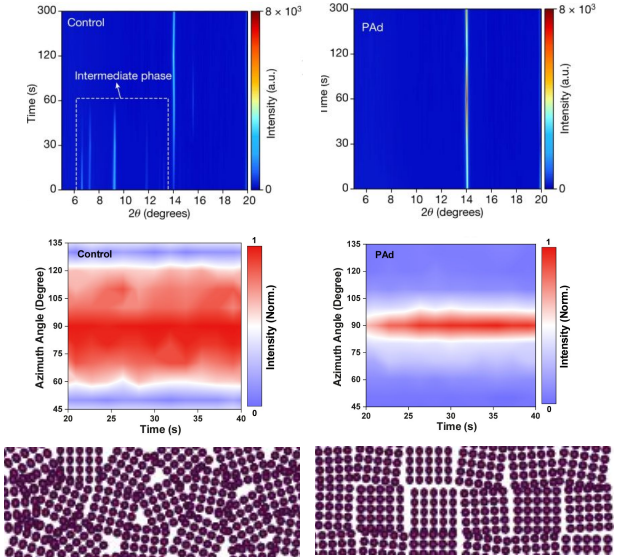
Some Perovskite Highlights

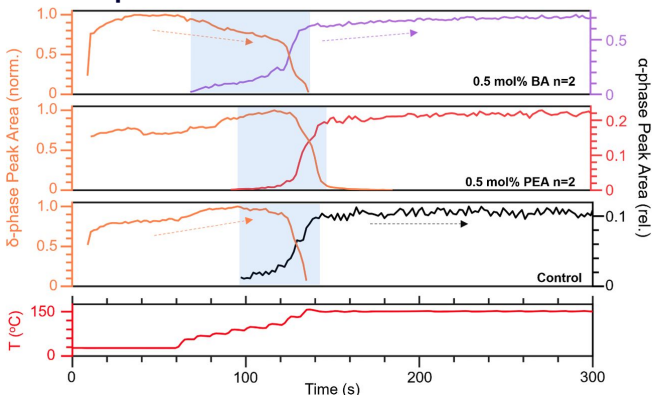
Correlation of intermediate phase formation and crystal orientation



Random Orientation Preferential Orientation

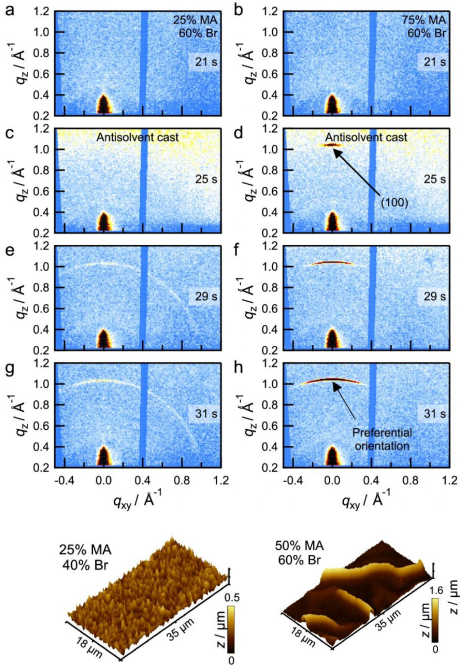
P. Shi, T. Kodalle, et al., Nature 620 (7973), 323-327, 2023.

Controlling phase transitions via precursor additives



S. Sidhik, I. Metcalf, T. Kodalle, et al., Science 384 (6701), 1227-1235, 2024.

Compositional engineering of film adhesion and roughness



K. Datta, T. Kodalle, et al., Nature Comm. 16 (1967), 2025.

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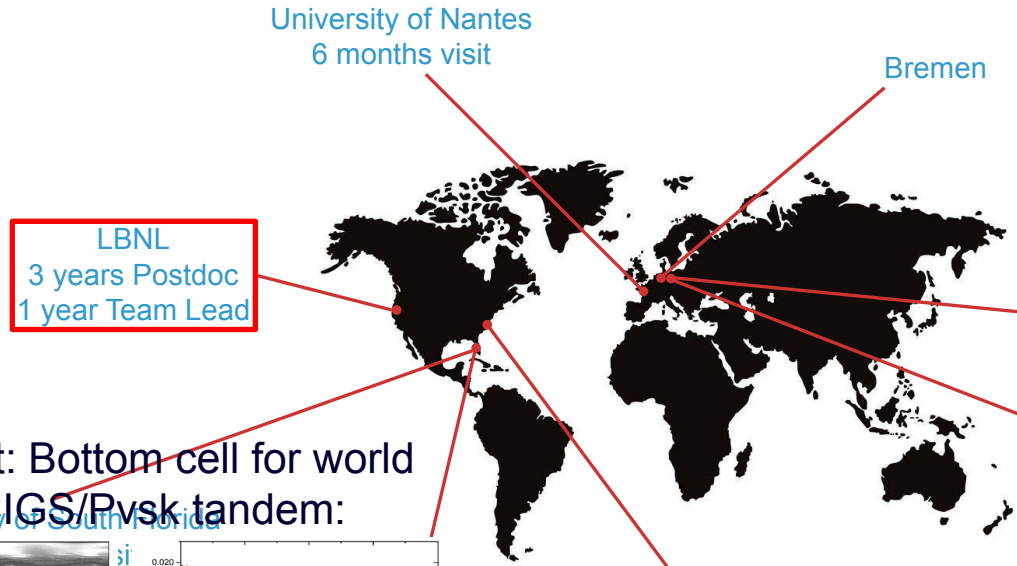
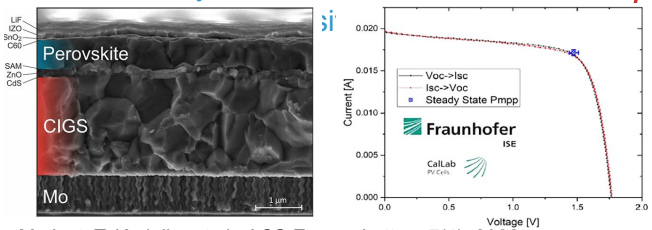
Things I've done in the (academic) world



Highlight: Bottom cell for world record CIGS/Pvsk tandem:



M. Jost, T. Kodalle, et al., ACS Energy Letters 7(4), 2022.

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