Georgia Tech

COPE Georgia Tech

NSF

IMOD

Juan-Pablo Correa-Baena

Goizueta Associate Professor
Initiative Lead on Solar Energy Conversion
Co-Director Center for Photonics and Electronics (COPE)

School of Materials Science and Engineering

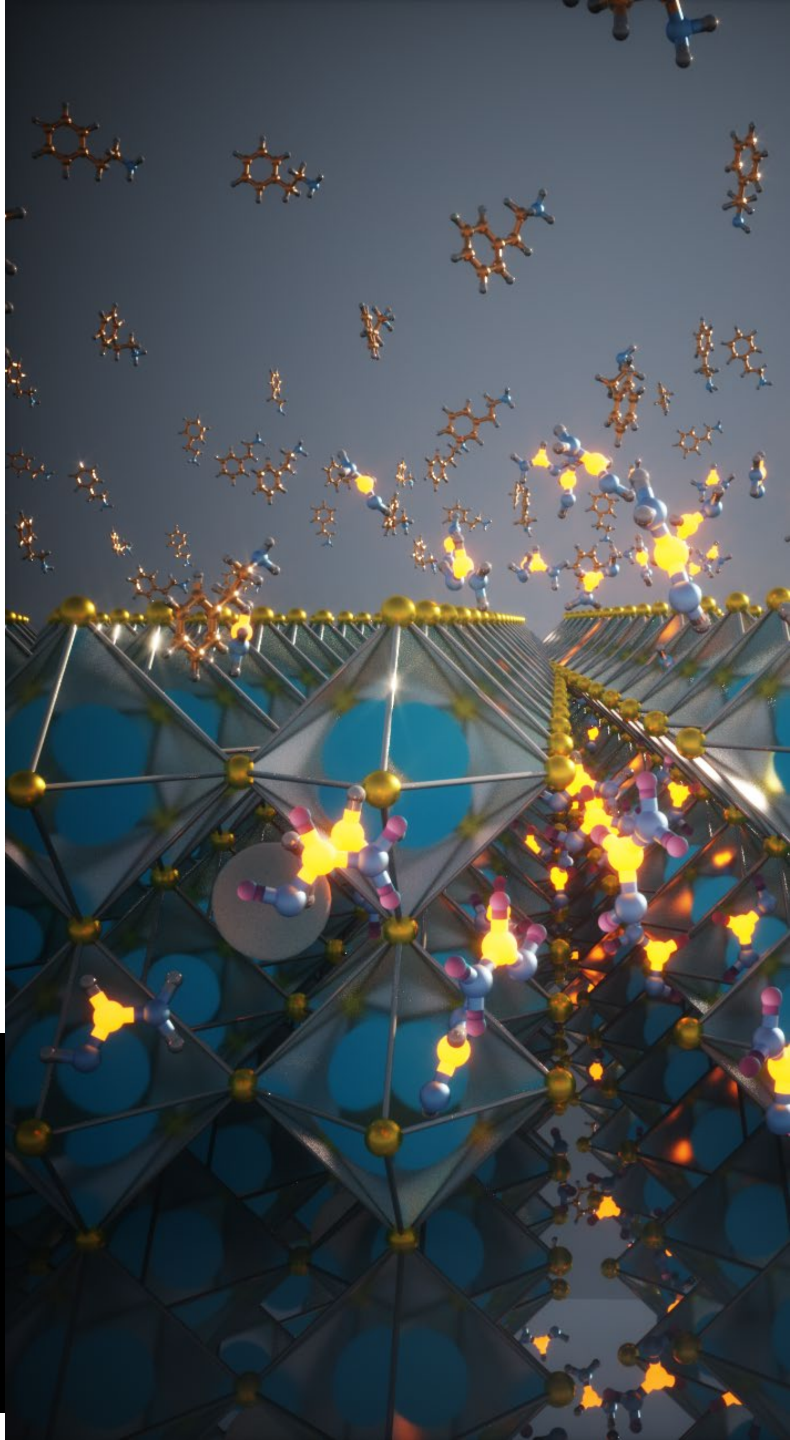
CHALLENGES AND OPPORTUNITIES IN PEROVSKITE SOLAR CELLS

Energy Materials Laboratories

HBCU Clean Energy Education Seminar Series on Solar Energy

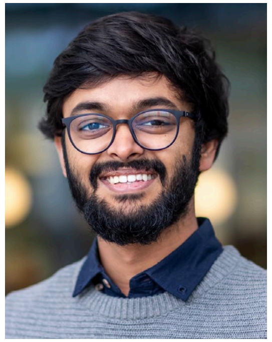
Atlanta GA

Wednesday, June 4, 2025



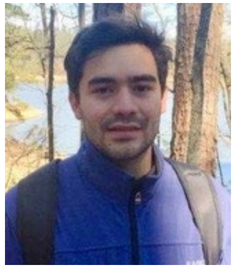
Research Scientist

Postdoctoral Researchers



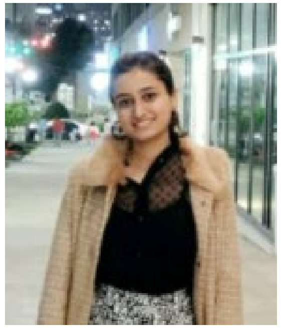
Alumni

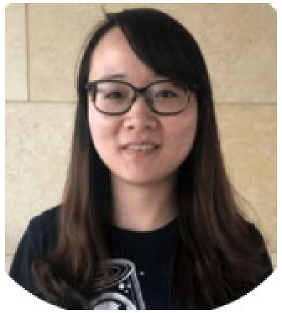
Dr. Juanita Hidalgo, Currently a postdoc at MIT

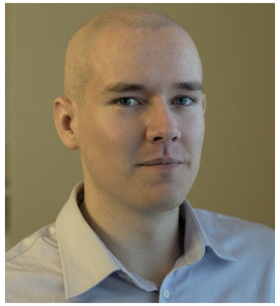


Dr. Andres Castro, currently a postdoc at University of Potsdam

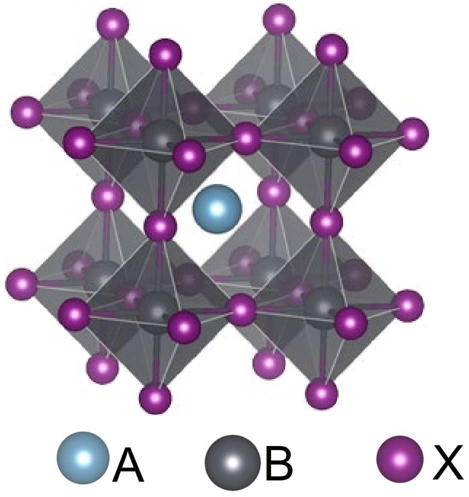
Graduate students

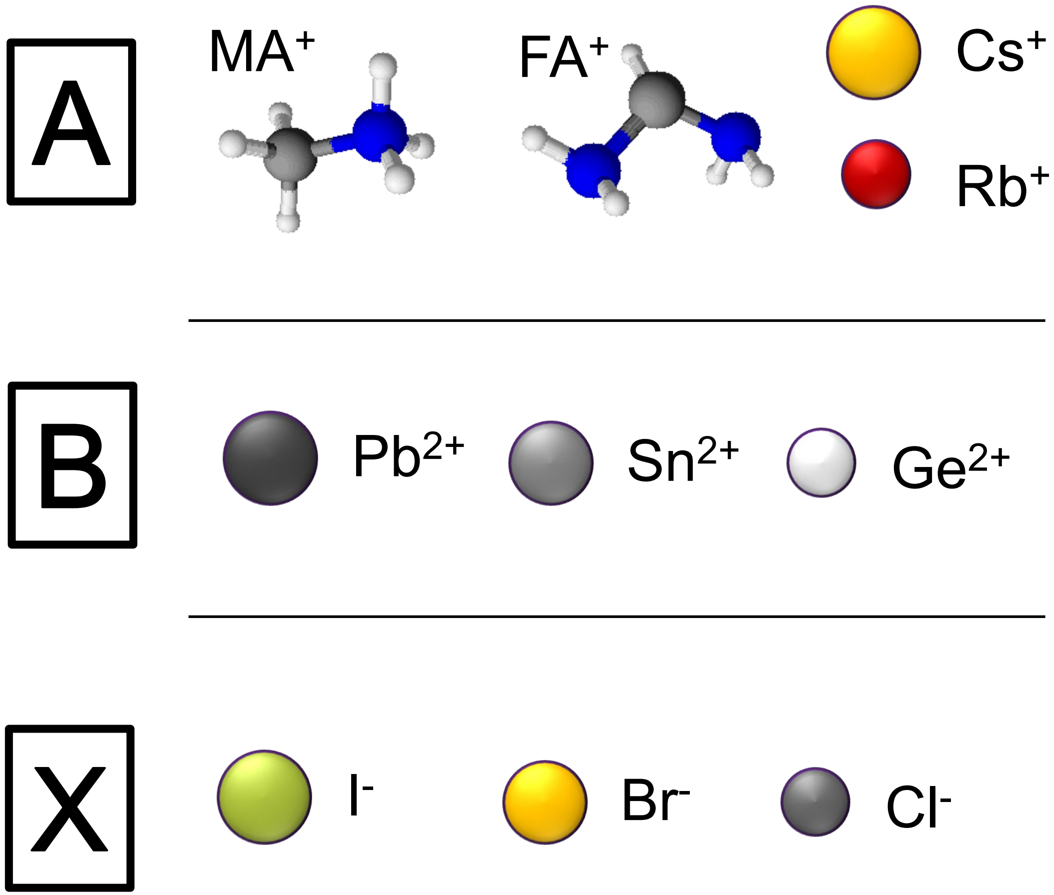






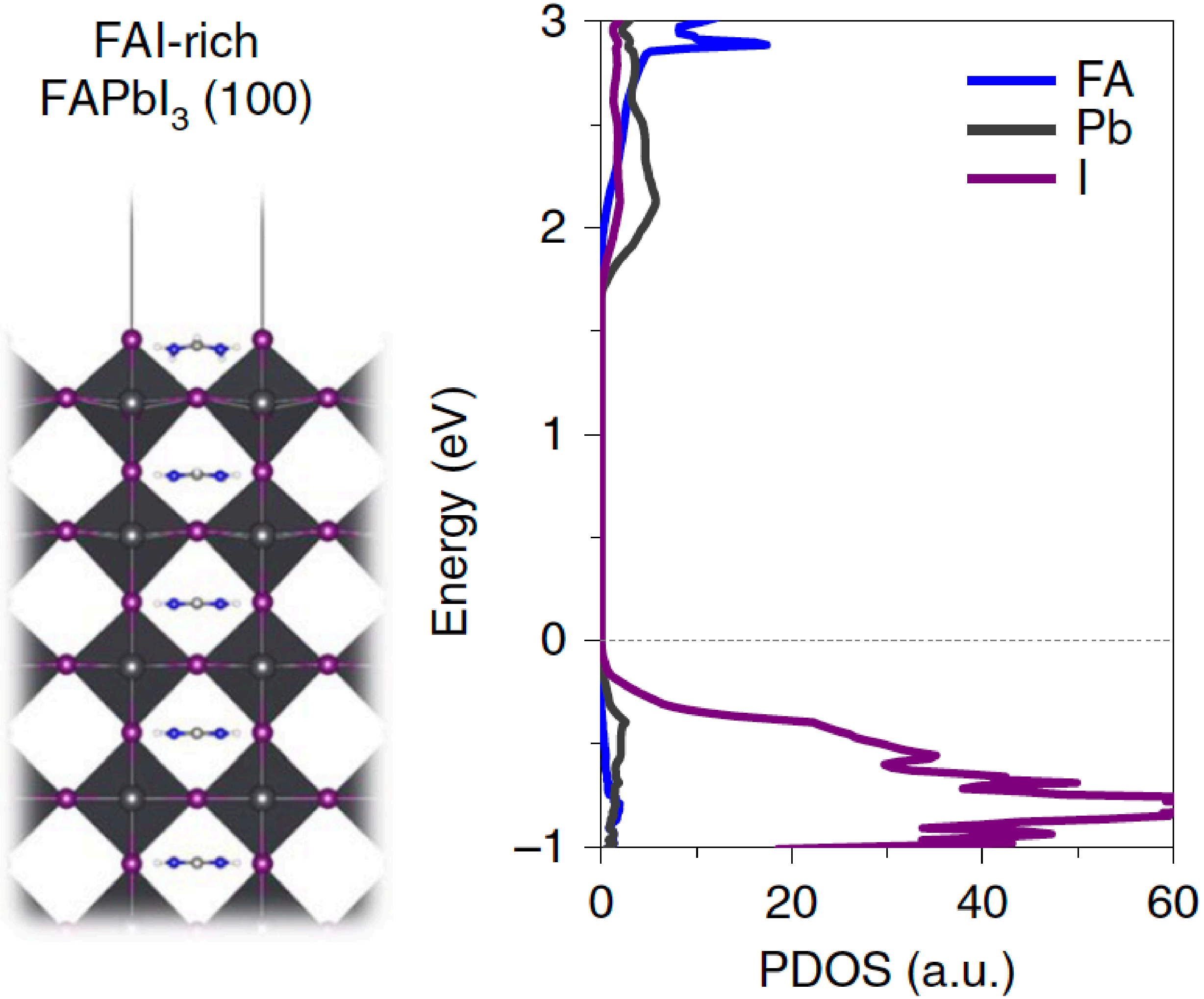
ABX_3 Halide Perovskites





CONTRIBUTION OF THE ORGANIC TO DOS

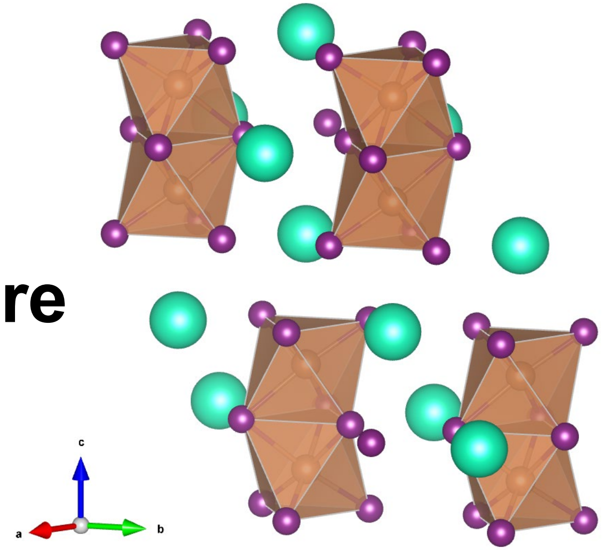
Surface: organic rich

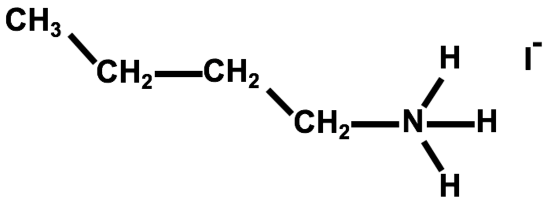


Zheng, X., …, Bakr, O. M. et al. (2020). *Nature Energy*, *5*(2), 131–140.

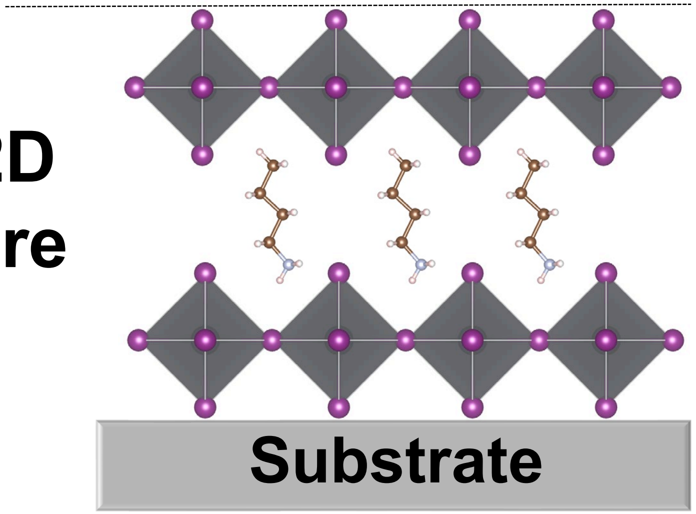
WHAT IS THE CONTRIBUTION OF THE ORGANIC OR INORGANIC CATION?

0D Structure





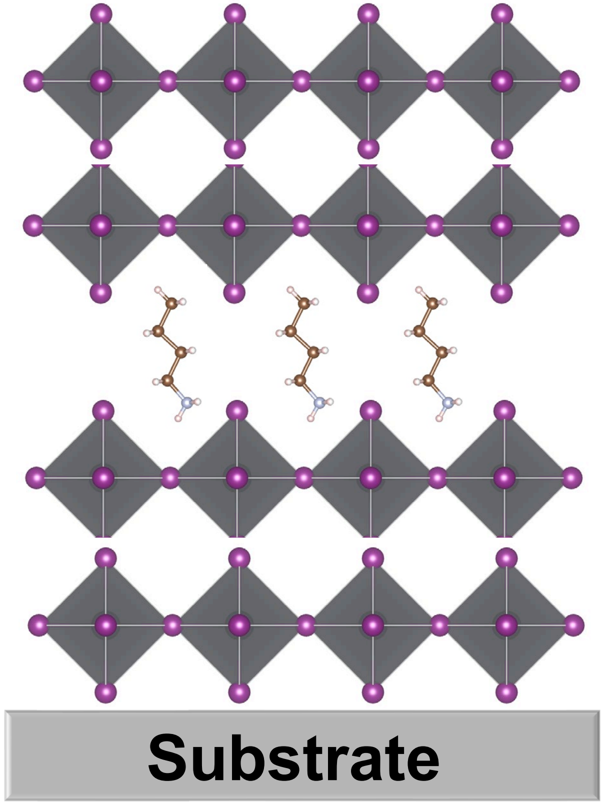
1D or 2D Structure



n = 1

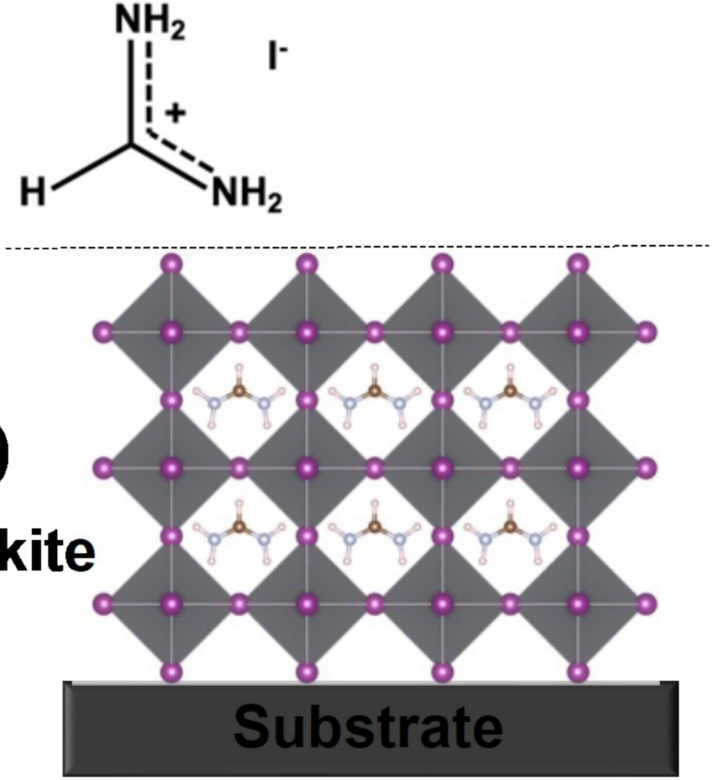
WHAT IS THE CONTRIBUTION OF THE ORGANIC OR INORGANIC CATION?

2D
Structure



n = 2

3D
Perovskite

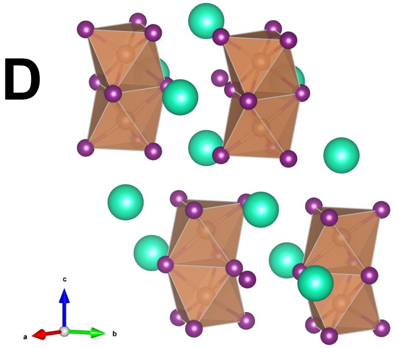


STRUCTURAL DIMENSIONALITY AFFECTS MATERIALS PROPERTIES

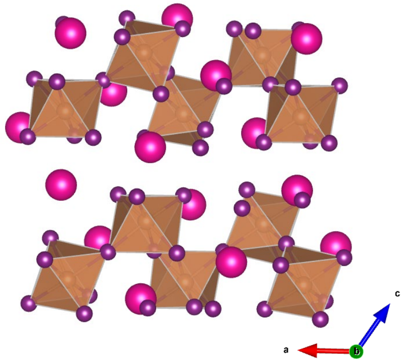
non 3D Perovskite-related

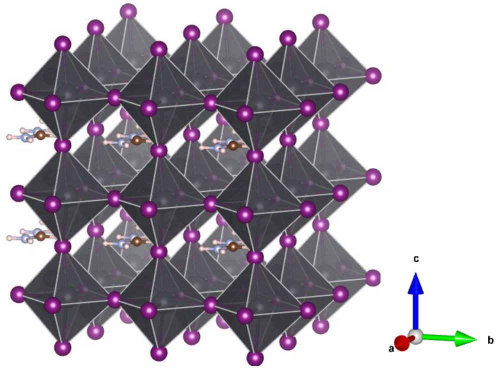
3D Perovskites

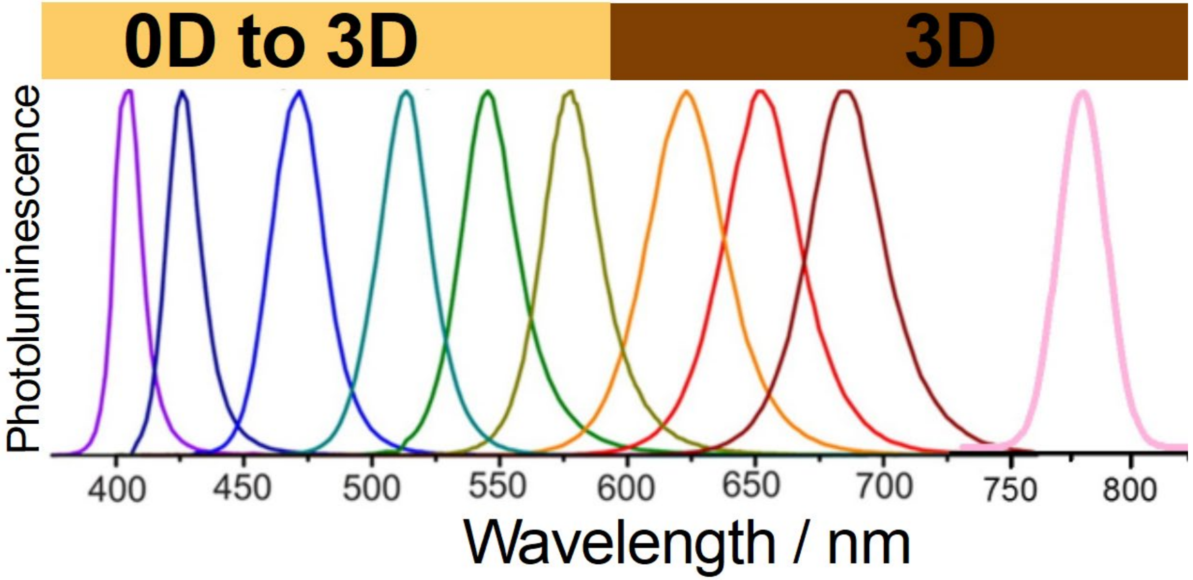
0D



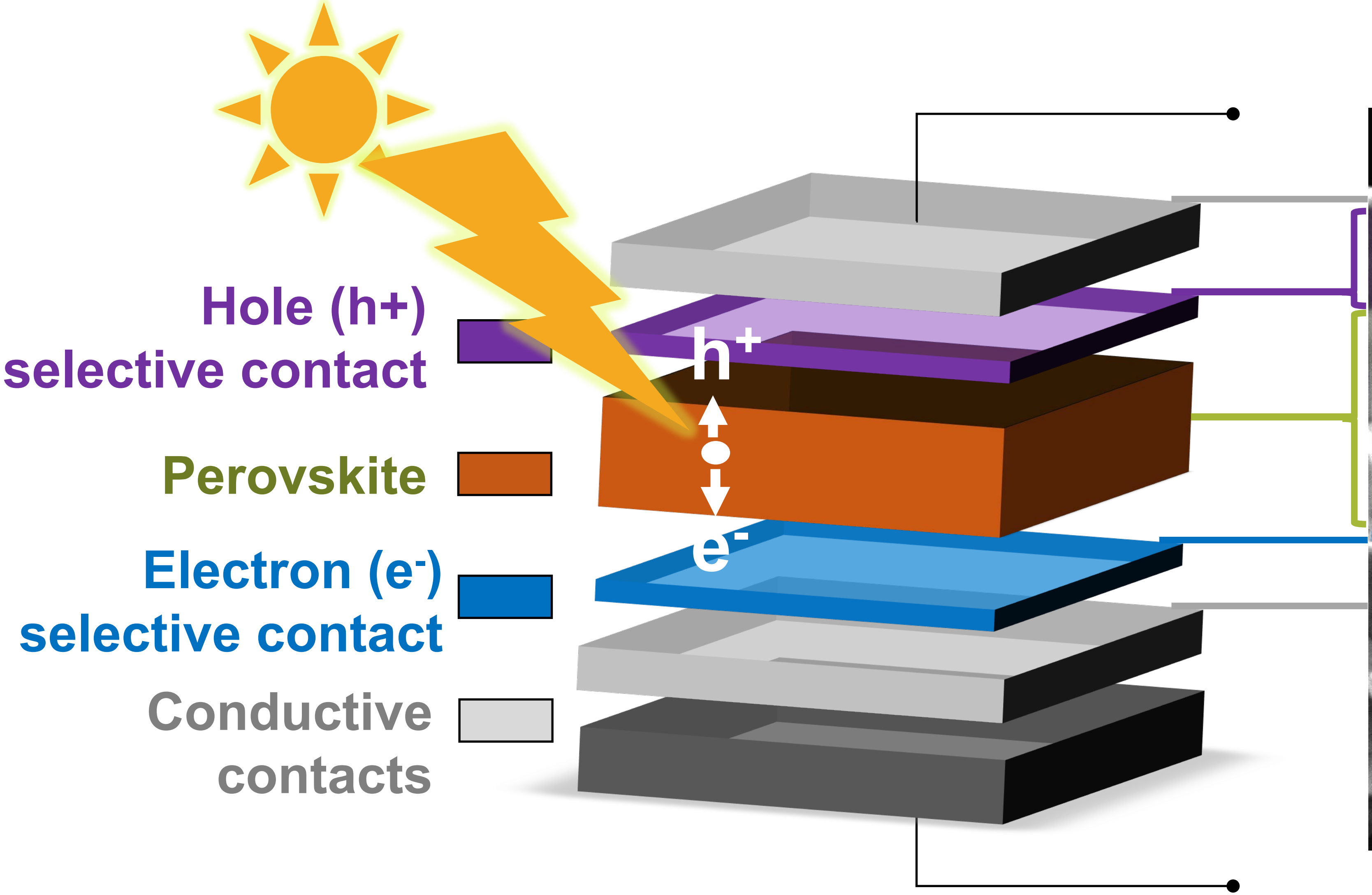
2D

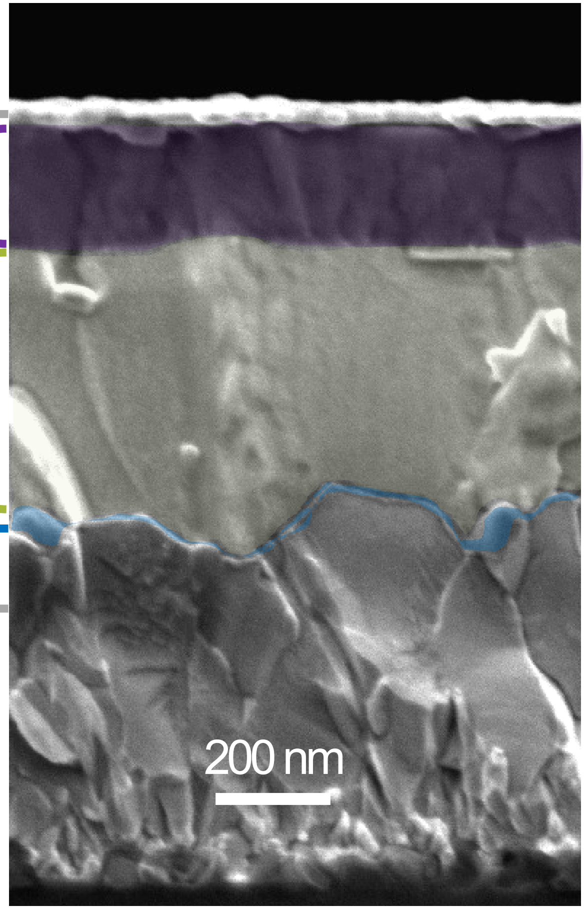






PEROVSKITES FOR SOLAR CELLS & PHOTODETECTORS





CORRESPONDING CROSS-SECTIONAL SEM

Correa-Baena, J.-P., et al., Energy & Environmental Science, 2017, 10 (3), 710-727.
Correa-Baena, J.-P., Science, 2017, 358 (6364), 739-744.

OUTLINE

01. INTRODUCTION TO PEROVSKITE DEFECTS

02. SURFACE MODIFICATION OF THE PEROVSKITE THIN FILM

03. PHASE TRANSFORMATIONS UNDER EXTERNAL STIMULI

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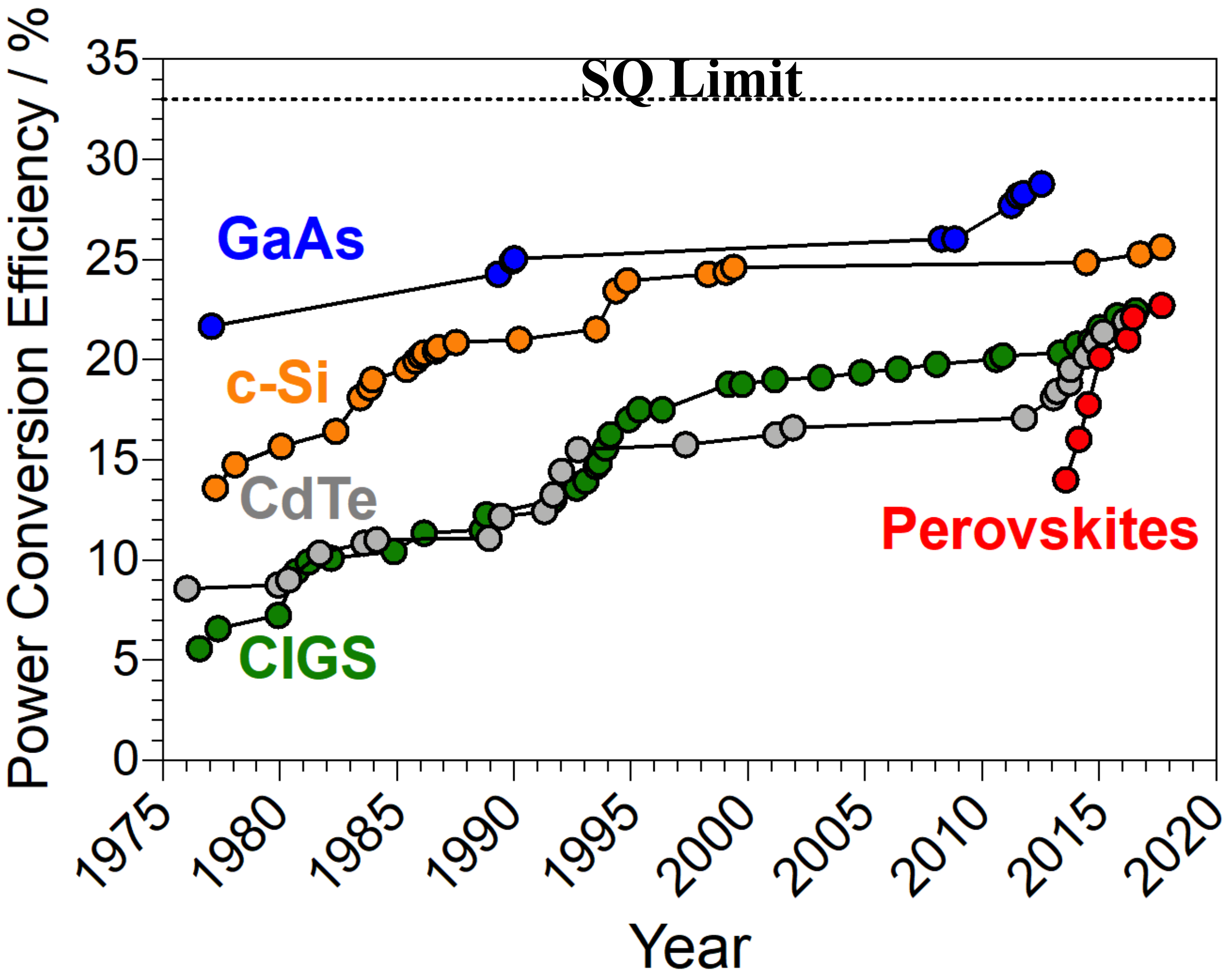
05. CONCLUSIONS

Progress of Solar Cell Efficiencies

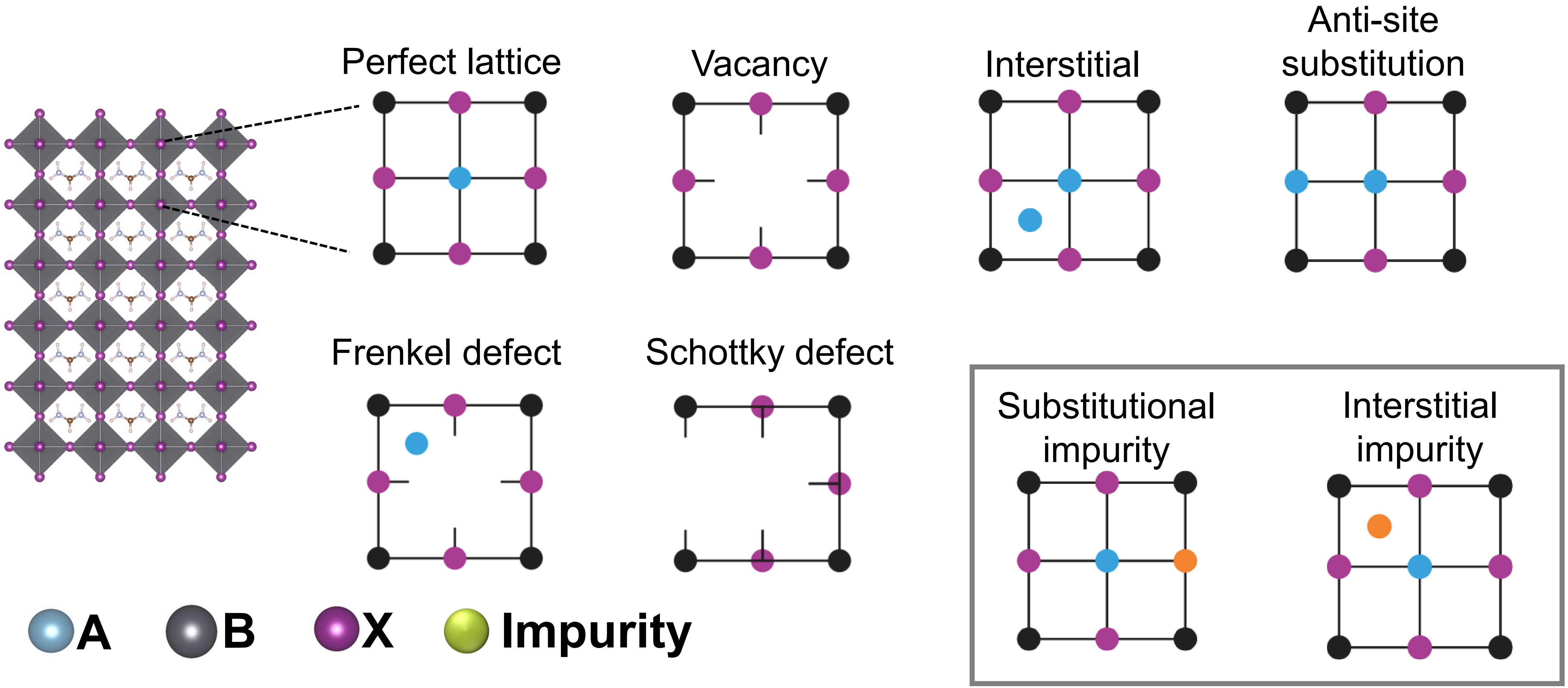


- Development of a new solar cell technology used to take decades
- Perovskites are an exception

Why?

NREL: National Center For Photovoltaics Home

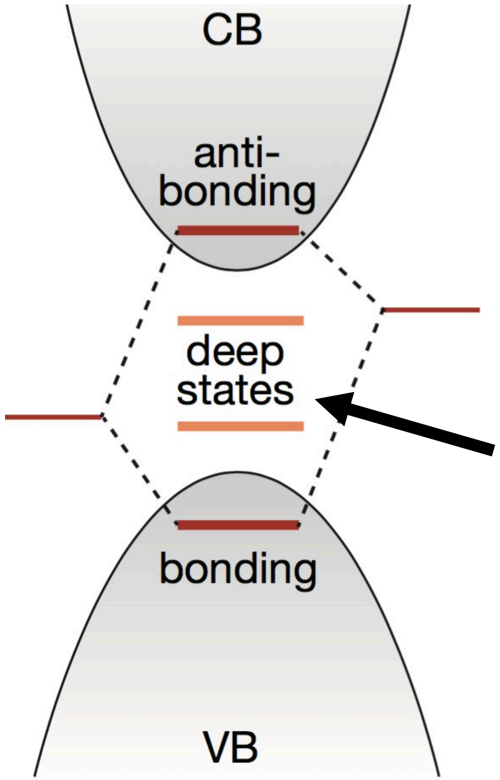
Point Defects in Perovskites



J. M. Ball, A. Petrozza, Nature Energy 1, 16149 (2016).

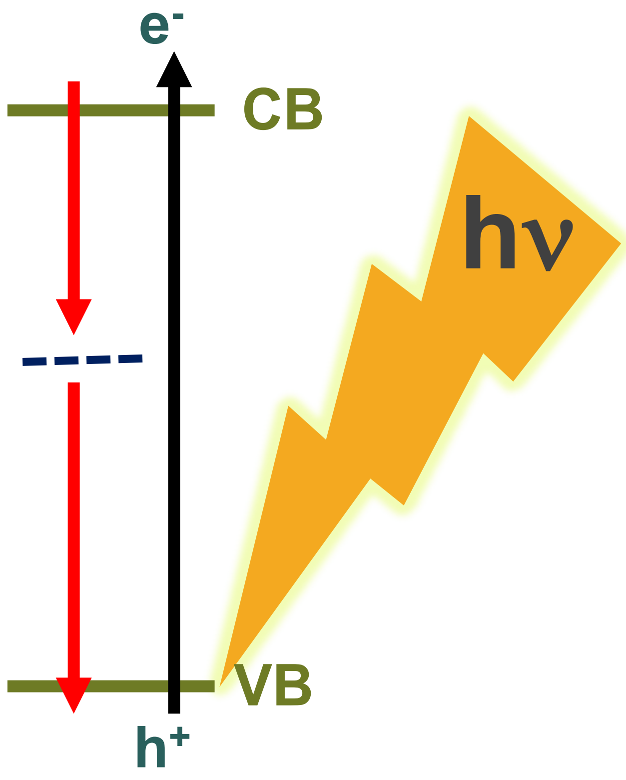
Defects Affect Electronic Trap States

most semiconductors



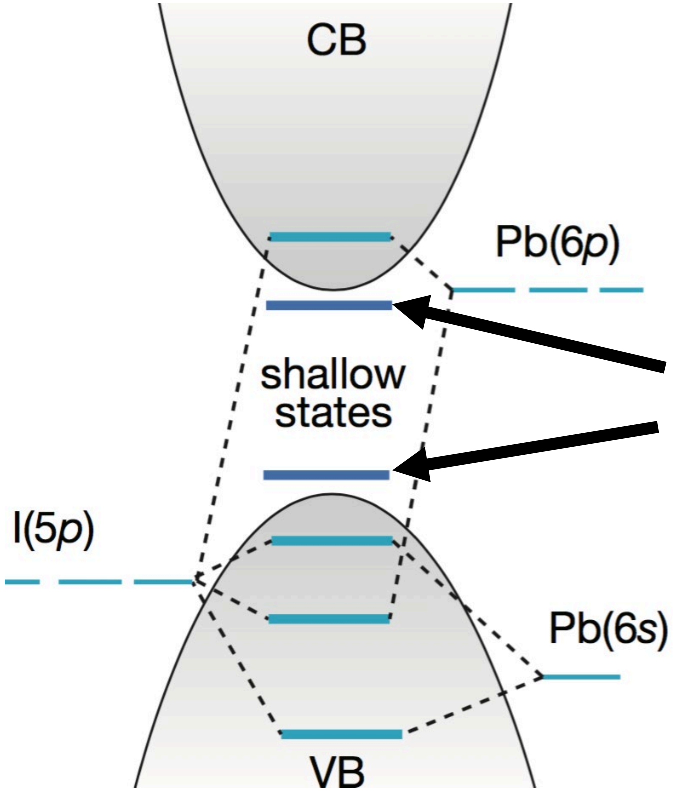
Trap assisted recombination

deep trap state



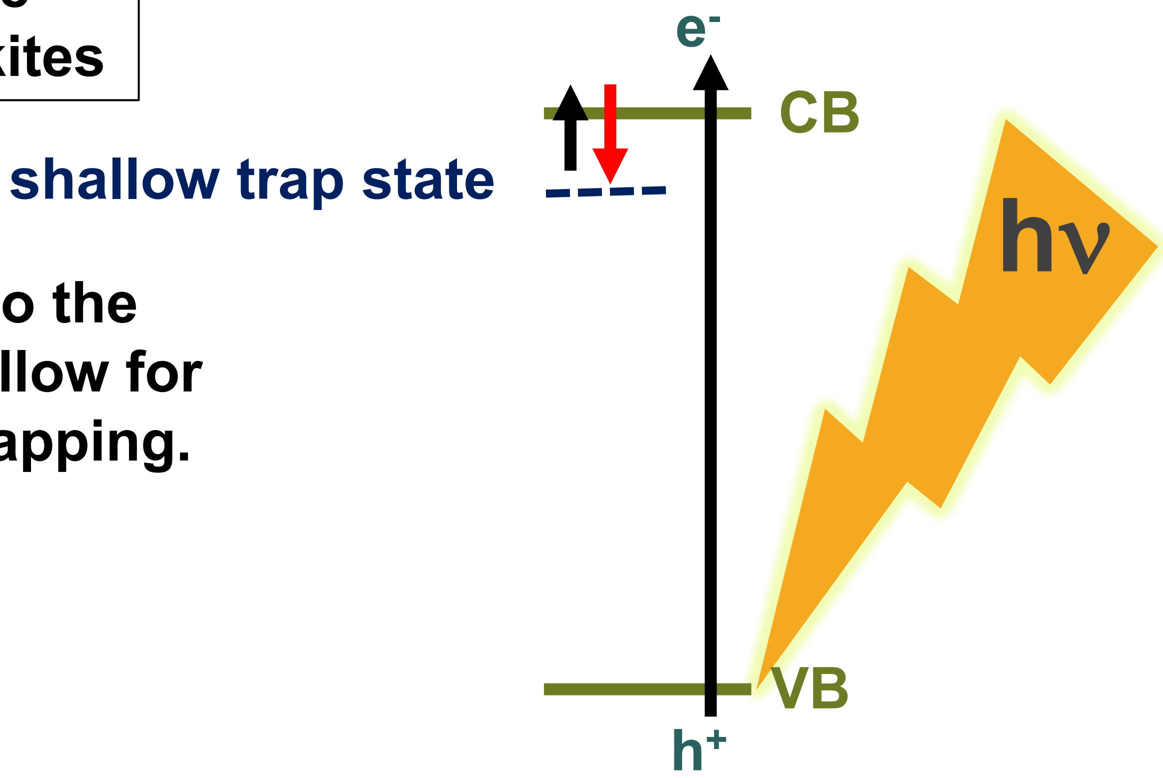
T. Umebayashi, et al., Physical Review B 67, 155405 (2003).

In Halide Perovskites: Mostly Shallow Traps



Halide Perovskites

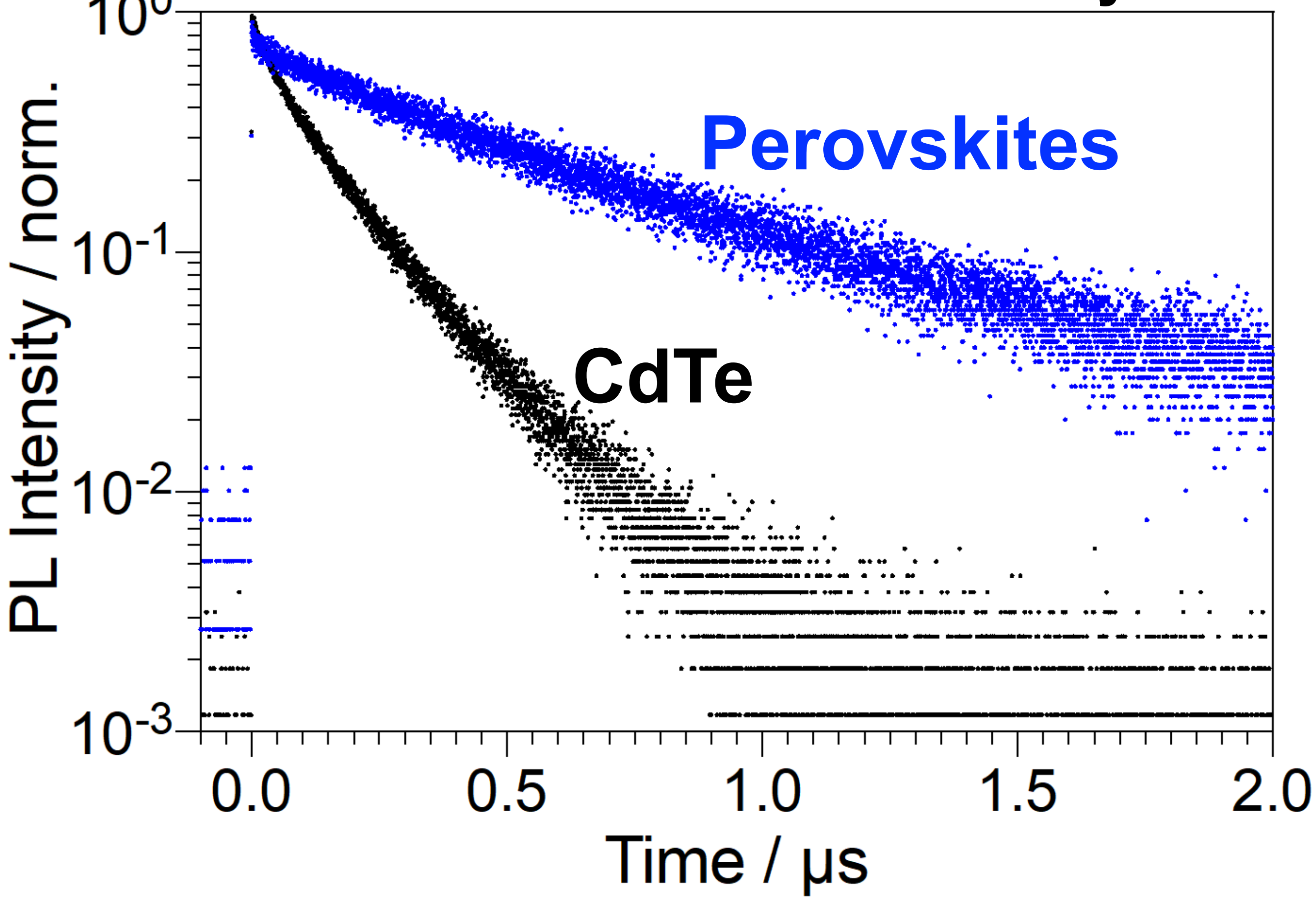
States close to the band edges allow for trapping-detrapping.



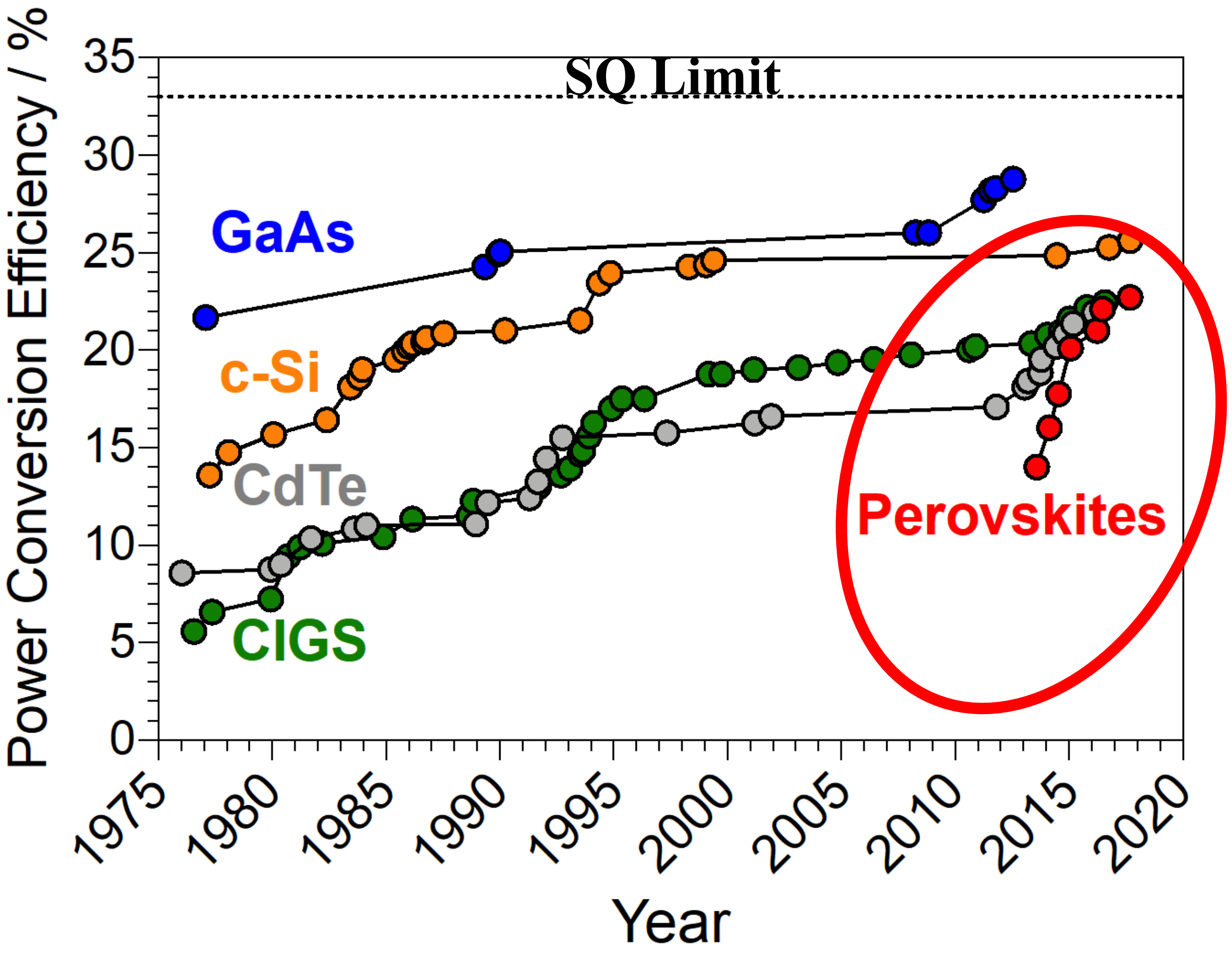
T. Umebayashi, et al., Physical Review B 67, 155405 (2003).
R. E. Brandt,…, Kurchin, et al., Chemistry of Materials, 2017, 29, 4667-4674.

Long-lived Charge Carrier Dynamics

Microsecond Photoluminescence decay



Progress of Solar Cell Efficiencies

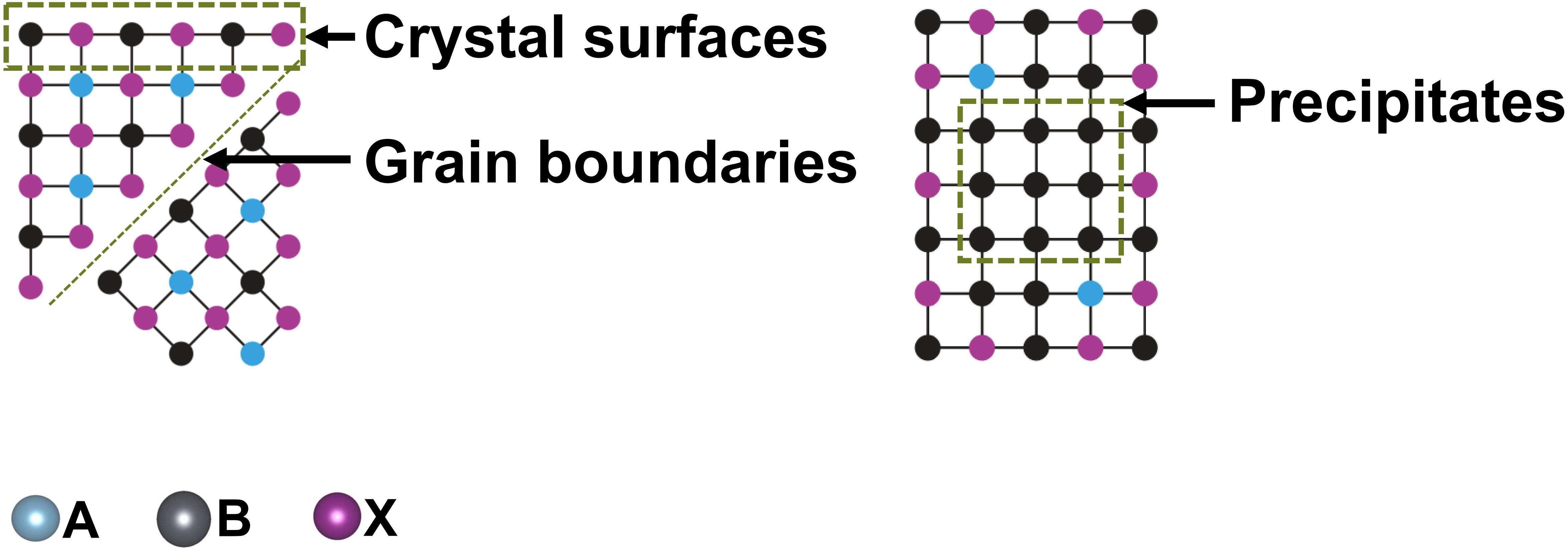


Why?

Some degree of defect tolerance

NREL: National Center For Photovoltaics Home

2D and 3D Defects in Perovskite Thin Films



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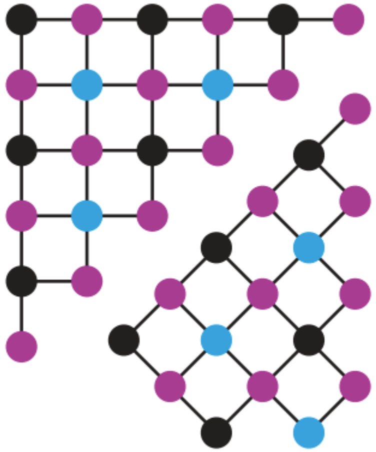
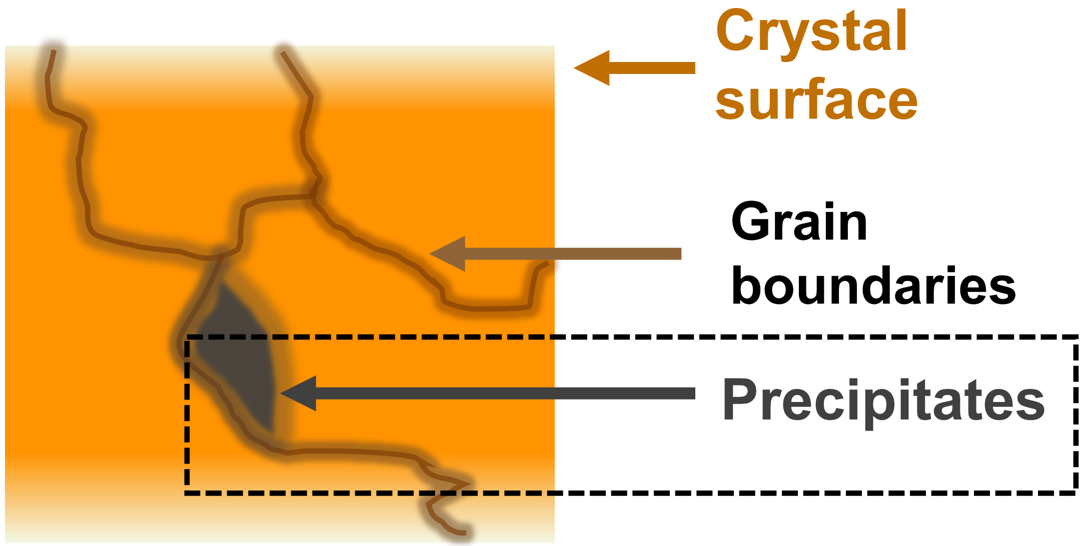
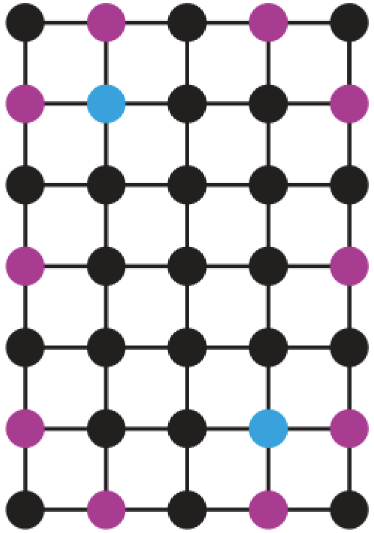
2D and 3D Defects in Perovskite Thin Films

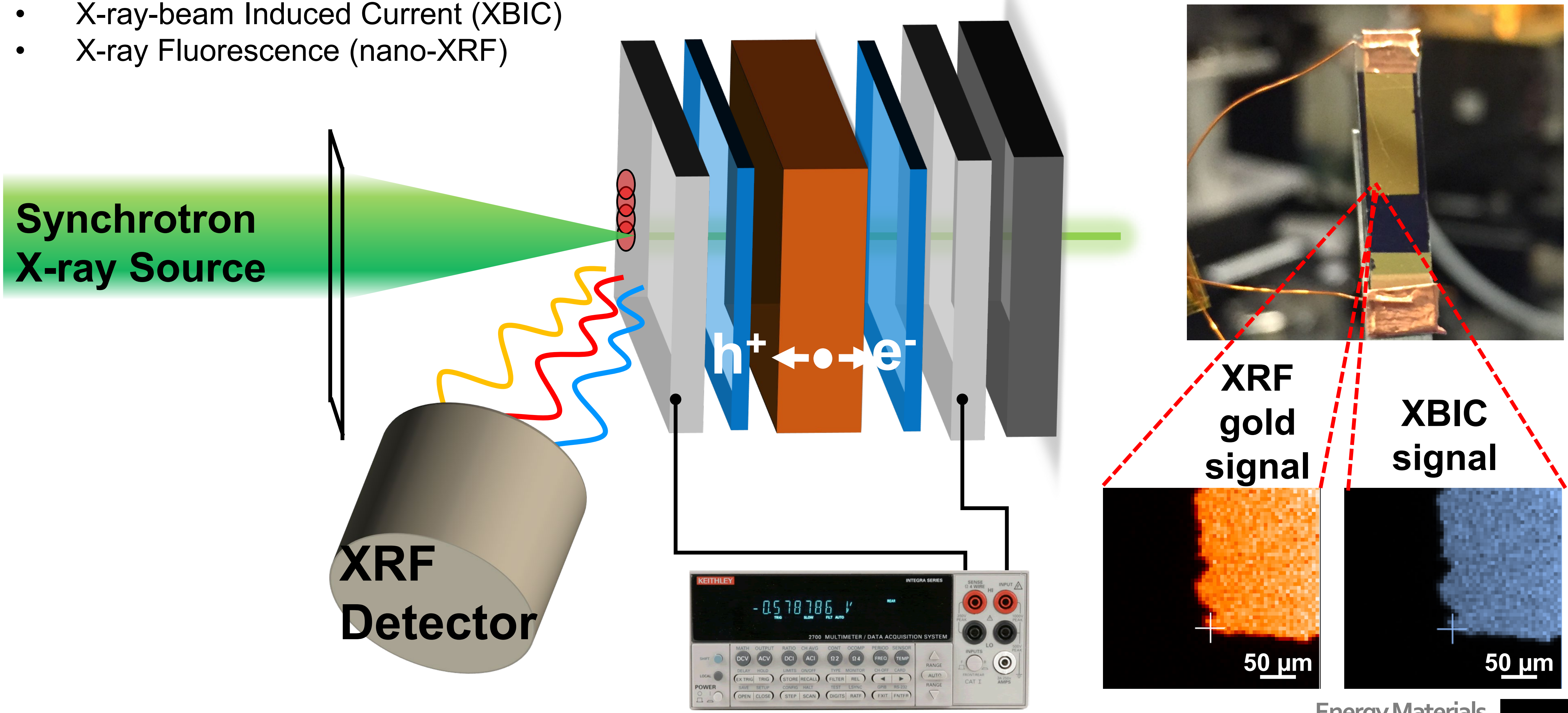






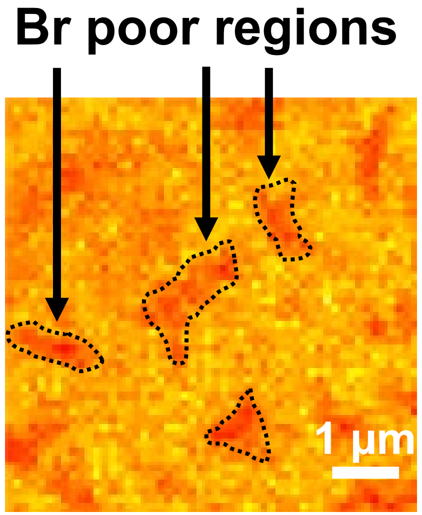
Effects of precipitates on electronic properties

- X-ray-beam Induced Current (XBIC)
- X-ray Fluorescence (nano-XRF)



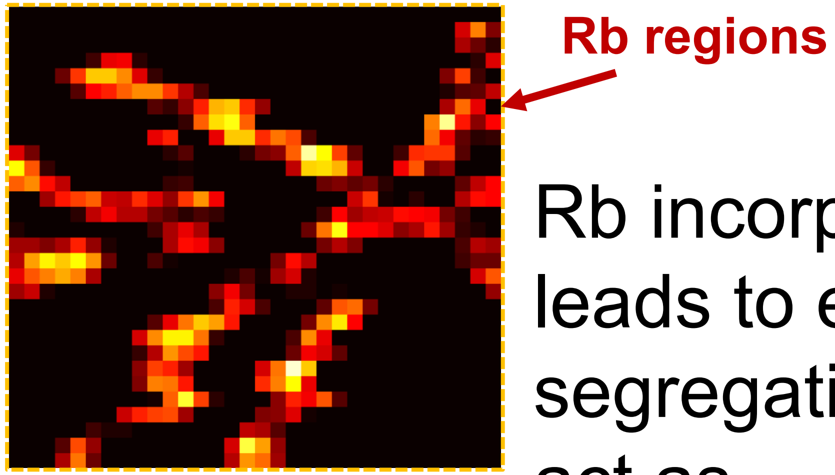
Correa-Baena, J.-P., Fenning, D., Buonassisi, T., et al. Science 2019, 363, 627-631.

"Additives" Affect Compositional Distribution



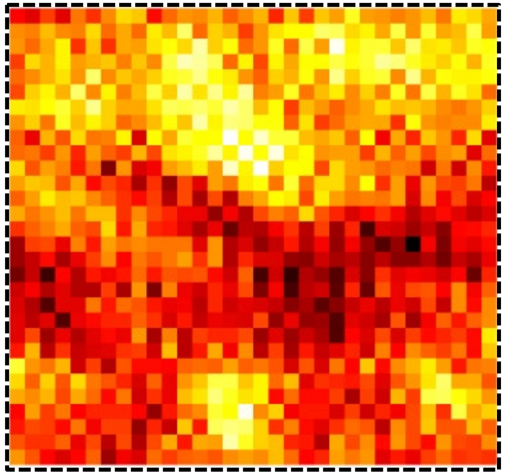
XRF

Cs and/or Rb incorporation in solution leads to homogenous halides in the thin film



XRF (chemistry)

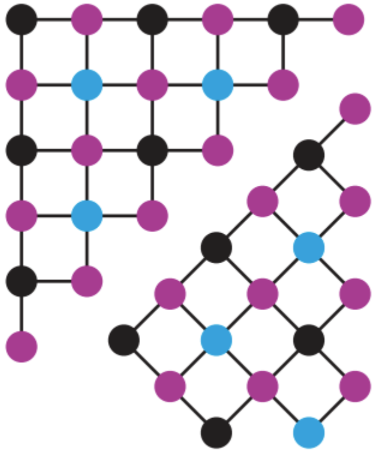
Rb incorporation leads to element segregation that act as recombination centers

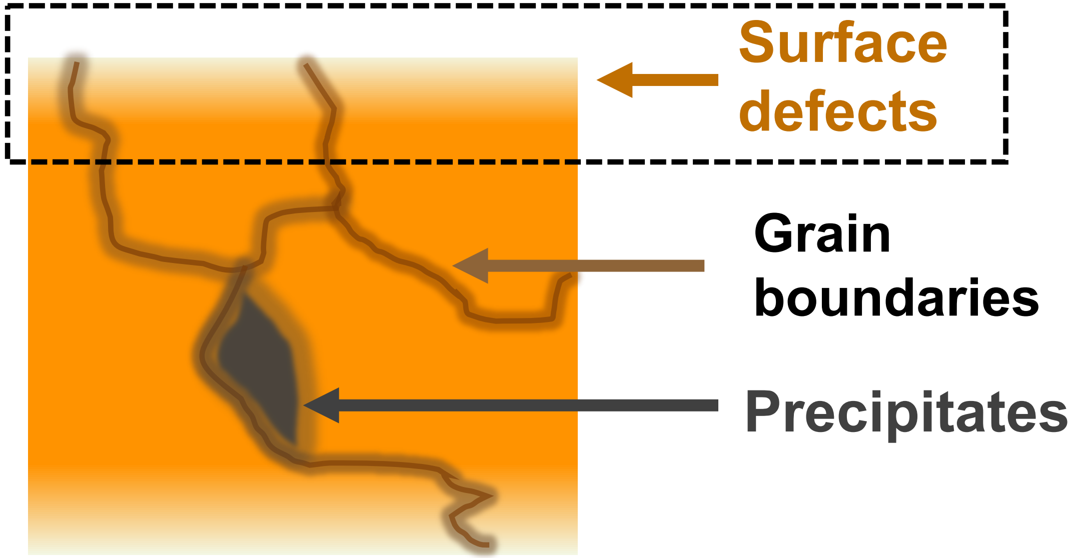


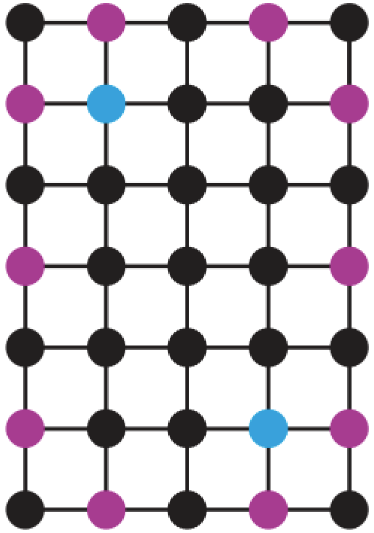
XBIC (local performance)

Correa-Baena, J.-P., Fenning, D., Buonassisi, T., et al. Science 2019, 363, 627-631.

The Role of Surfaces in Perovskite Thin Films







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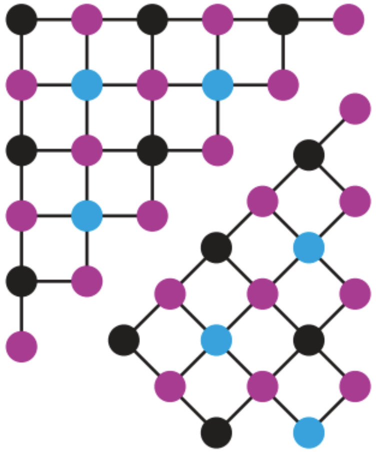
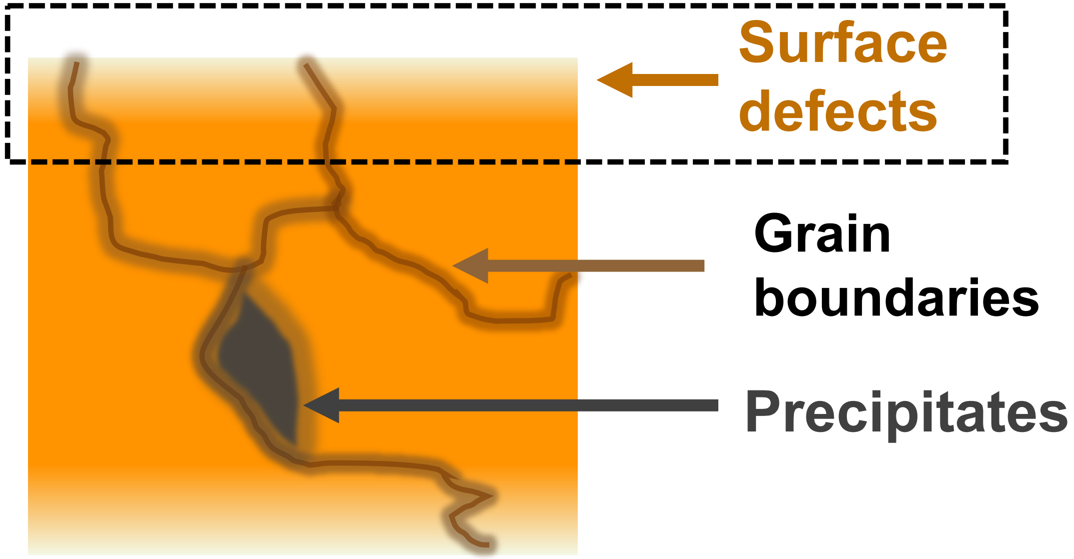
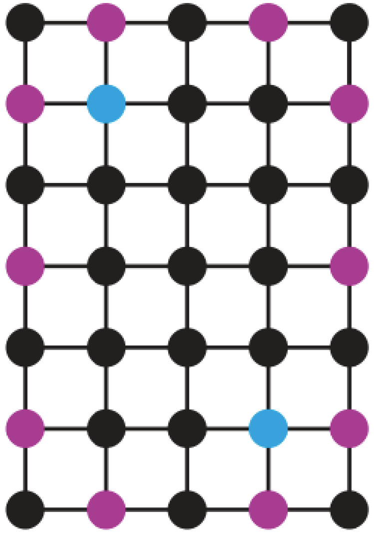
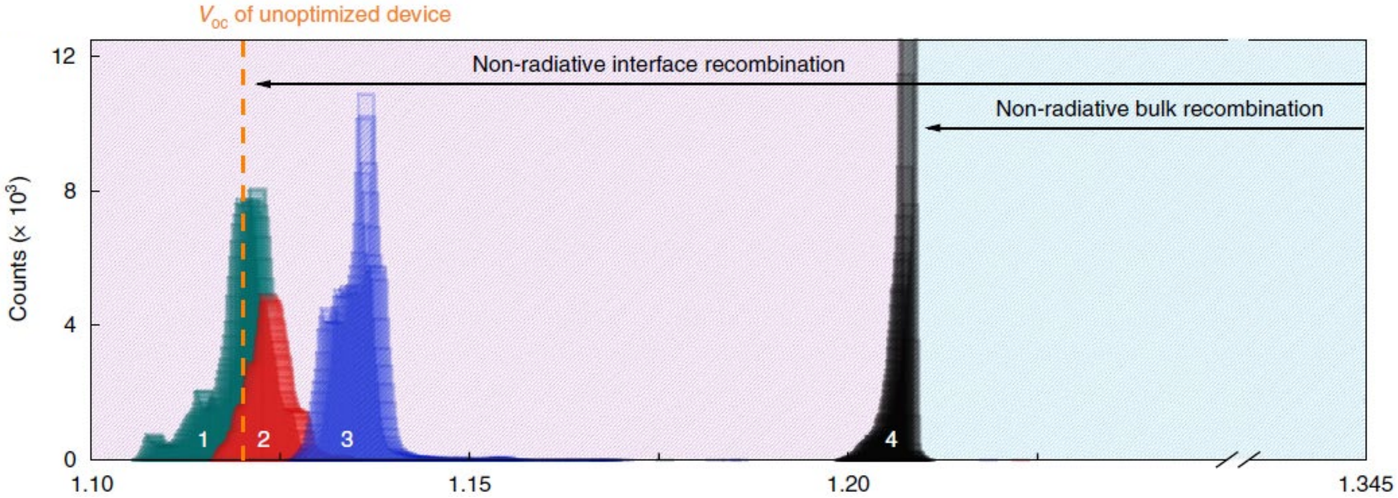
The Role of Surfaces in Perovskite Thin Films



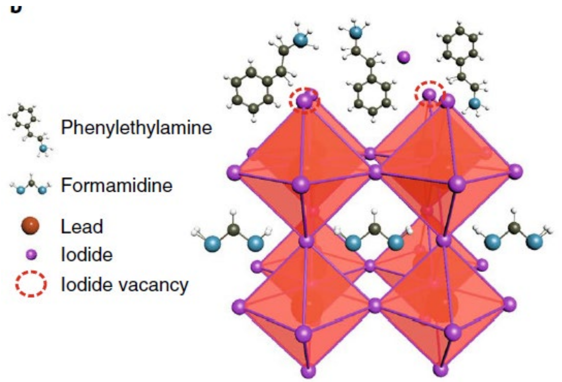


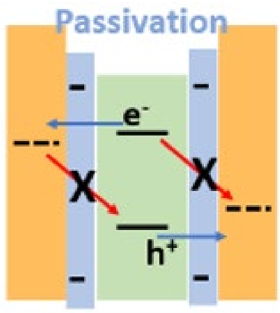




Interface recombination is still major cause of performance loss (V_{oc} drop);

Nature Energy, 3, (2018), 847–854





Large organic molecules (e.g. PEAI) can passivate defects at perovskite interfaces

Broad range of reported results:

(PVK composition, annealing, 2D deposition route)

- Correct band alignment is beneficial
- Accurate control on thickness to avoid series resistance losses

J. Phys. Chem. Lett., 11, (2020), 5115–5119

J. Phys. Chem. Lett., 10, (2019), 5713−5720

ACS Energy Lett., 4, (2019), 2893–2901

Nature Photonics, 13, (2019), 460–466

Nano Lett. 20, (2020), 3992–3998

QUESTIONS

1. What structures form at the surface of the perovskite thin film?

2. How stable is this interface given its "soft" nature?

3. What is the mechanism by which surface passivation happens?

QUESTIONS

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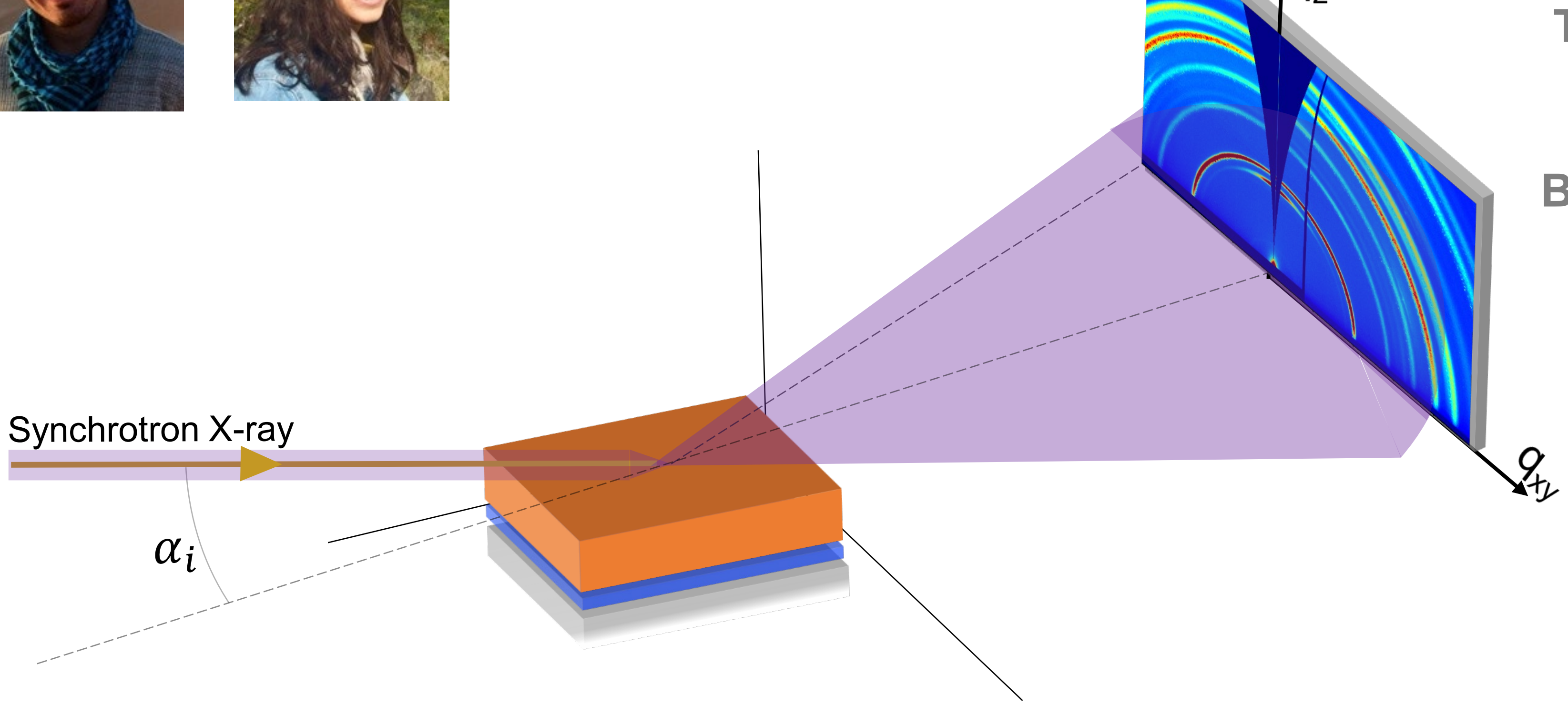
2. How stable is this interface given its "soft" nature?

3. What is the mechanism by which surface passivation happens?

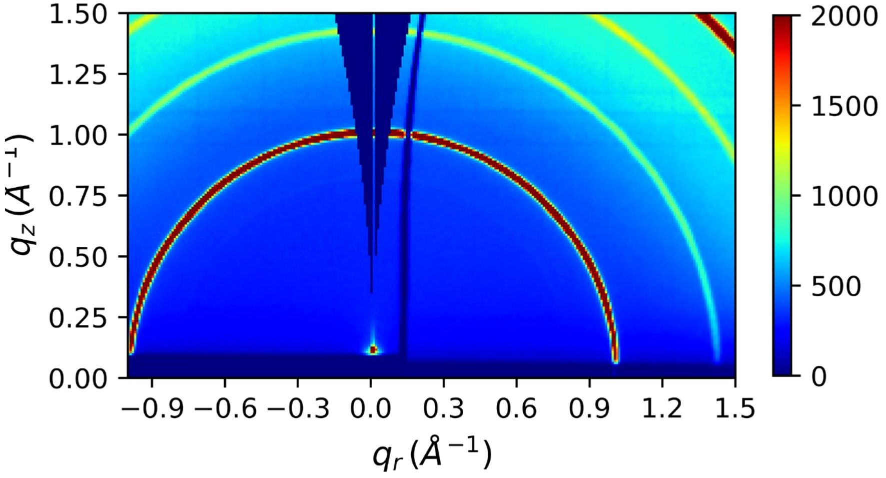
GRAZING-INCIDENCE WIDE-ANGLE X-RAY SCATTERING (GIWAXS)



The National Synchrotron Light Source (NSLS)

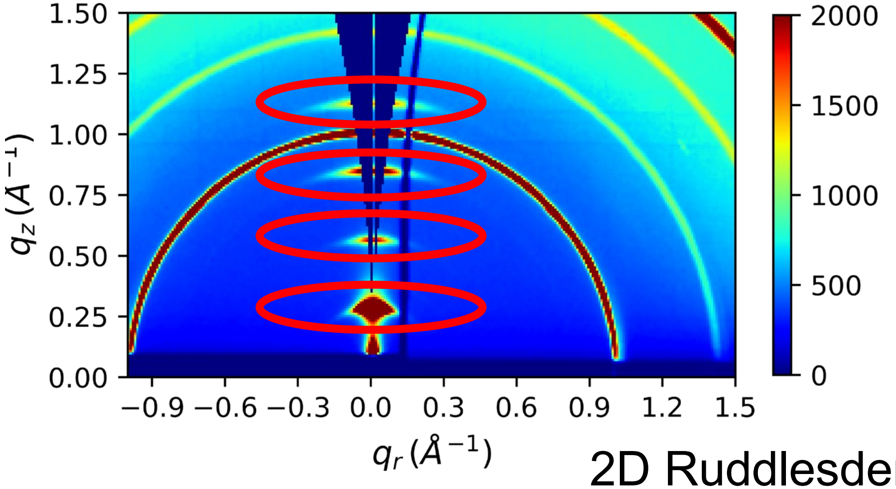
Brookhaven National Laboratory (BNL)

CsFAMA/Pb/IBr



PEAI

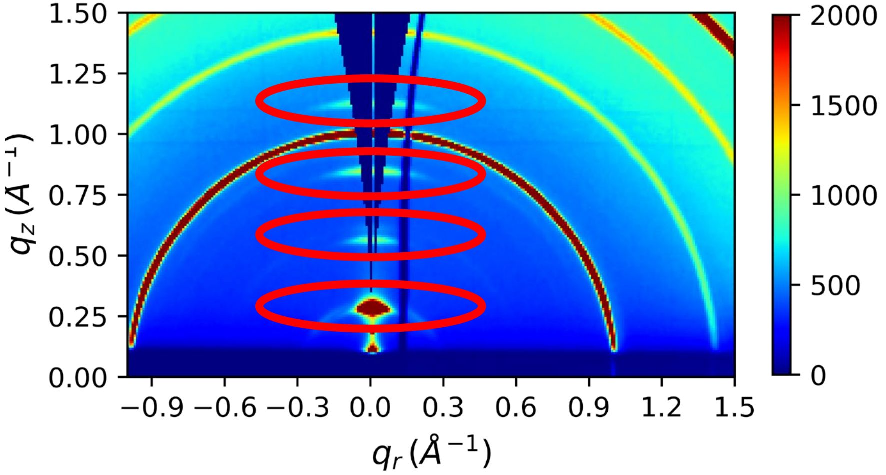
PEAI



2D features appear

2D Ruddlesden-Popper $(PEA)_2(A)_{n-1}Pb_nI_{3n+1}$ with n = 2

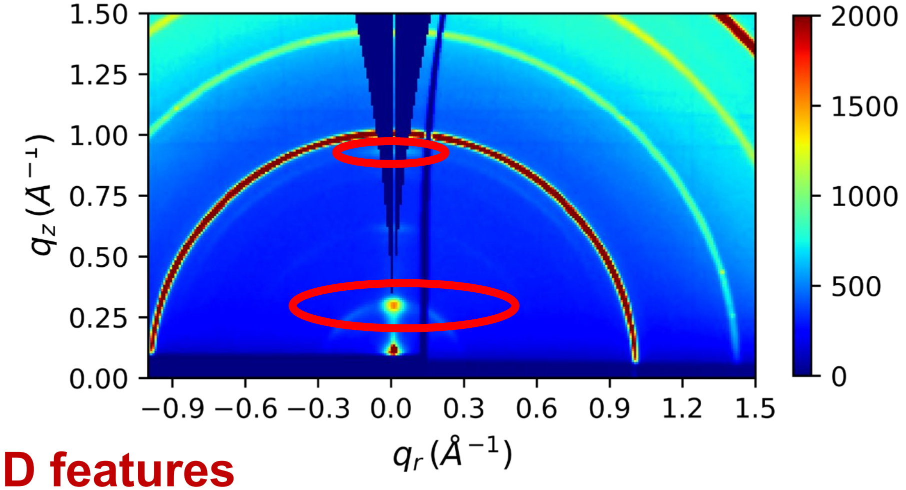
PEAI + 100 ºC for 10 min



2D features fade
Increase in q_r

2D Ruddlesden-Popper with n = 2 towards n = 1

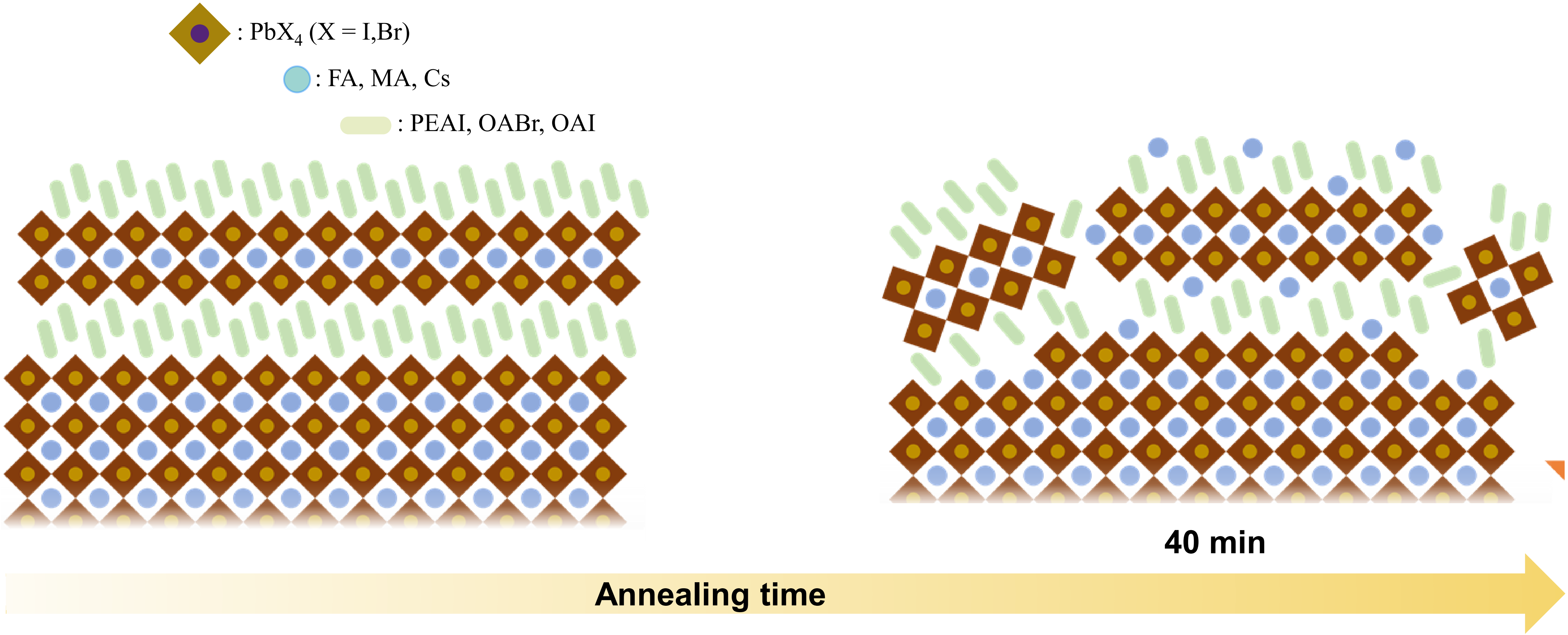
PEAI + 100 ºC for 40 min



2D features fade further

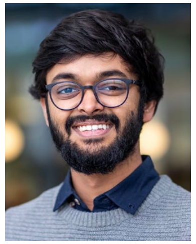
Perini, C. A. R., Correa-Baena, J.-P. et al. (2022). **Advanced Materials**. 2204726

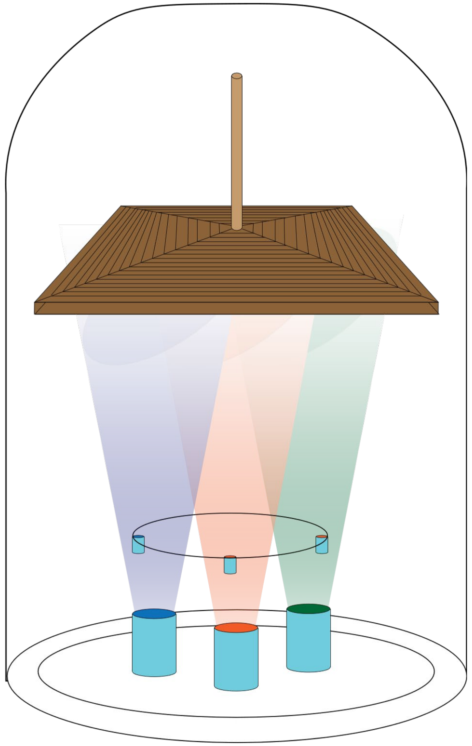
BULKY CATION PASSIVATION + DIFFUSION

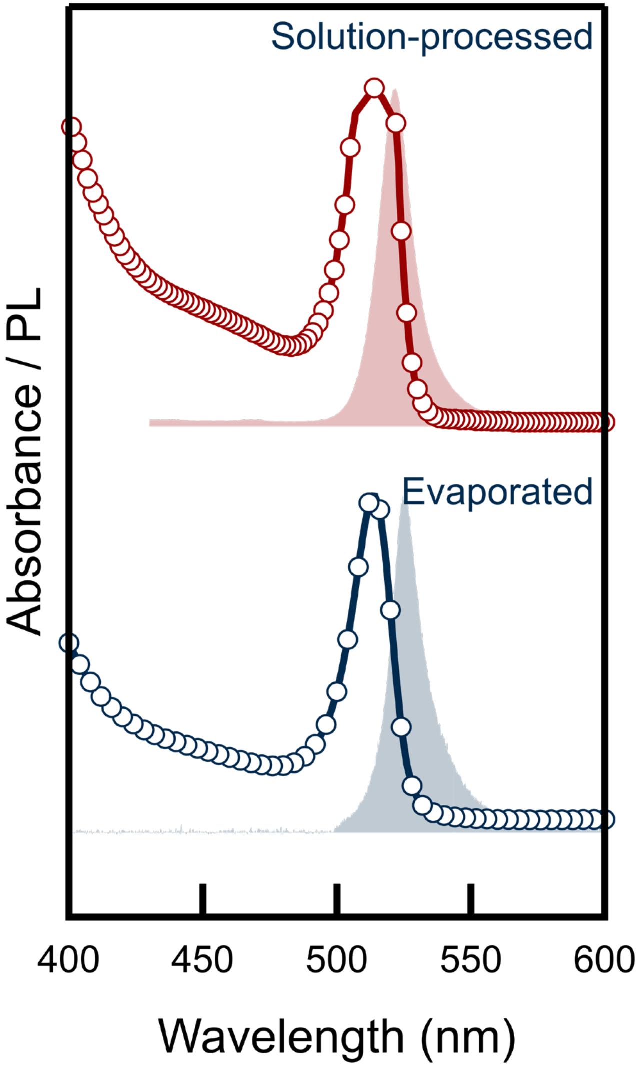


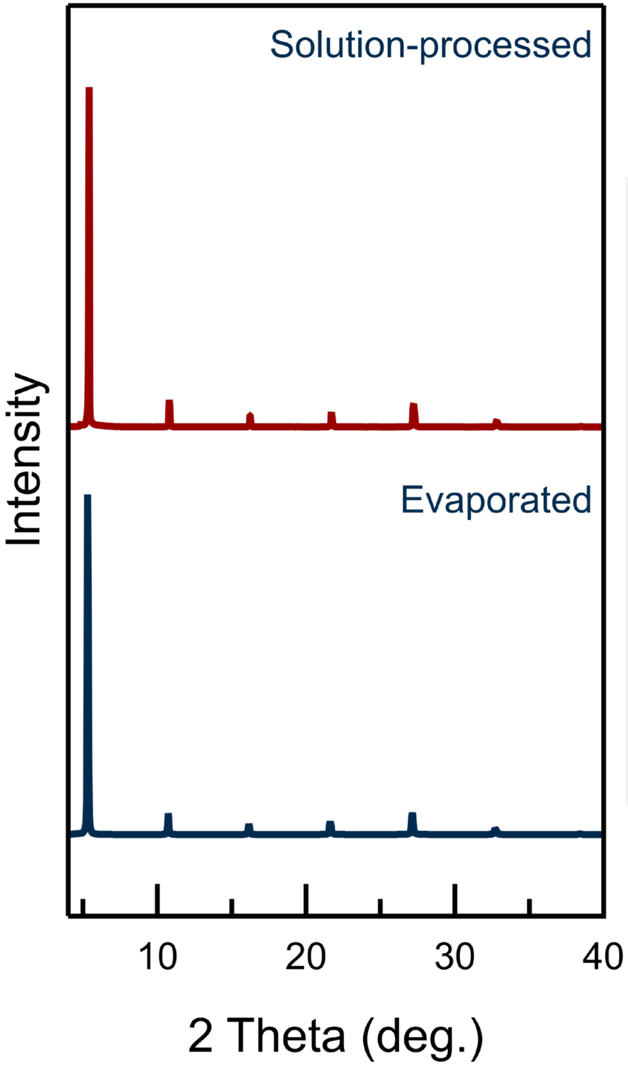
Perini, C. A. R., Correa-Baena, J.-P. et al. (2022). ***Advanced Materials***. 2204726

VAPOR PROCESSING OF A RP (2D PEROVSKITE) N=1 THIN FILM





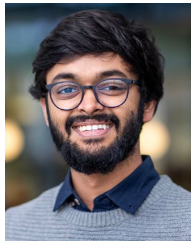


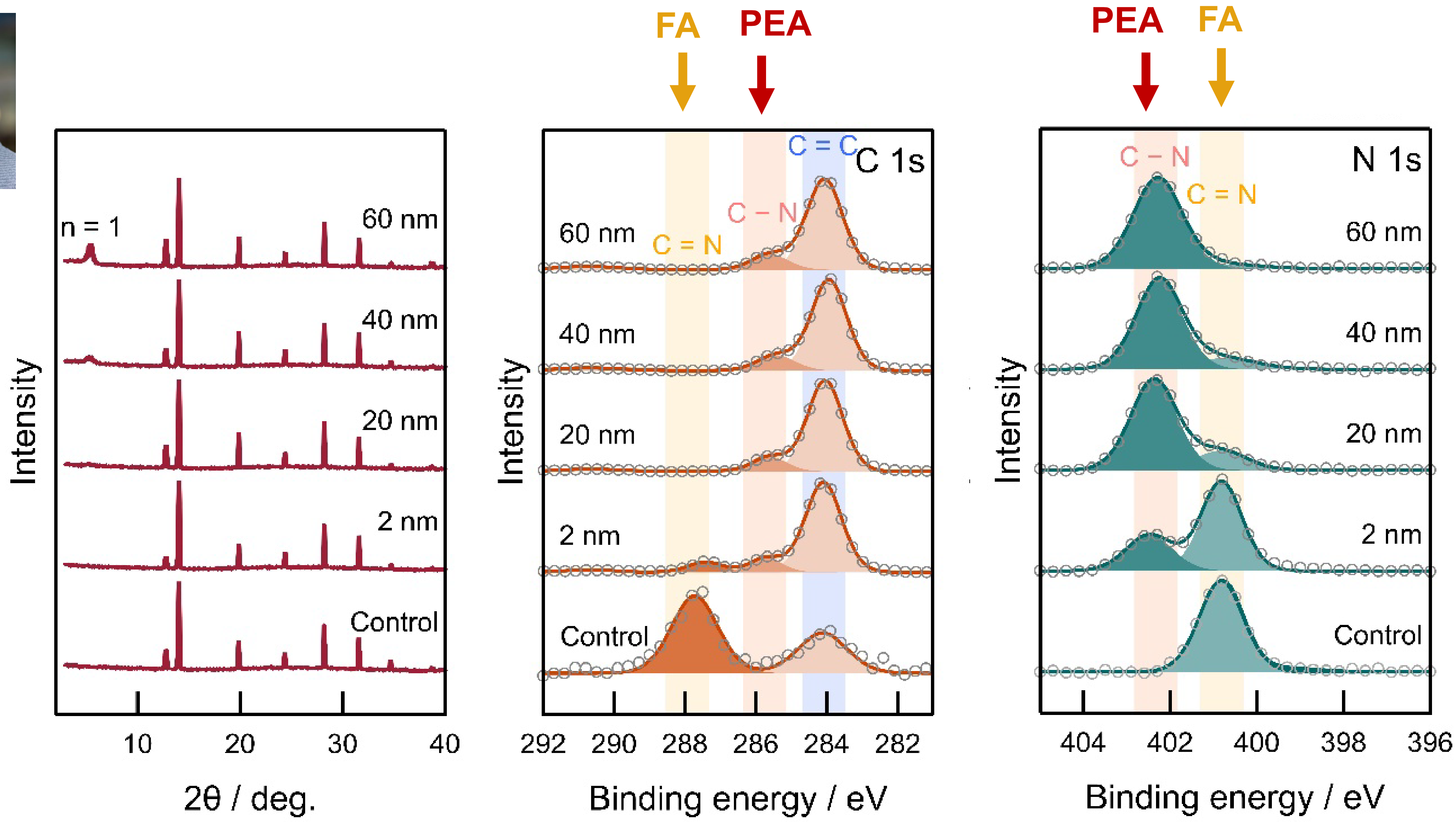


UV-vis-NIR and PL spectroscopy, and XRD show nearly identical PEA_2PbI_4 prepared using solution-processing or thermal co-evaporation

Perini, Carlo A. R., Correa-Baena, J.-P. et al. (2023). ***ACS Energy Letters,*** 2023, 8, 3, 1408−1415.
Datta, Kunal, Correa-Baena, J.-P. et al. (2024). ***Advanced Materials***. 36 (35), 2404795.

VAPOR PROCESSING OF A 2D/3D HETEROSTRUCTURE





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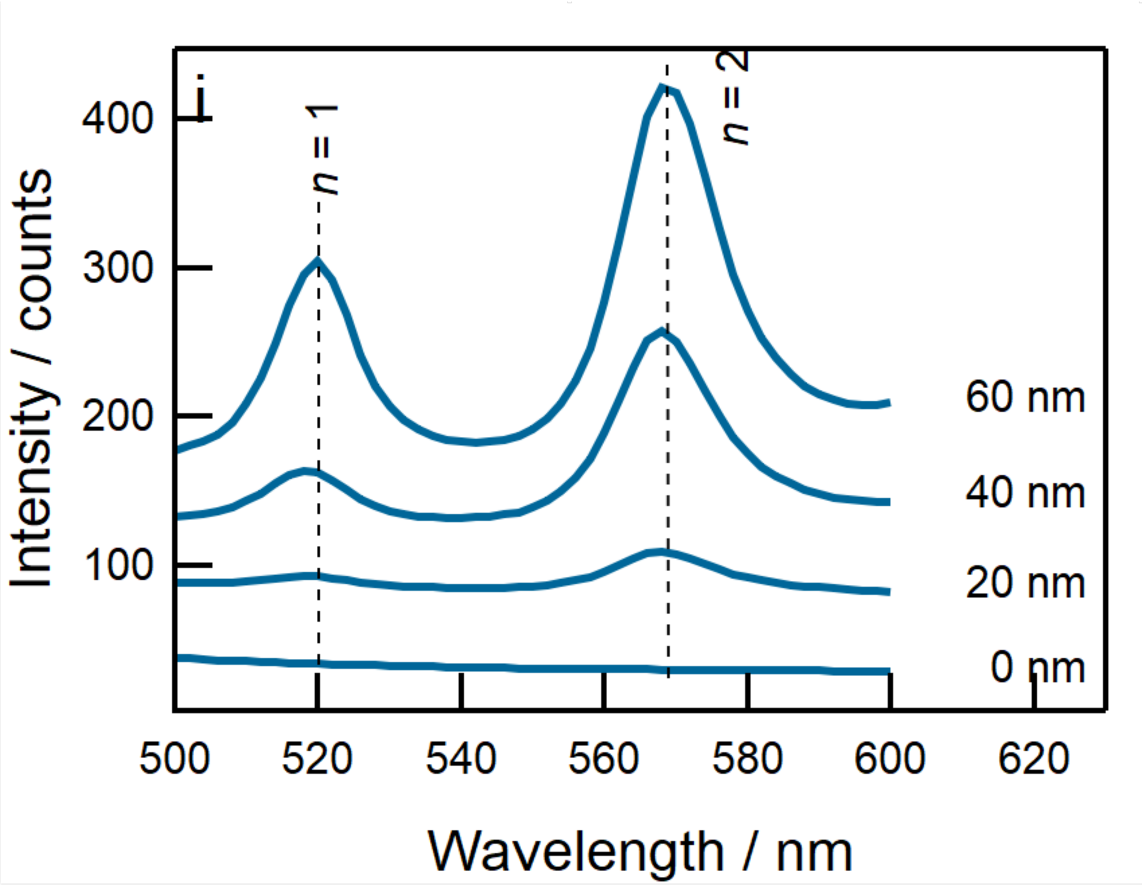
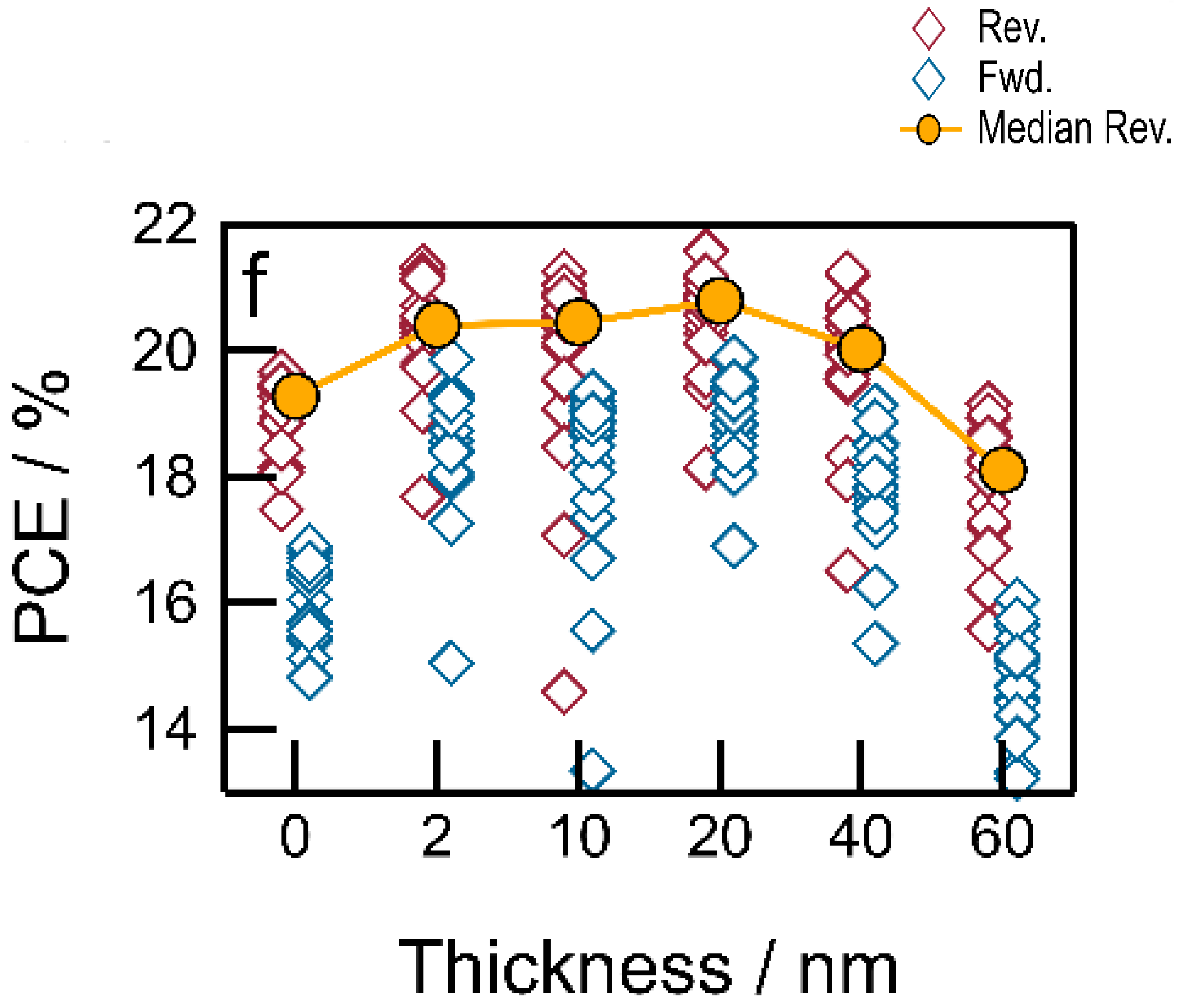
VAPOR PROCESSING OF A 2D/3D HETEROSTRUCTURE





Perini, Carlo A. R., Correa-Baena, J.-P. et al. (2023). ***ACS Energy Letters,*** 2023, 8, 3, 1408−1415 .
Datta, Kunal, Correa-Baena, J.-P. et al. (2024). ***Advanced Materials***. 36 (35), 2404795.

QUESTIONS

1. What structures form at the surface of the perovskite thin film?

2. How stable is this interface given its "soft" nature?

3. What is the mechanism by which surface passivation happens?

OUTLINE

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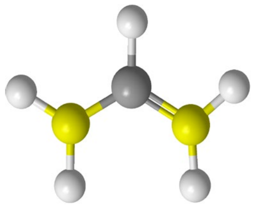
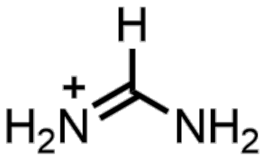
FORMAMIDINIUM LEAD HALIDE PEROVSKITES

FA





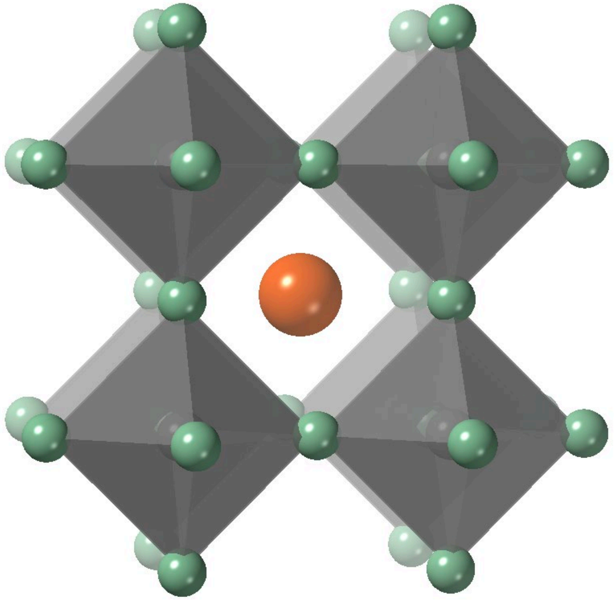
$FAPbI_3$

Ideal bandgap for solar cells 1.48 eV

Eperon, et al. *Energy Environm. Sci.* ***2014****, 7, 982*

Perovskite

corner-sharing



ABX_3

single or mixed ion

- **A** **FA^+** / MA^+ / Cs^+
- **X** I^- / Br^-
- **B** Pb^{2+}

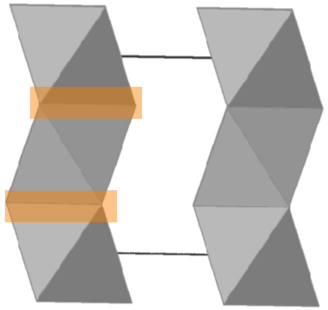
THE PEROVSKITE STRUCTURE IS UNSTABLE

Polymorphism into non-perovskite phases

$FAPbI_3$

2H

$P6_3/mmc$

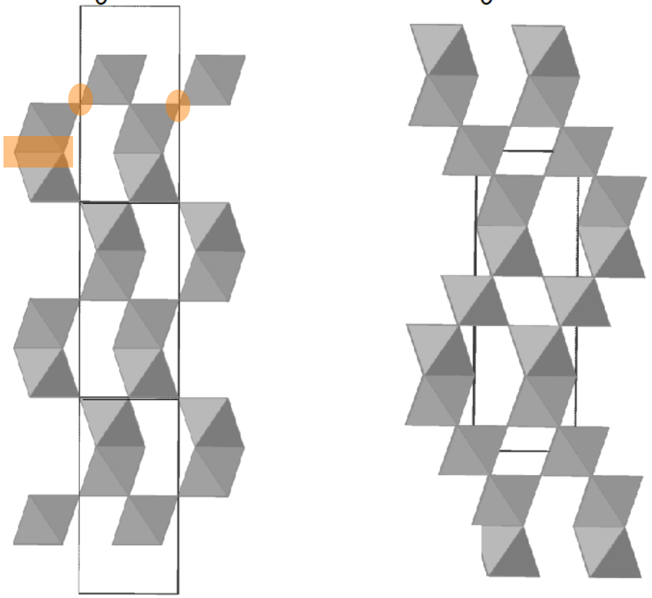


face-sharing

Charles, *et al. Chem. Mater.* ***2020***, *32, 2282-2291.*

Hexagonal polytypes H: $APbX_3$

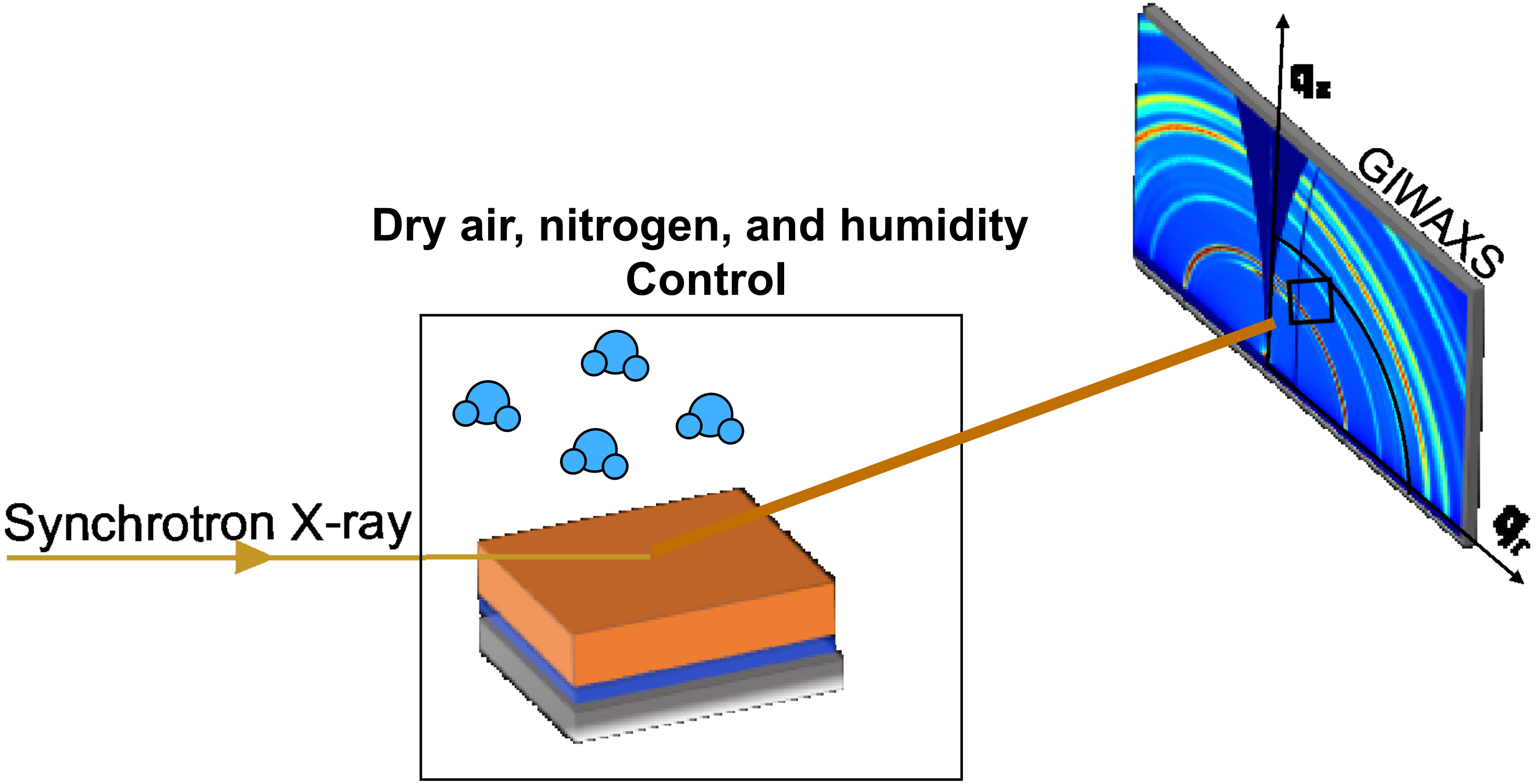
4H | 6H
$P6_3/mmc$ | $P6_3/mmc$



corner- and face-sharing

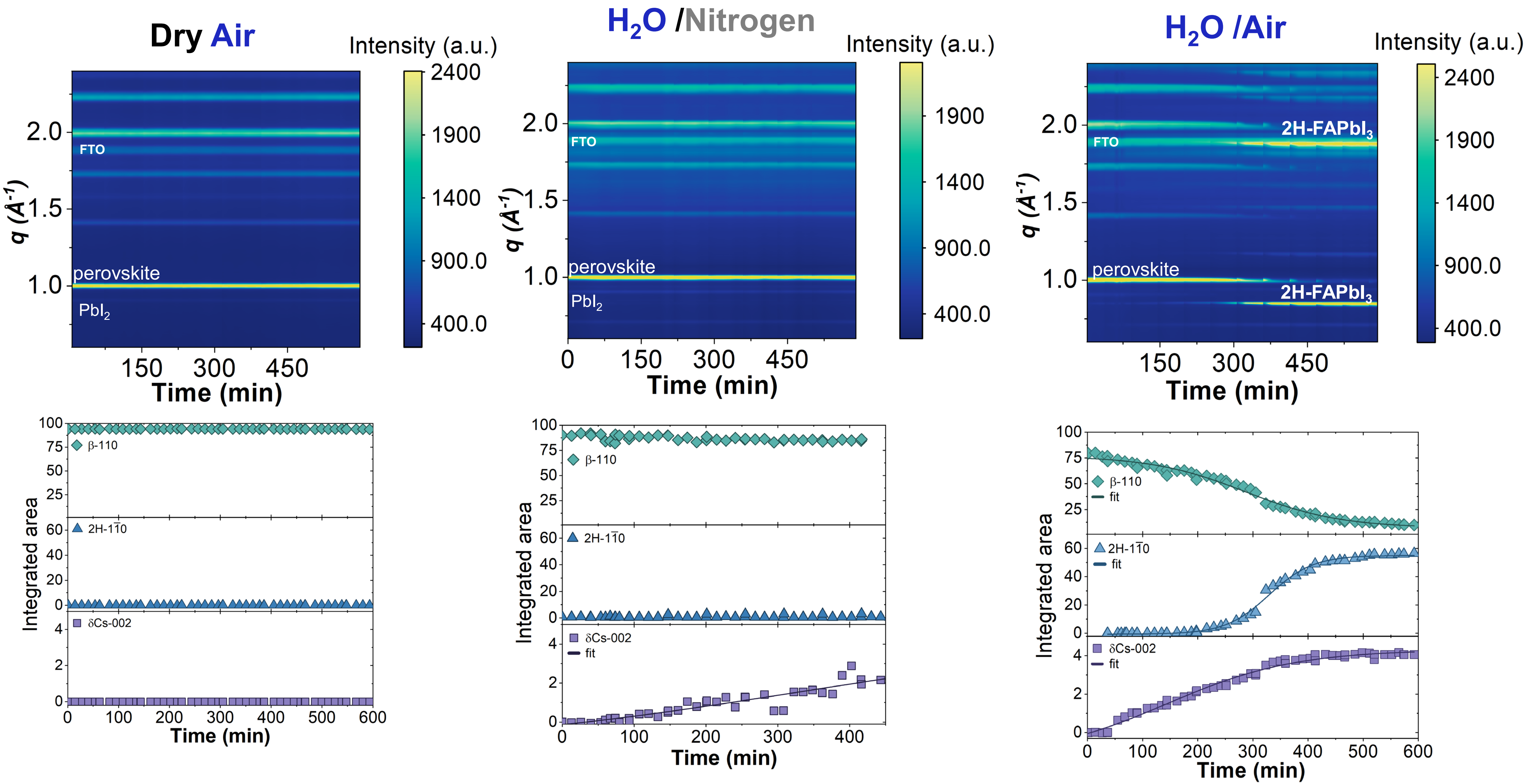
Gratia, et al. *ACS Energy Lett.* ***2017***, *2, 12, 2686-2693*

IN-SITU GIWAXS: UNDERSTANDING PHASE TRANSFORMATIONS UNDER DIFFERENT ENVIRONMENTS



Hidalgo, J., …, Correa-Baena, J. P. **Materials Today**, 2023, 68, 13–21

Hidalgo,…Correa-Baena. **J. Am. Chem. Soc**. 2023, 145, 45, 24549–24557



Hidalgo, J., …, Correa-Baena, J. P. **Materials Today**, 2023, 68, 13–21

Hidalgo,…Correa-Baena. **J. Am. Chem. Soc**. 2023, 145, 45, 24549–24557

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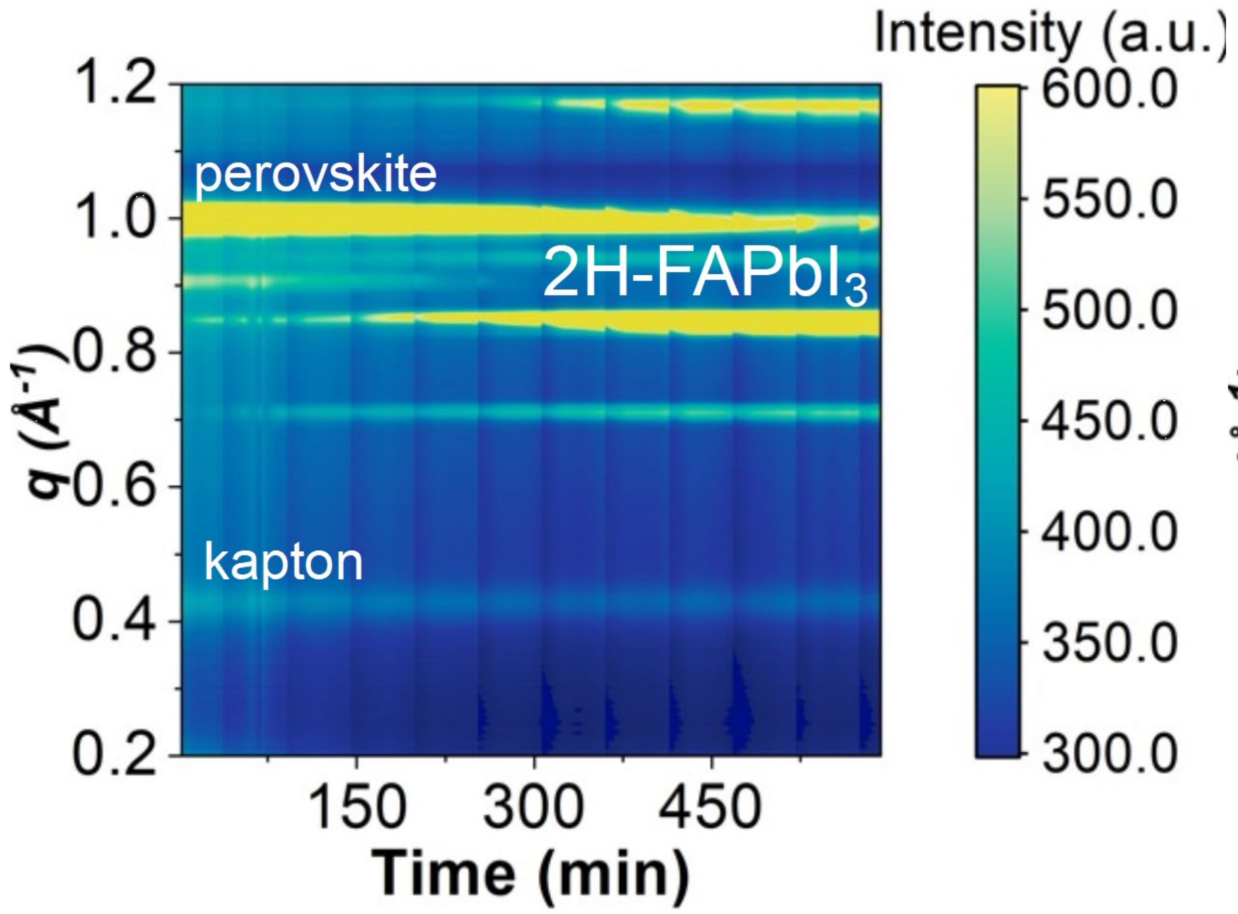
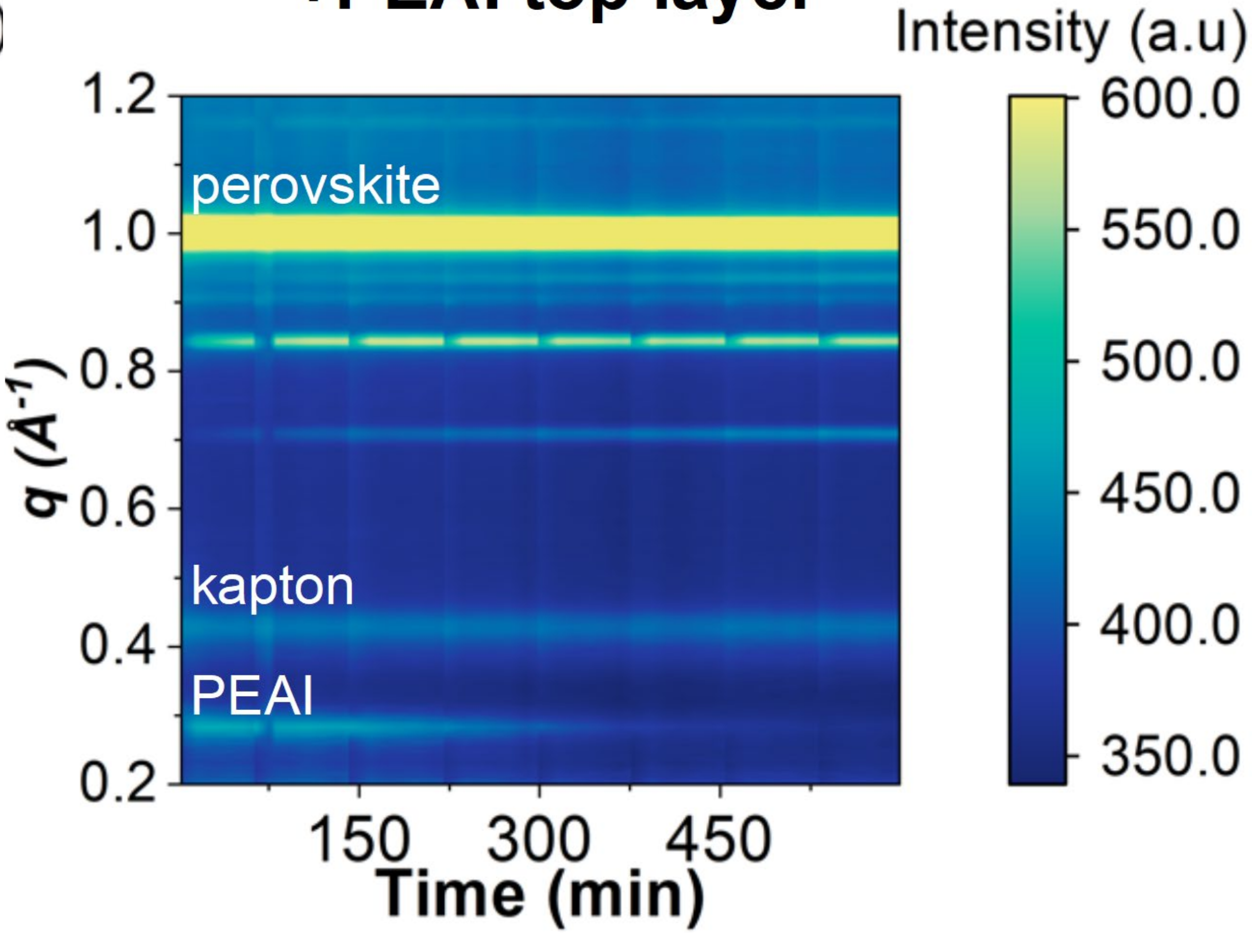
IN-SITU GIWAXS STUDIES CORROBORATE THIS

H_2O /Air



+PEAI top layer

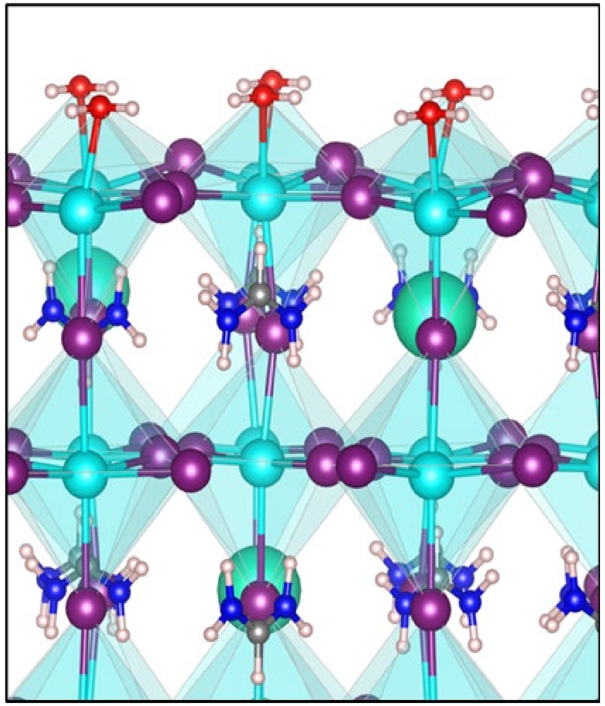


Hidalgo, J., …, Correa-Baena, J. P. ***Materials Today****, 2023, 68, 13–21*

Hidalgo,…Correa-Baena. ***J. Am. Chem. Soc****. 2023, 145, 45, 24549–24557*

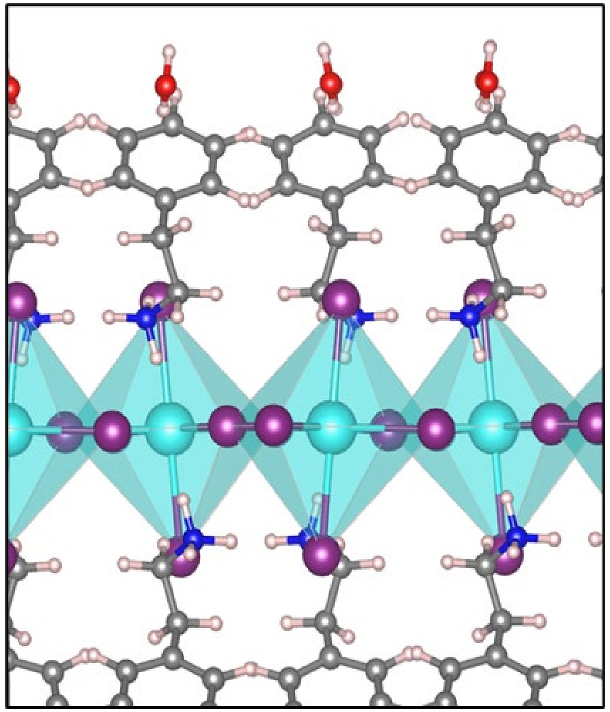
PEAI REPELS WATER

H_2O Adsorption



$E_{ads} = -0.50$ eV

PEA



$E_{ads} = -0.19$ eV

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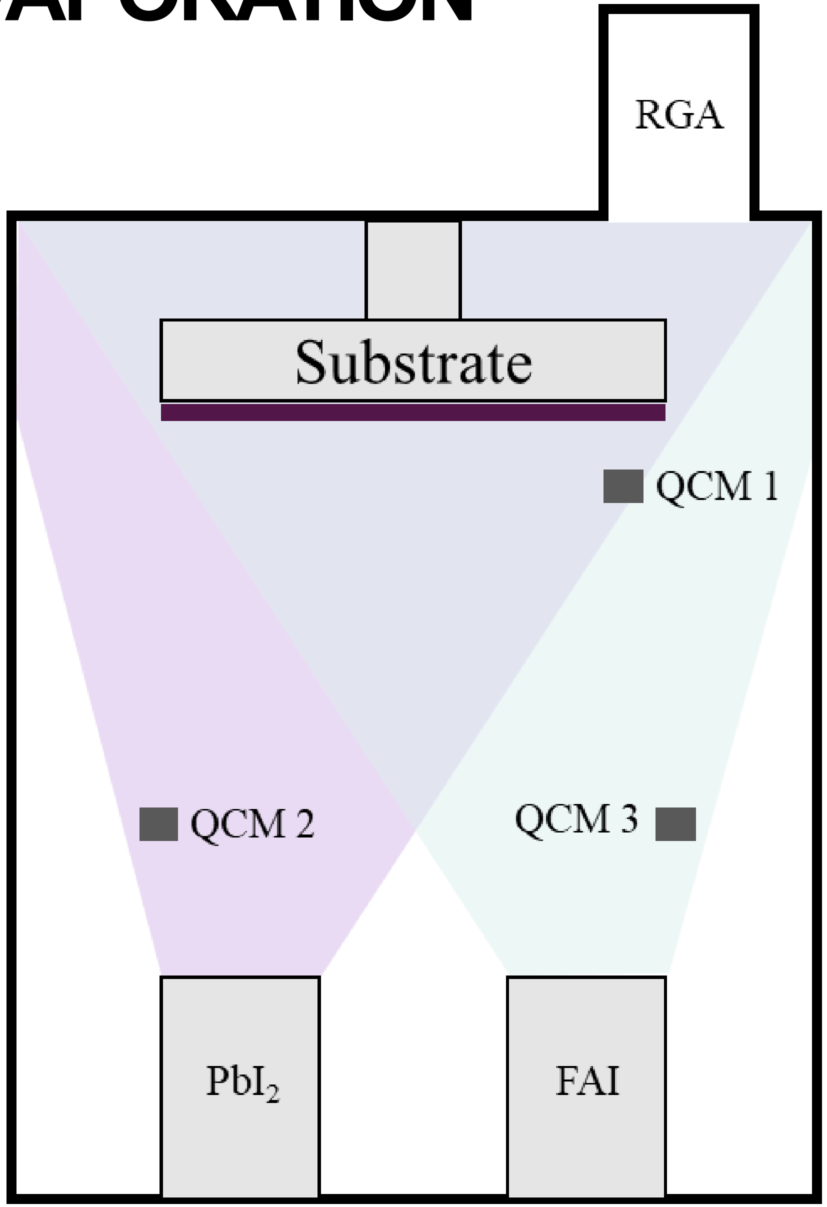
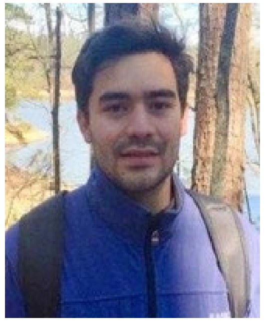
PHASE TRANSFORMATIONS FROM THE VAPOR PHASE:

WHAT HAVE WE LEARNED FROM THE INTERFACE AND ITS EFFECT ON PHASE TRANSFORMATIONS?

CONTROL OF PHASE PURITY FOR FAPI BY THERMAL EVAPORATION

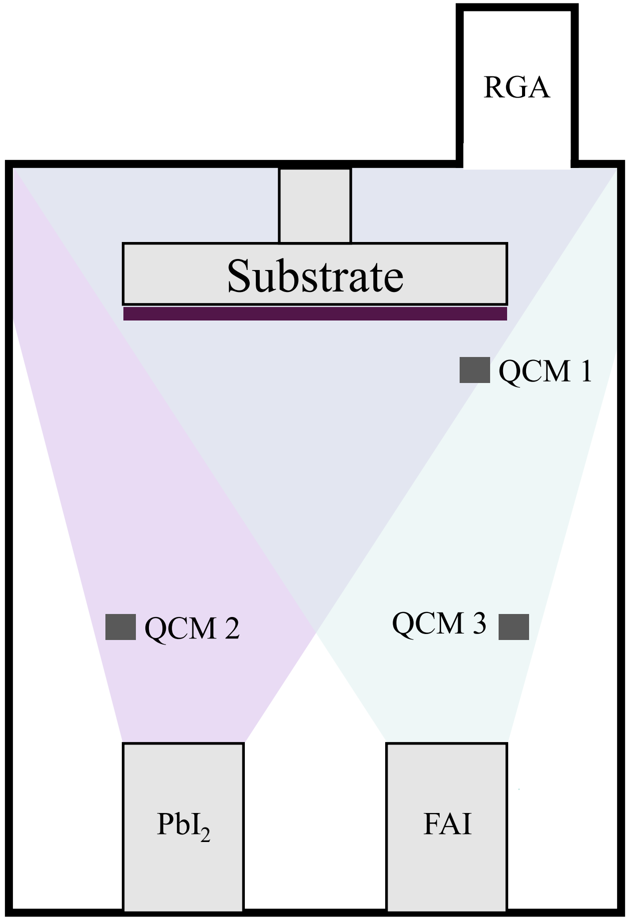


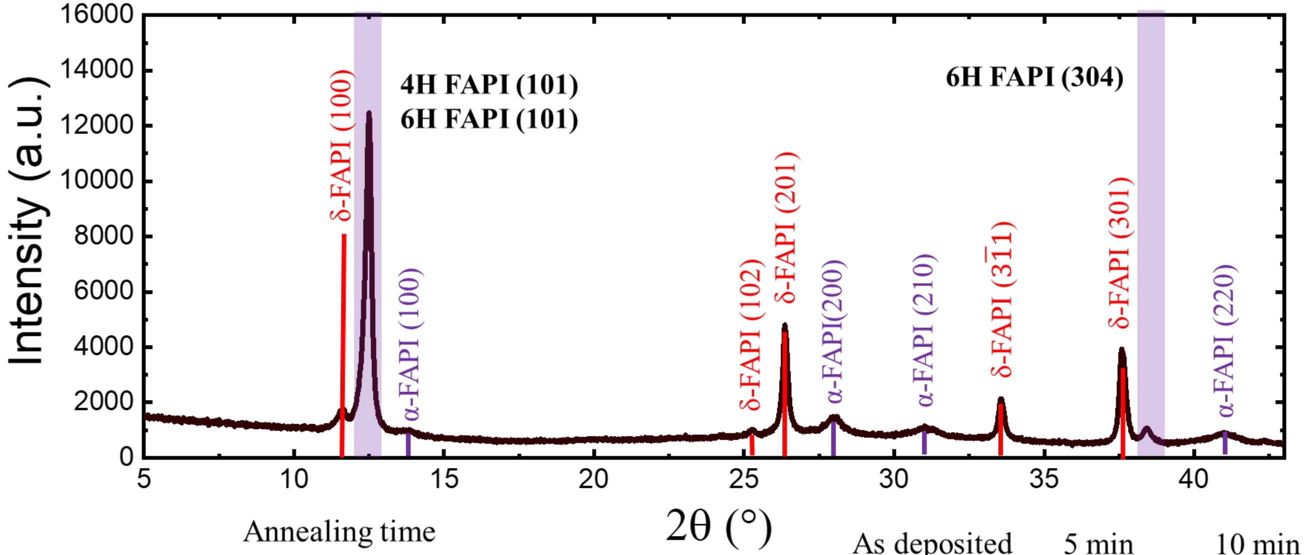
Andres-Felipe
Castro-Mendez

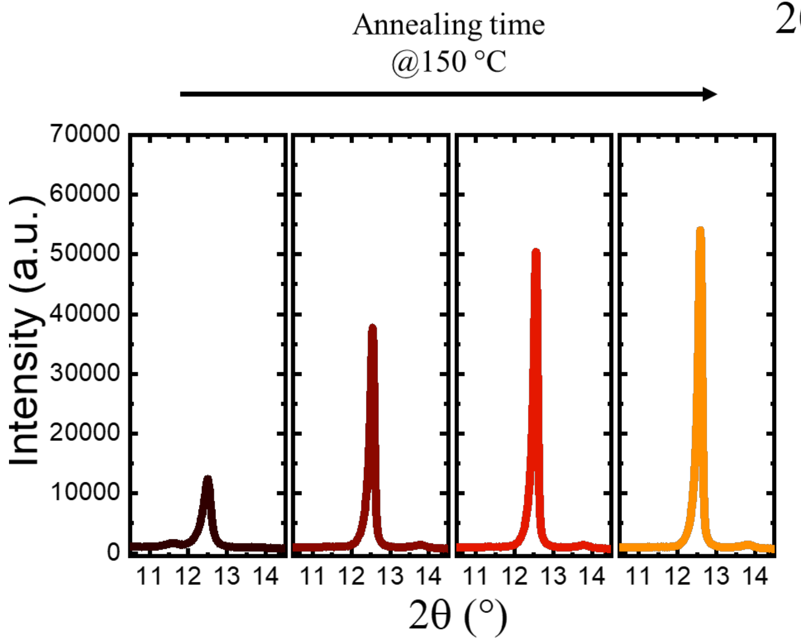


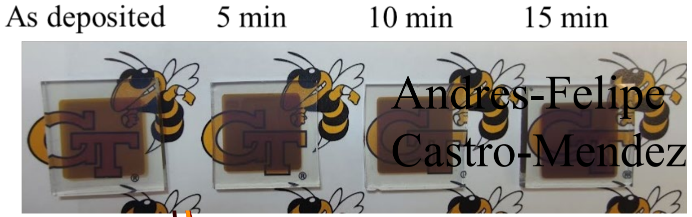
Castro-Méndez, A. F., …, Correa-Baena, J. P. (2022). ***ACS Applied Materials and Interfaces*** **2022**, 14, 30, 34269–34280.

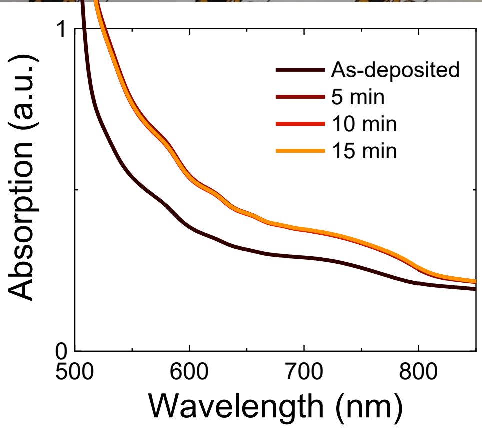
EVAPORATION OF FAPBI3 LEADS TO HEXAGONAL PHASES DIFFICULT TO CONVERT TO CUBIC





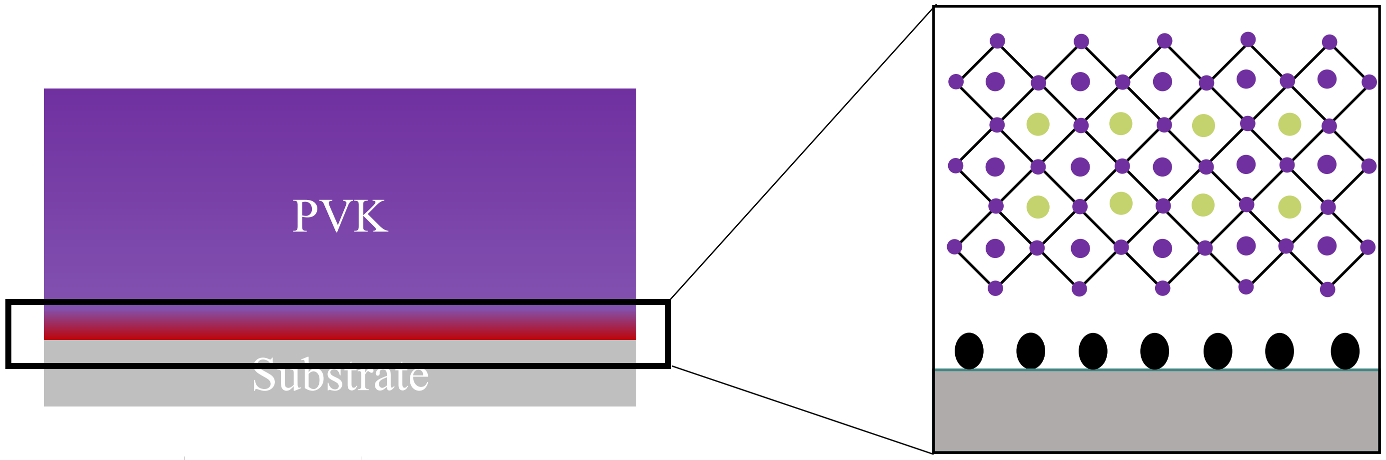


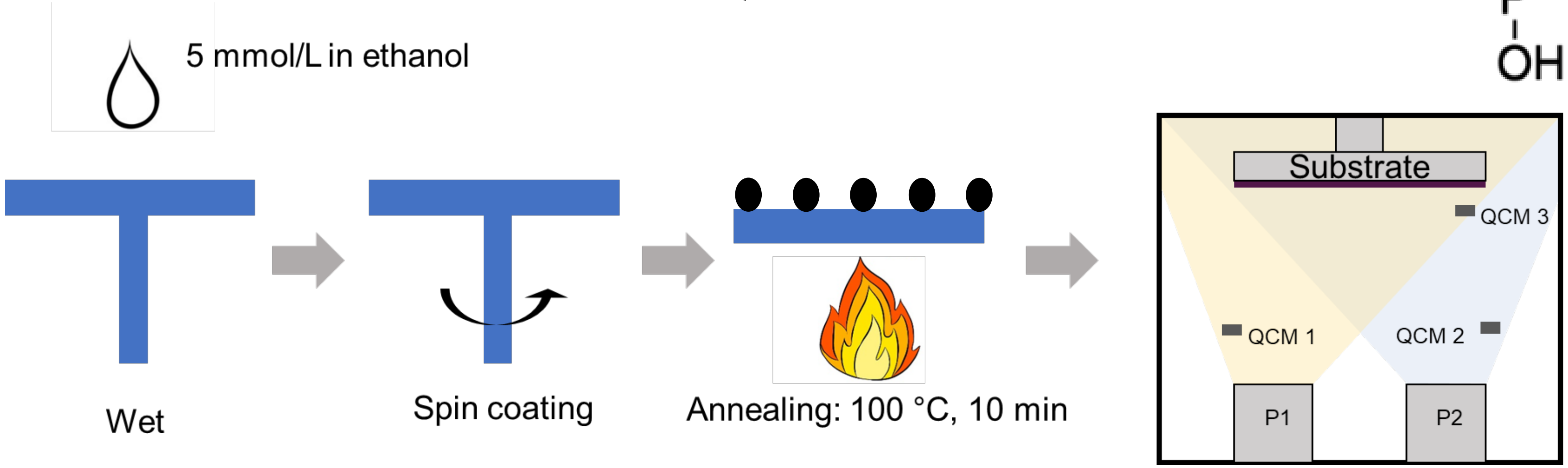




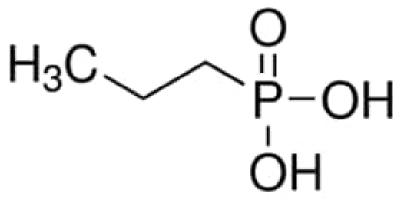
Castro-Méndez, A. F., …, Correa-Baena, J. P. (2024). ***JACS.*** 146 (27), 18459-18469

TEMPLATING THE GROWTH OF FAPI PEROVSKITES VIA PHOSPHONIC ACIDS

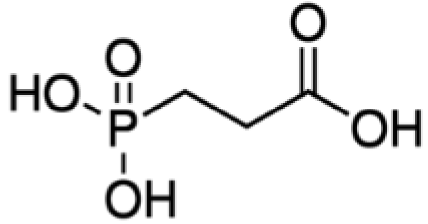




Propyl phosphonic acid (PPAc)



3-phosphonopropionic acid (3PPAc)

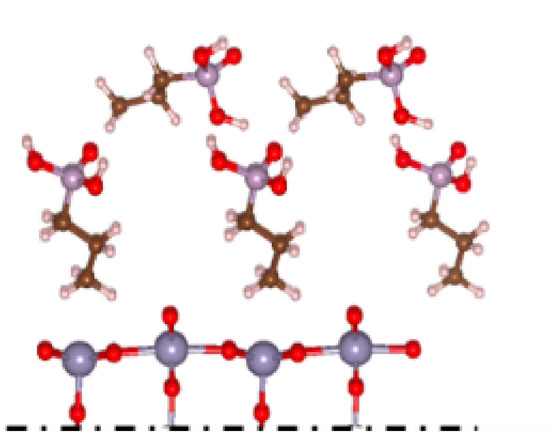


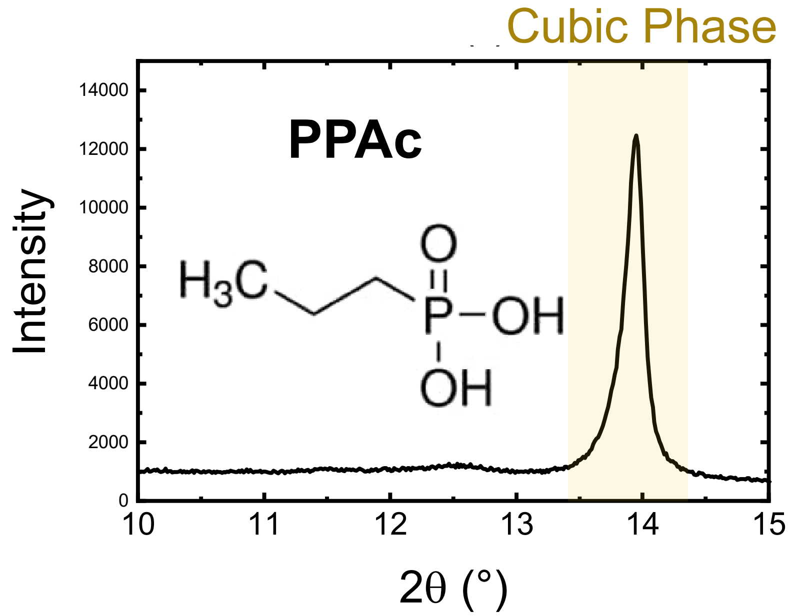
Castro-Méndez, A. F., …, Correa-Baena, J. P. (2024). ***JACS.*** 146 (27), 18459-18469.

PPA HELPS FORM CUBIC PEROVSKITE

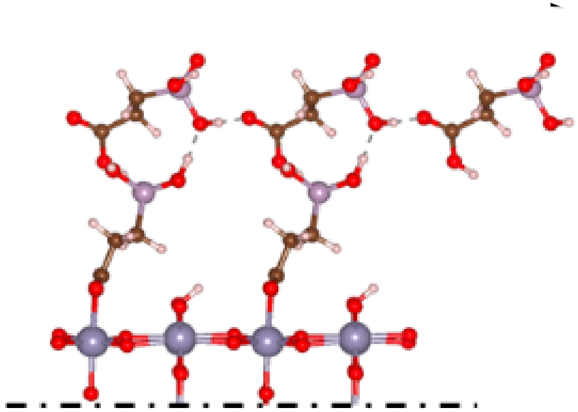
In collaboration with
Prof. Andrew Rappe at **U Penn**

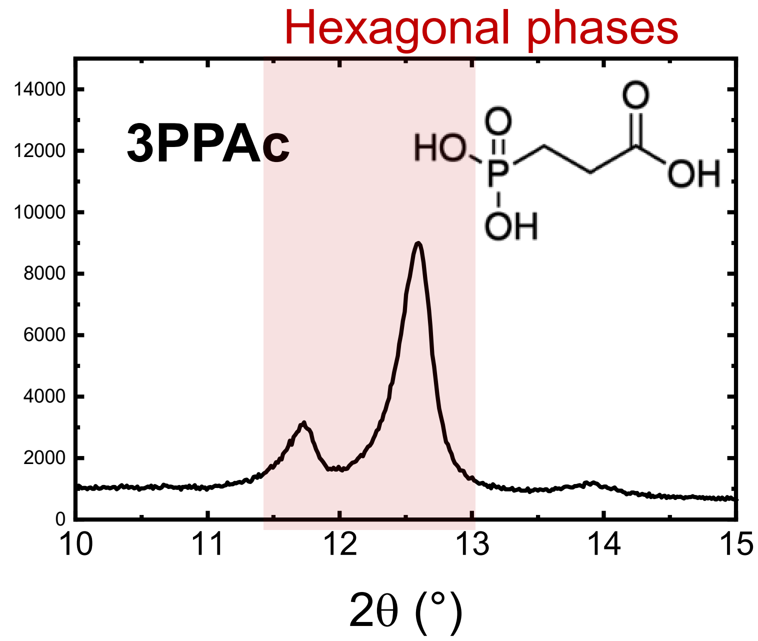
CH_3-PA-CH_3-PA





COOH-PA-COOH-PA

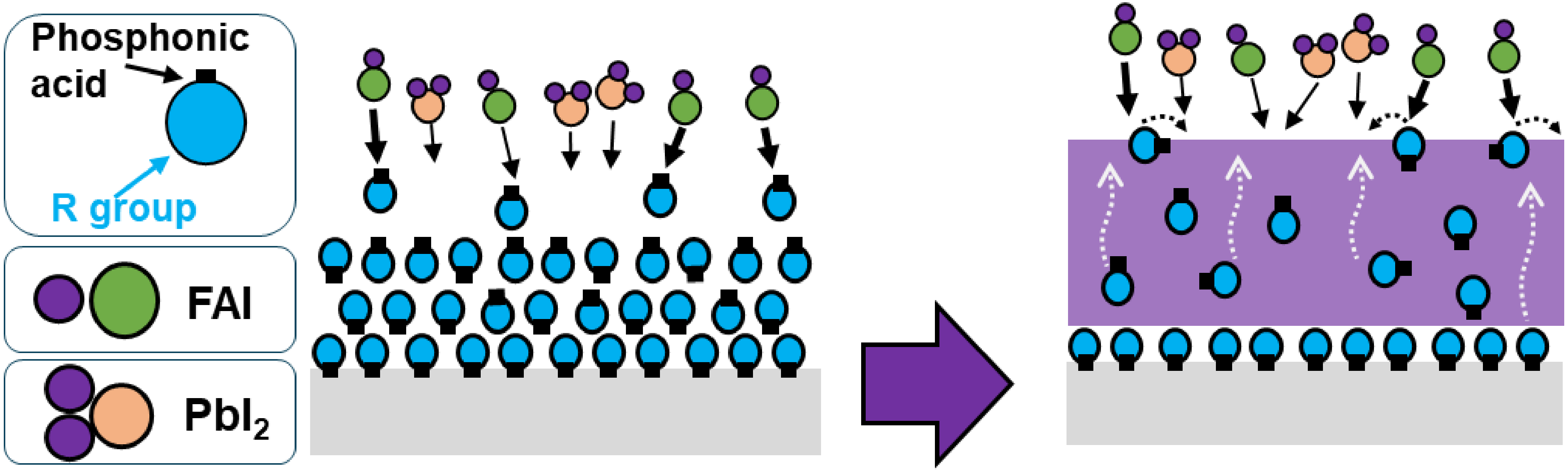




3PPAc has stronger binding energy than PPAc

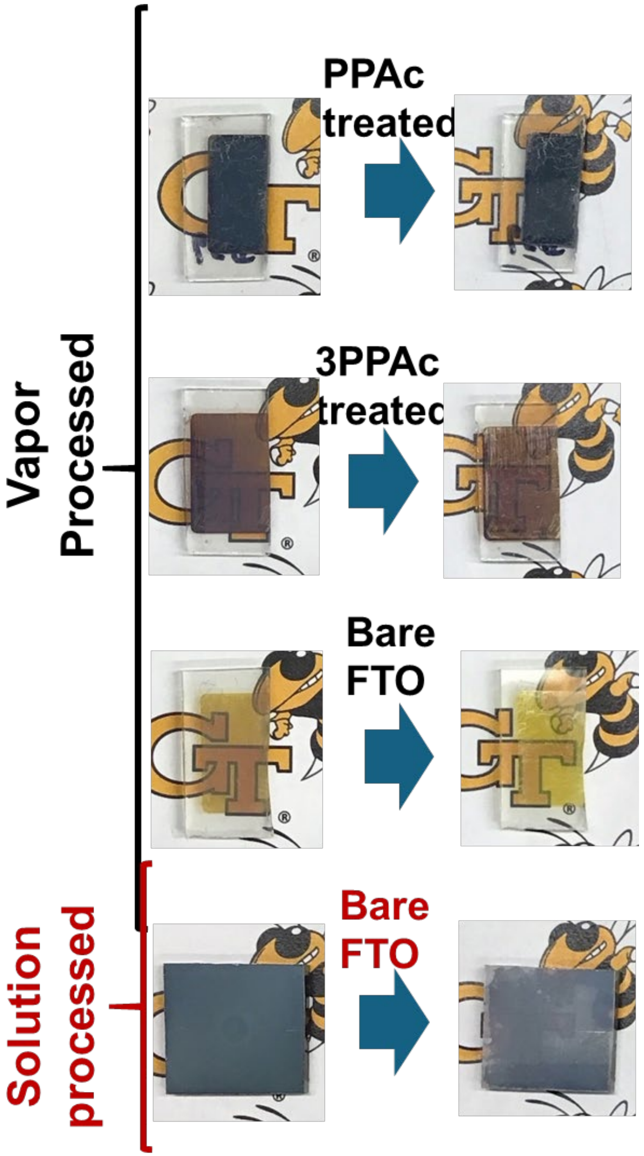
Castro-Méndez, A. F., …, Correa-Baena, J. P. (2024). ***JACS.*** 146 (27), 18459-18469

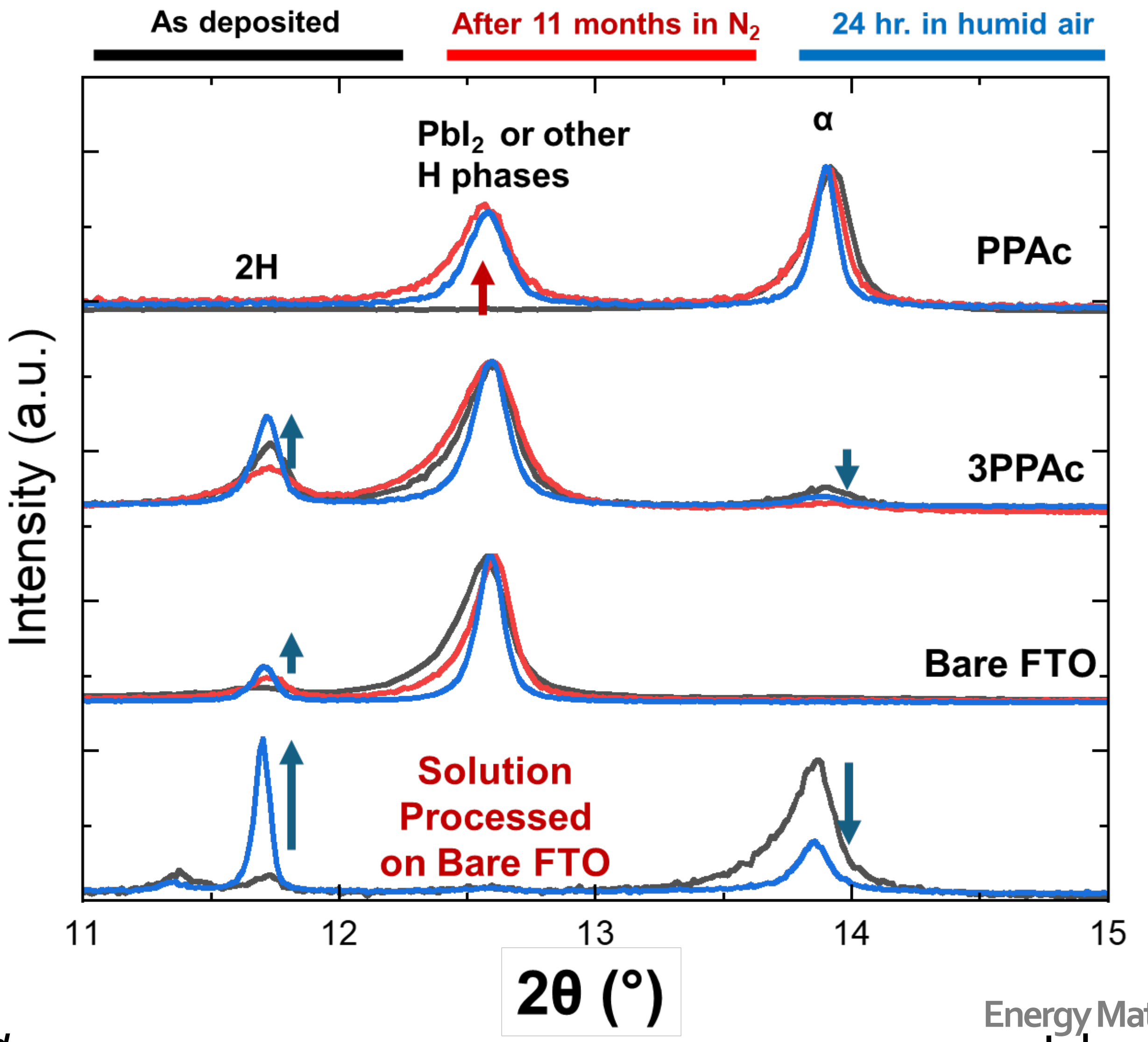
PROPOSED MECHANISM:



- PHOSPHONIC ACIDS HELP TRAP FAI TO FORM CUBIC PEROVSKITES
- LOW BINDING ENERGY BETWEEN PHOSPHONIC ACID MOLECULES MAY LEAD TO THEIR MIGRATION DURING EVAPORATION

STABILITY OF FAPI BY EVAPORATION IN HUMID AIR





Castro-Méndez, A. F., …, Correa-Baena, J. P. (2024). ***JACS.* Accepted**

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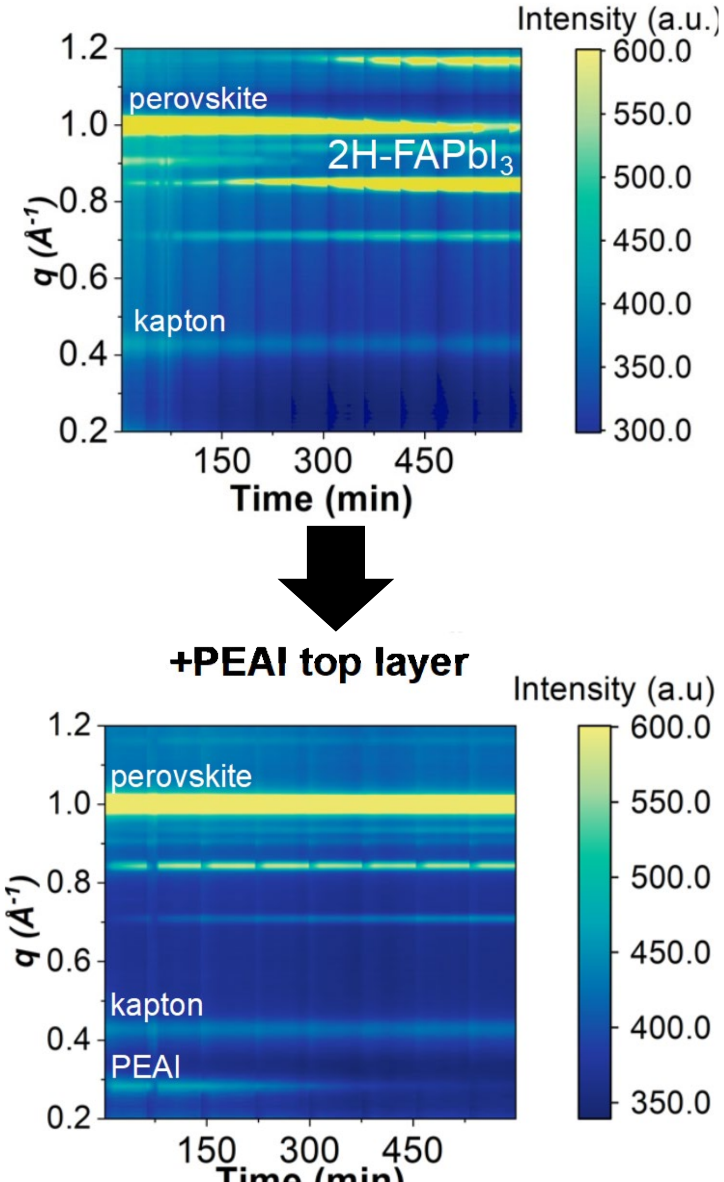
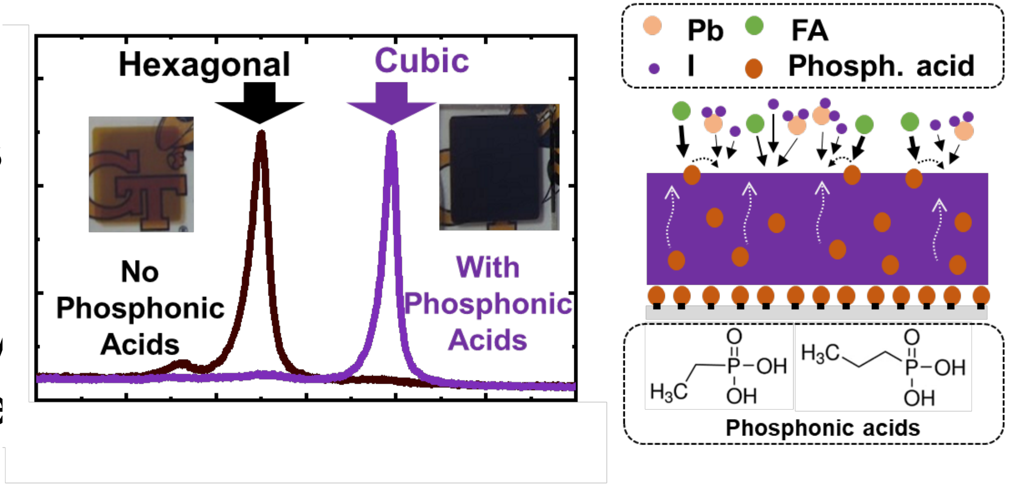
CONCLUSIONS: INTERFACES ENABLE PHASE STABILIZATION



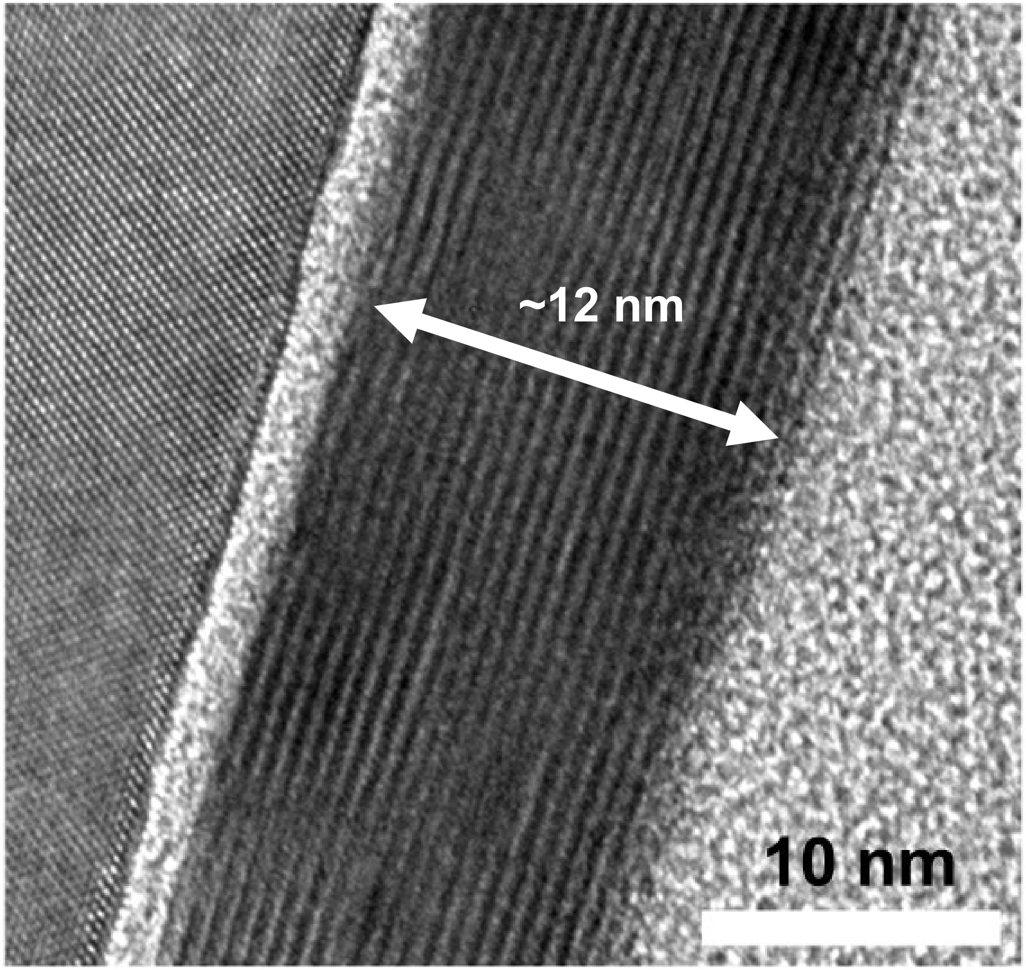
- Surface protection leads to preventing phase transformation
- Surface passivation may be overshadowed by the physical barrier from PEAI
- Hydrophobicity of PEAI may be the most important parameter to improve optoelectronic properties of the underlying perovskite



- The cubic phase only forms in the presence of excess phosphonic acids
- PAs lead to the adsorption of FA and thus the formation of a perovskite

BONUS!!
ALD/CVD OF LEAD HALIDES

75°C – 10 cycles



Vagott, J. N., …, Correa-Baena, J. P. (2022). ***Chemistry of Materials***, *34*(6), 2553–2561.

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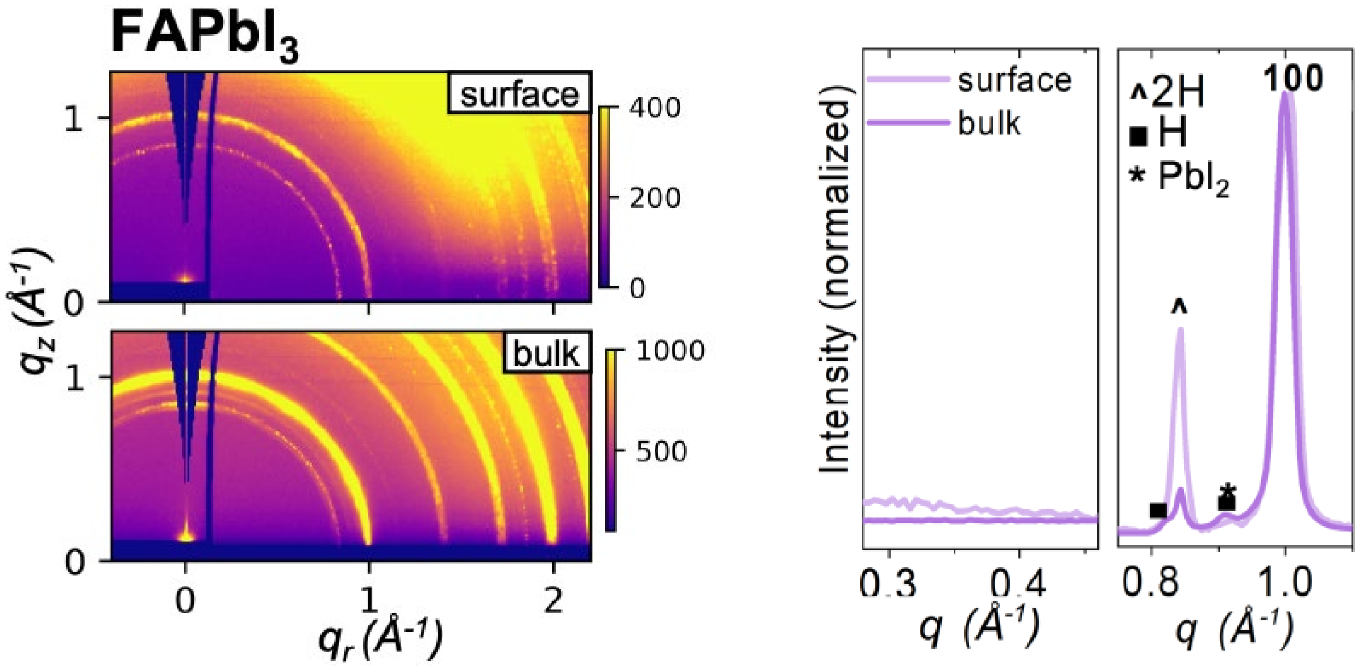
THANK YOU

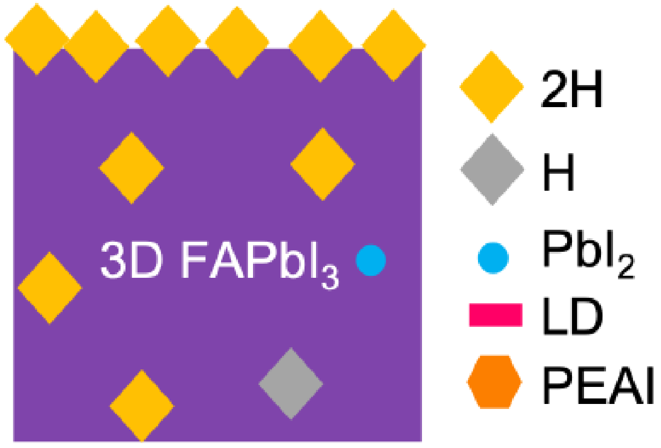
jpcorrea@gatech.edu

Baena.gatech.edu

@jpcorreabaena @baenalabs

INCREASED HEXAGONAL PHASES AT THE SURFACE

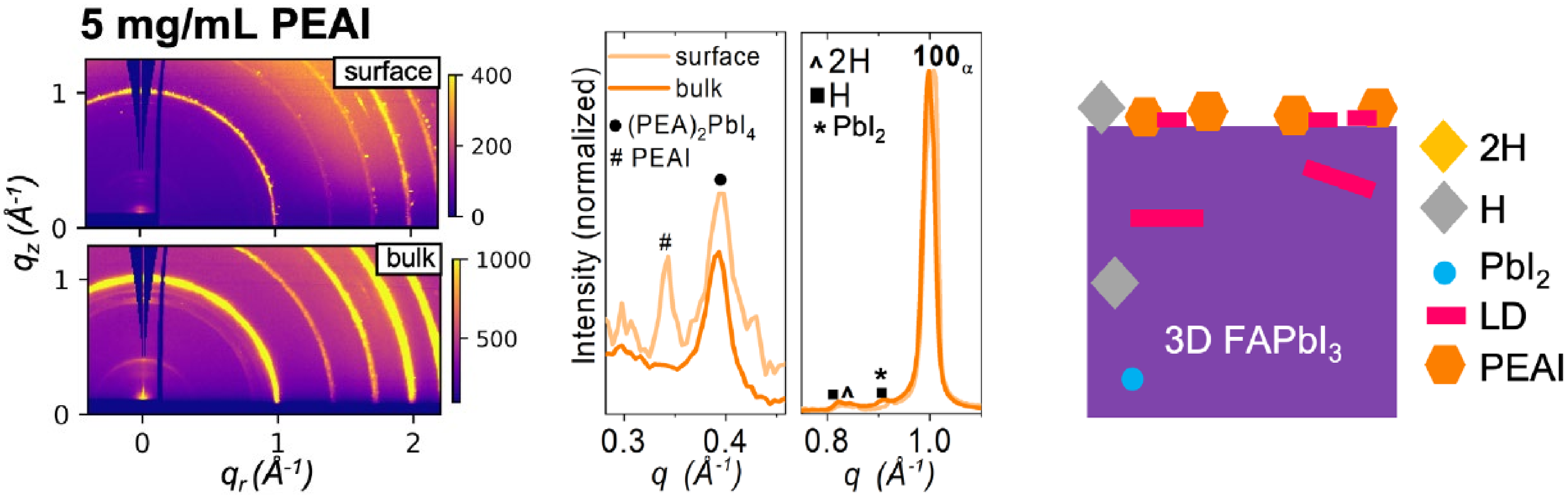




Hidalgo, J., …, Correa-Baena, J. P. ***Materials Today****, 2023, 68, 13–21*

Hidalgo,…Correa-Baena. ***J. Am. Chem. Soc****. 2023, 145, 45, 24549–24557*

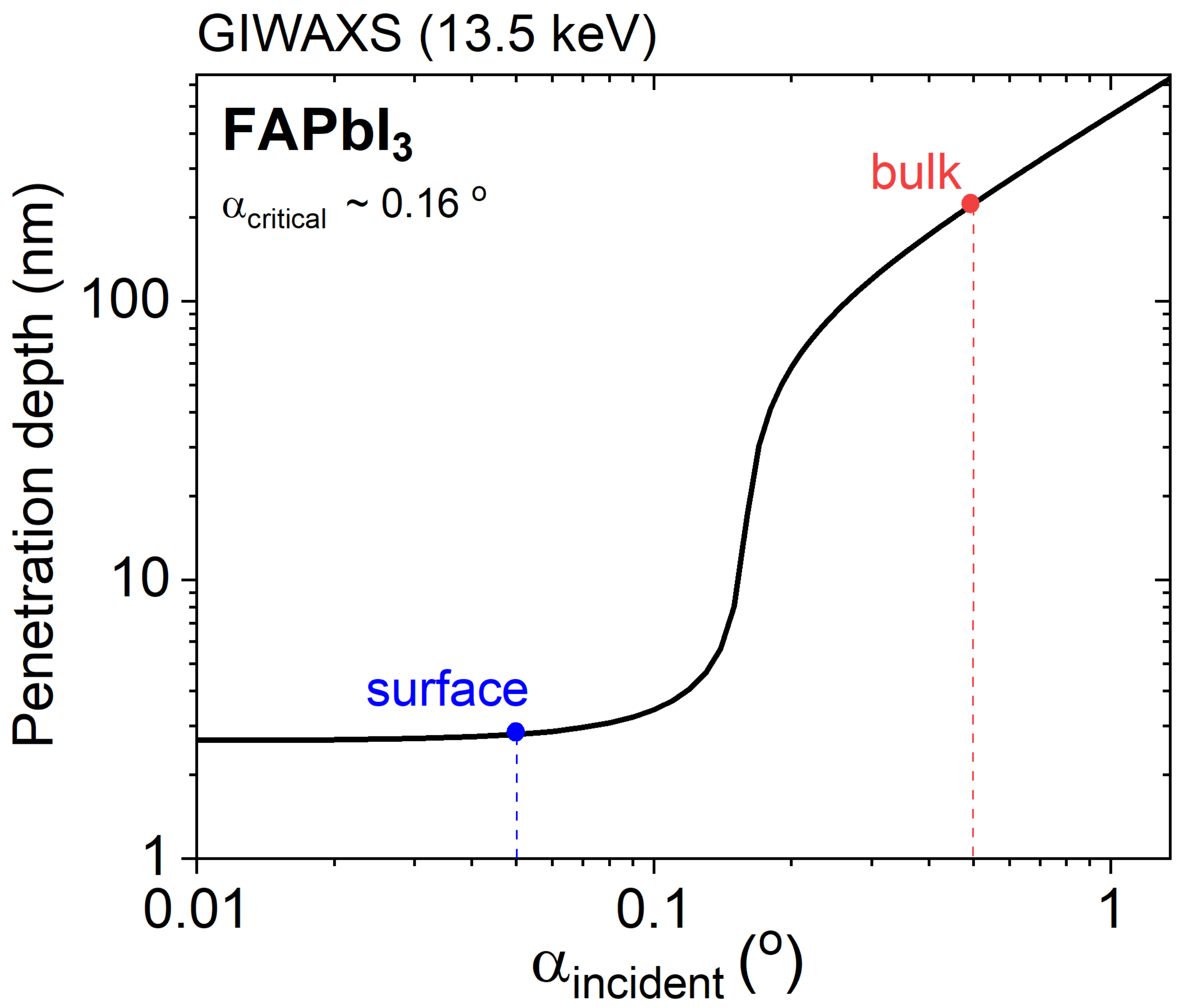
TOP LAYER OF PEAI REDUCES NON-PEROVSKITE PHASES



Hidalgo,…Correa-Baena. ***J. Am. Chem. Soc****. 2023, 145, 45, 24549–24557*

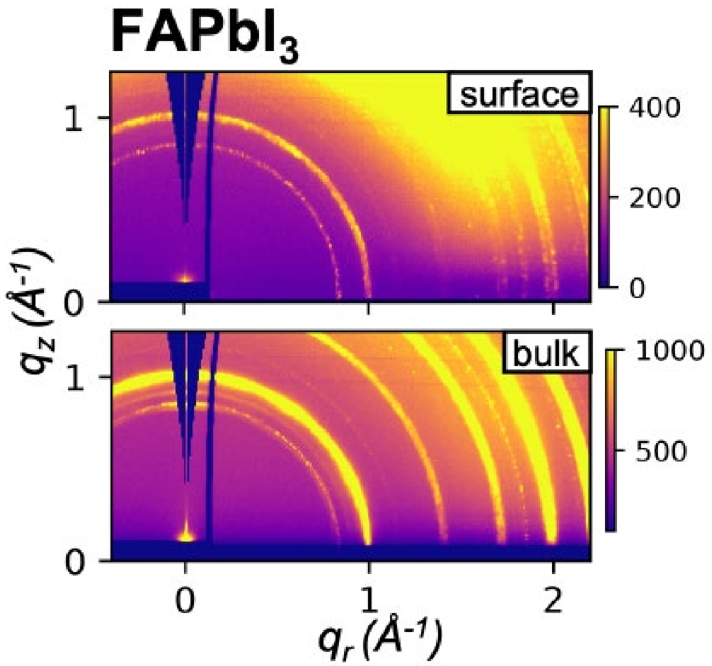
Hidalgo, J., …, Correa-Baena, J. P. ***Materials Today****, 2023, 68, 13–21*

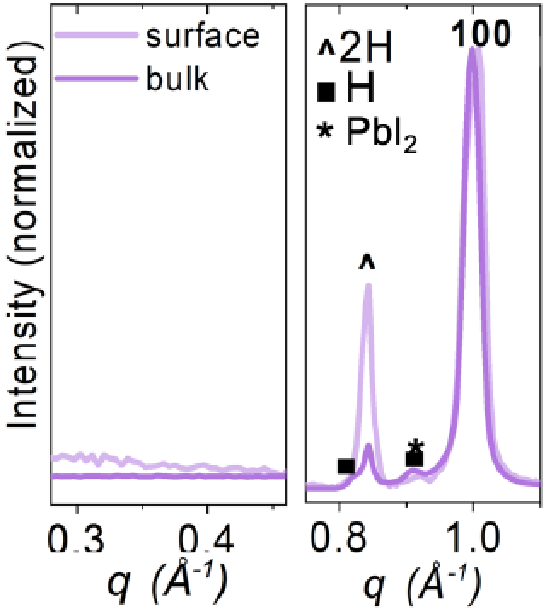
X-RAY PENETRATION DETPTH VS. INCIDENT ANGLE

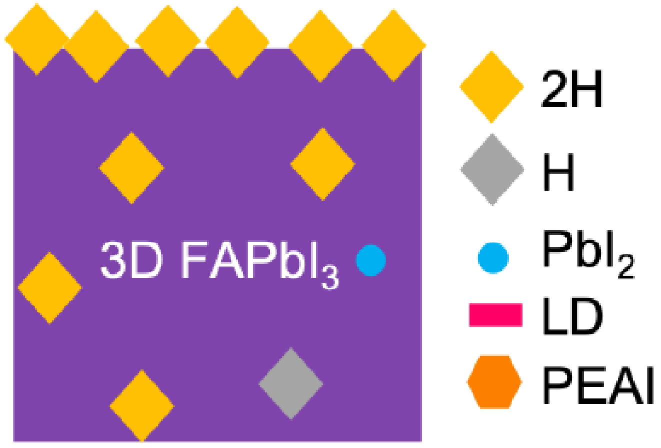


INCREASED HEXAGONAL PHASES AT THE SURFACE

$FAPbI_3$



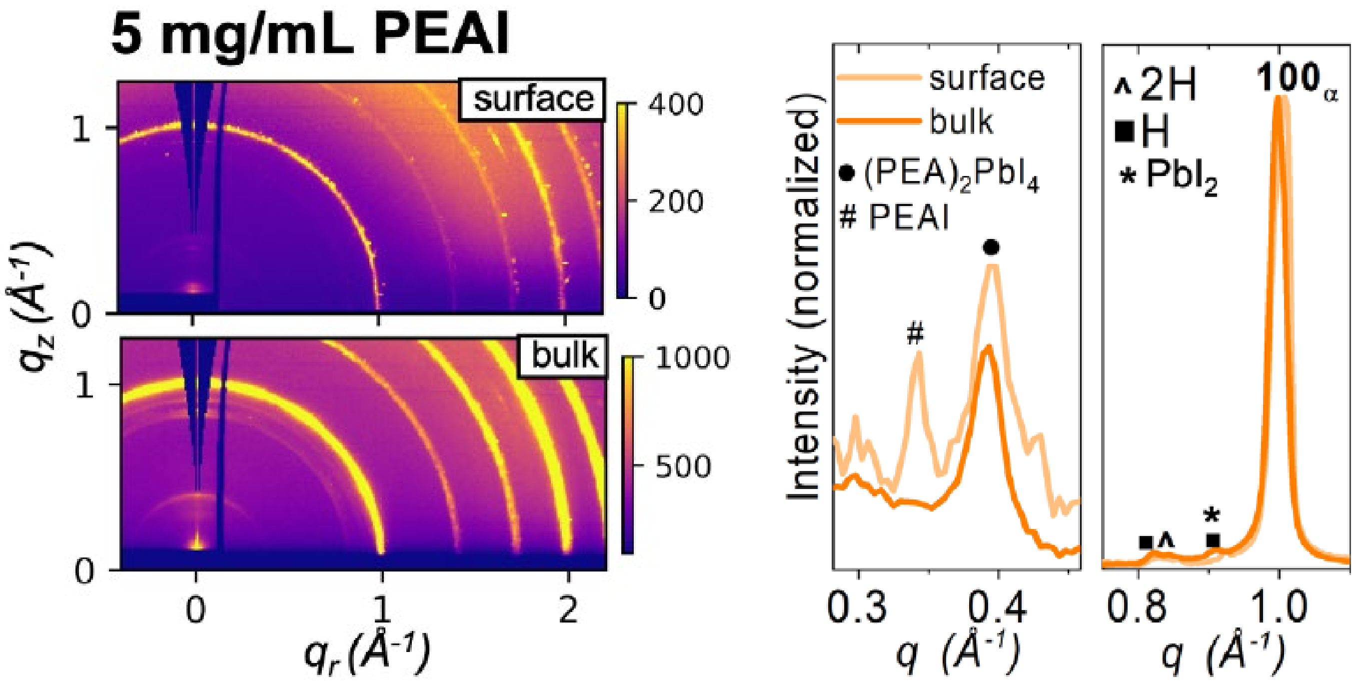


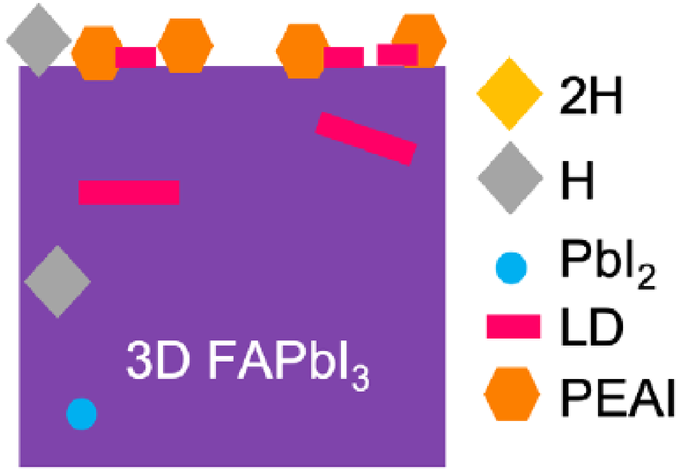


Hidalgo,…Correa-Baena. ***Materials Today 2023***

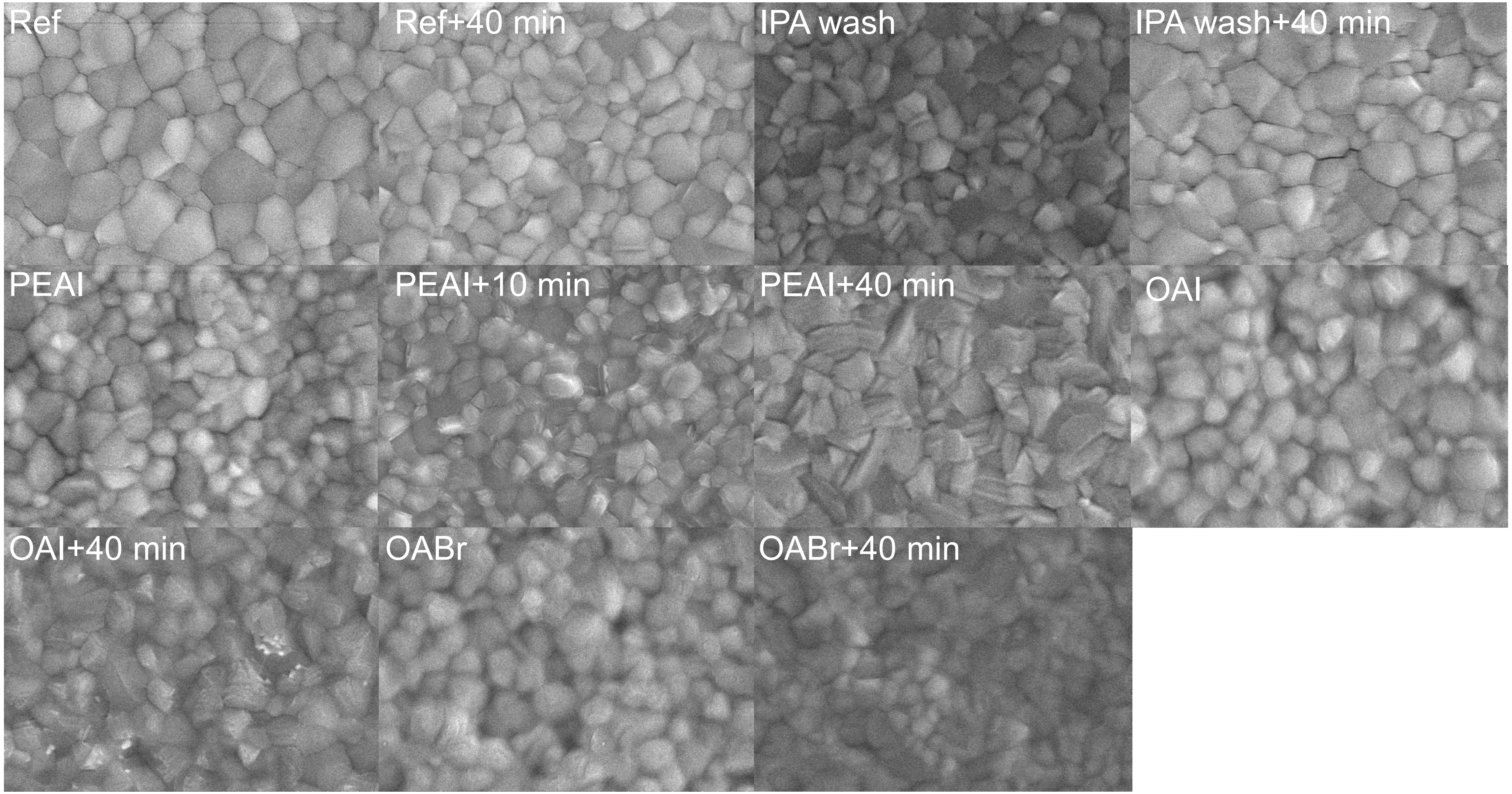
TOP LAYER OF PEAI REDUCES NON-PEROVSKITE PHASES

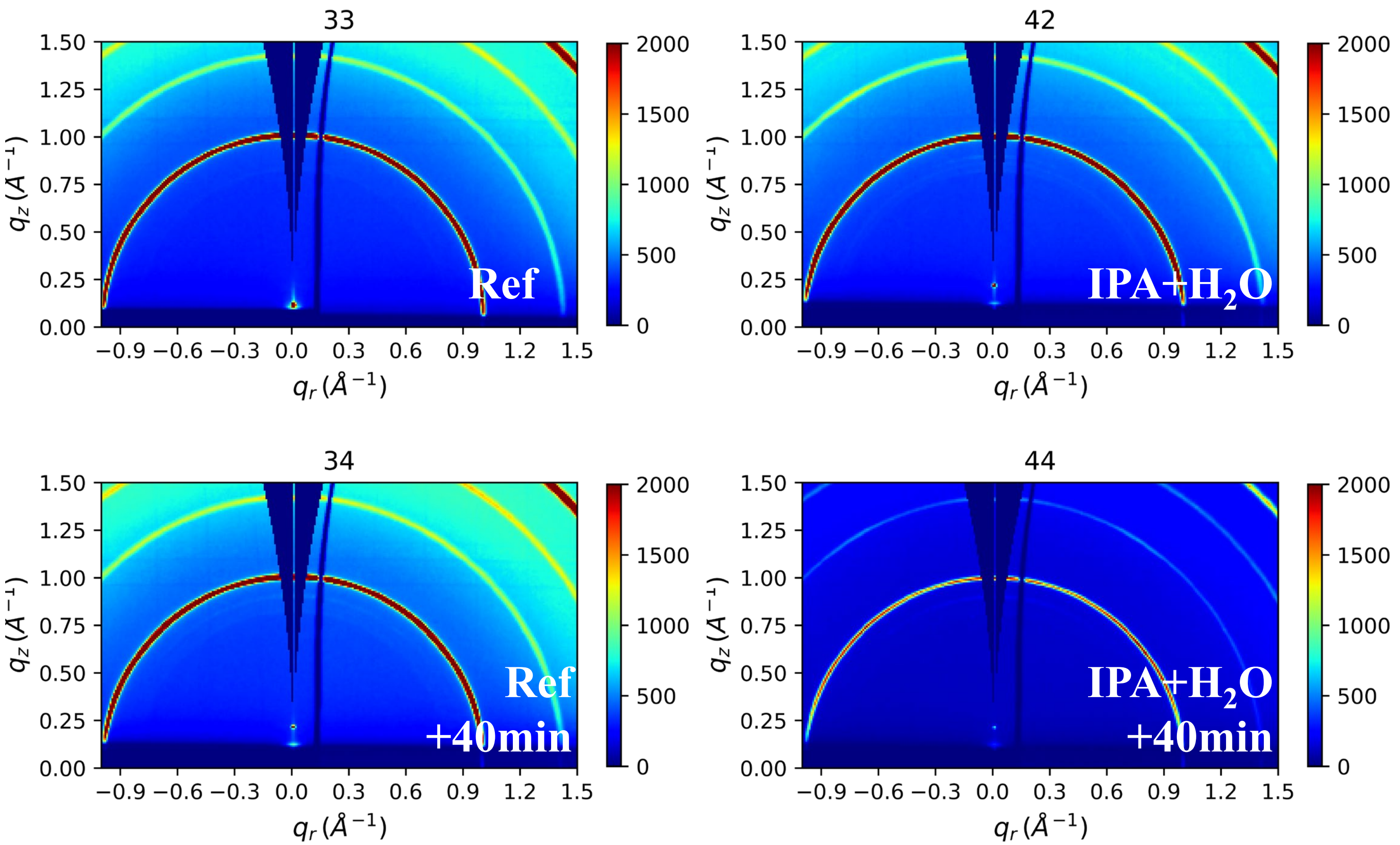
$FAPbI_3$

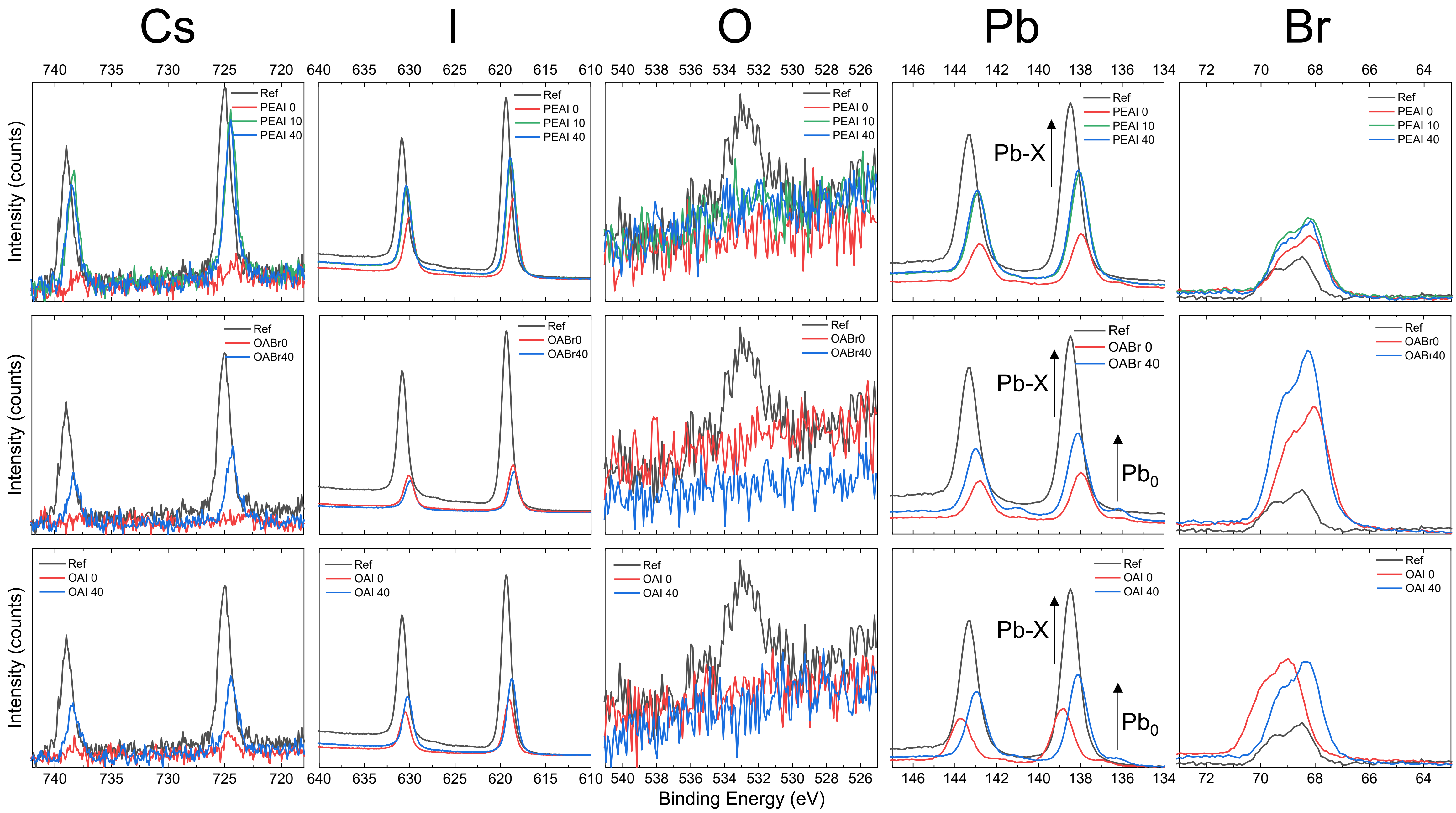




Hidalgo,…Correa-Baena. ***Materials Today 2023***


Ref
Ref+40 min
IPA wash
IPA wash+40 min
PEAI
PEAI+10 min
PEAI+40 min
OAI
OAI+40 min
OABr
OABr+40 min


33
42
34
44
Ref
IPA+H$_2$O
Ref
+40min
IPA+H$_2$O
+40min
q_z (Å^{-1})
q_r (Å^{-1})



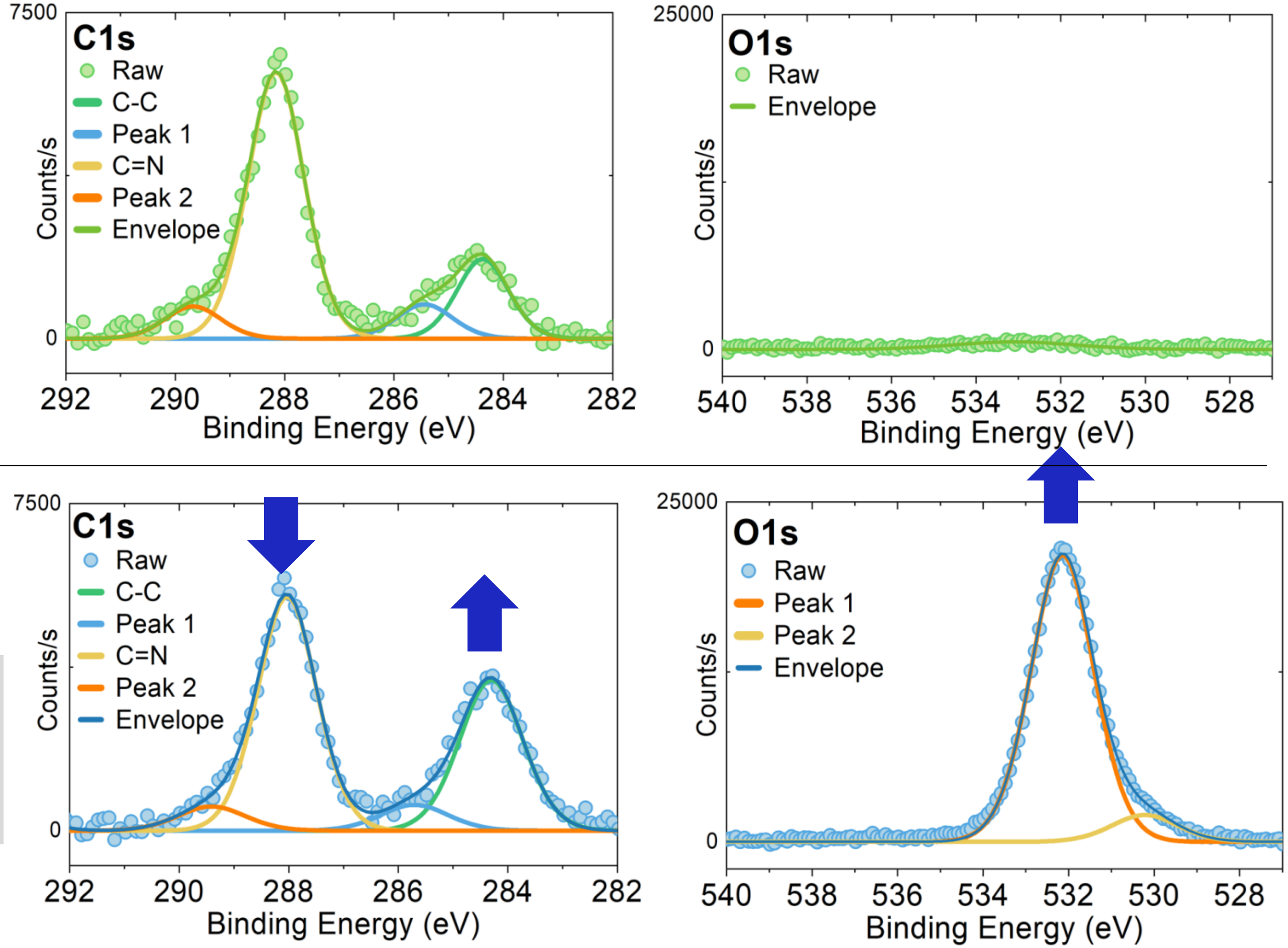
XPS EVOLUTION

EX-SITU XPS: OXYGEN ROLE IN THE PHASE TRANSFORMATION

H_2O and oxygen interaction starts on the surface

Pristine

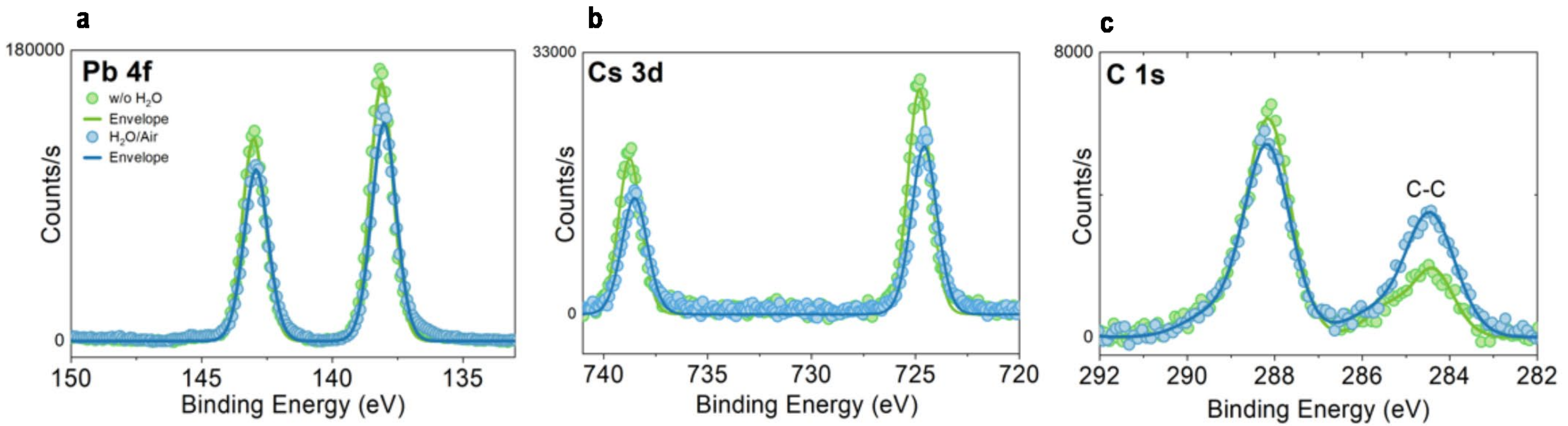
Exposed to H_2O and air

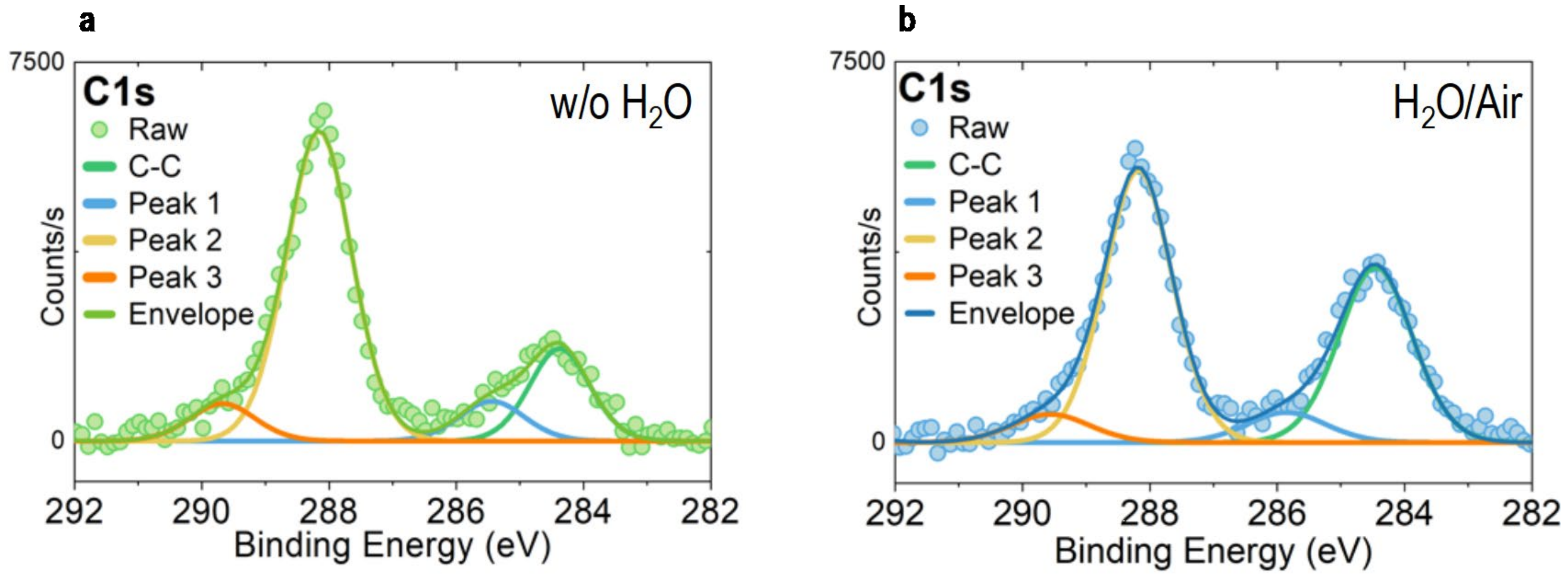


Bulky cation important to prevent oxygen interactions
Oxygen may be inducing undesired phase transformations from cubic perovskite to hexagonal non-perovskite

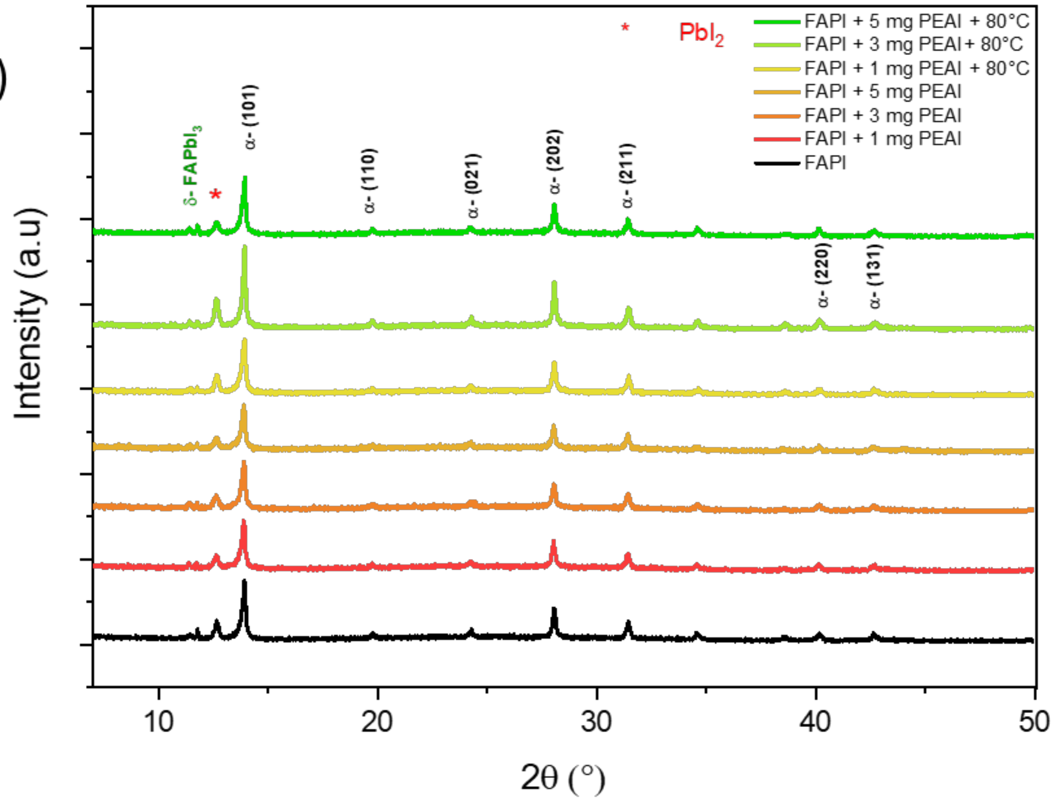
Hidalgo,…Correa-Baena. J. Am. Chem. Soc. 2023, 145, 45, 24549–24557

138.35 138.20


a
180000
Pb 4f
w/o H_2O
Envelope
H_2O/Air
Envelope
Counts/s
0
150
145
140
135
Binding Energy (eV)
b
33000
Cs 3d
Counts/s
0
740
735
730
725
720
Binding Energy (eV)
c
8000
C 1s
C-C
Counts/s
0
292
290
288
286
284
282
Binding Energy (eV)

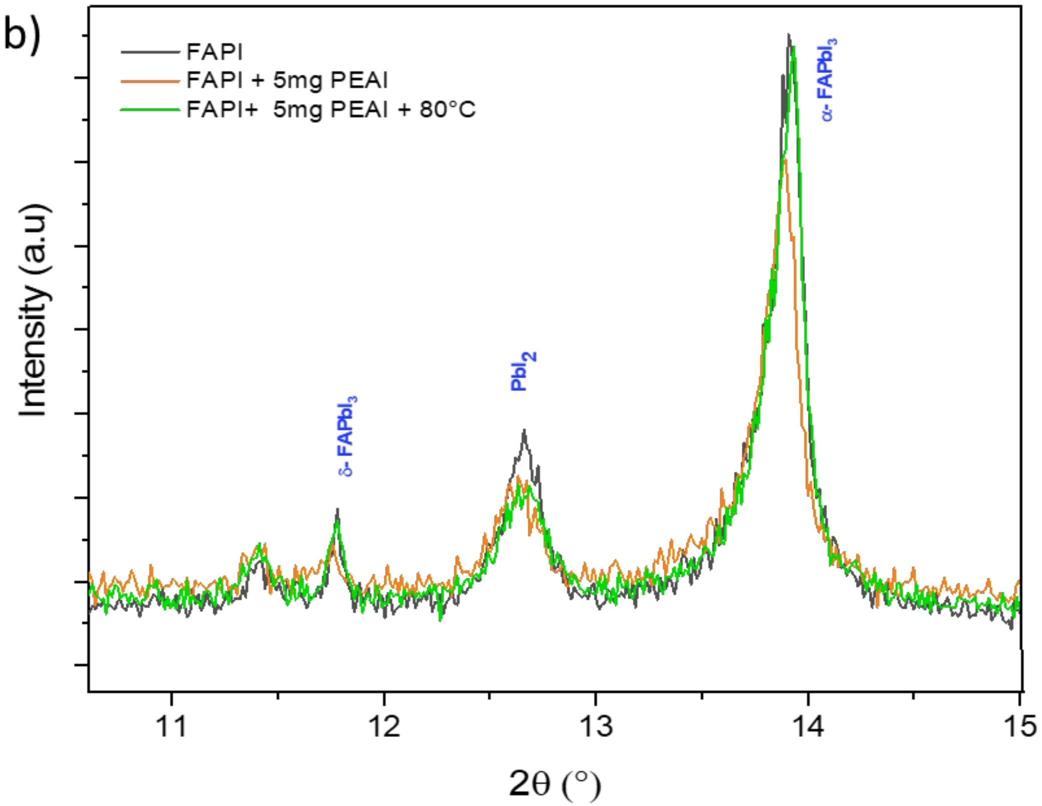

a
7500
C1s
w/o H_2O
Raw
C-C
Peak 1
Peak 2
Peak 3
Envelope
Counts/s
0
292
290
288
286
284
282
Binding Energy (eV)
b
7500
C1s
H_2O/Air
Raw
C-C
Peak 1
Peak 2
Peak 3
Envelope
Counts/s
0
292
290
288
286
284
282
Binding Energy (eV)

a)



FAPI + 5 mg PEAI + 80°C
FAPI + 3 mg PEAI + 80°C
FAPI + 1 mg PEAI + 80°C
FAPI + 5 mg PEAI
FAPI + 3 mg PEAI
FAPI + 1 mg PEAI
FAPI
* PbI2
δ- FAPbI3
α- (101)
α- (110)
α- (021)
α- (202)
α- (211)
α- (220)
α- (131)
Intensity (a.u)
10
20
30
40
50
2θ (°)

b)



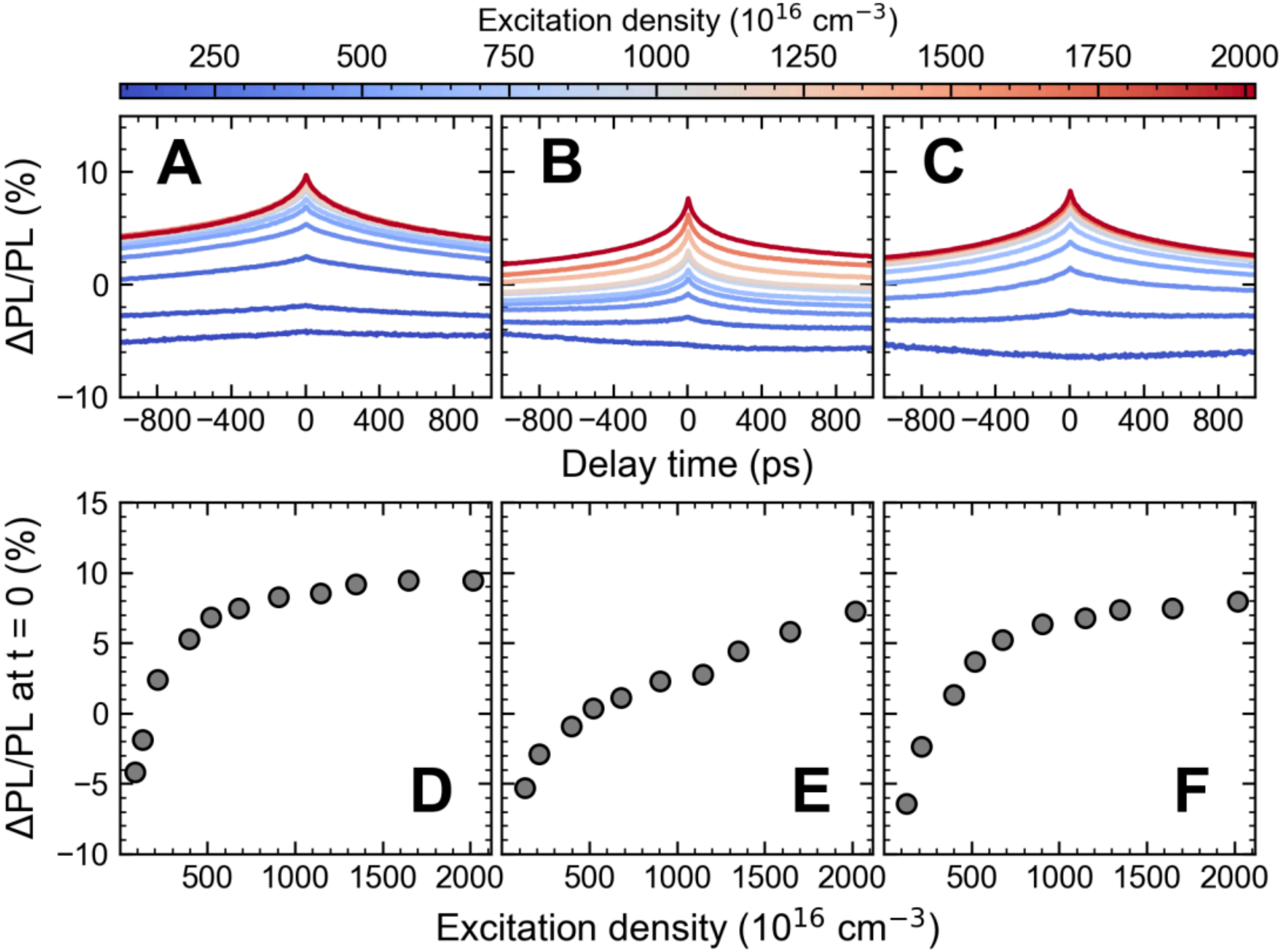
FAPI
FAPI + 5mg PEAI
FAPI+ 5mg PEAI + 80°C
δ- FAPbI3
PbI2
α- FAPbI3
Intensity (a.u)
11
12
13
14
15
2θ (°)

c)

WHAT ABOUT SHALLOW TRAPS?

- excitation correlation photoluminescence (ECPL) to understand shallow trap formation
- Defect assisted nonradiative recombination produces a positive ECPL signal, whereas auger processes would introduce a negative ECPL component.
- 2D Ruddlesden-Popper with n = 2 towards n = 1

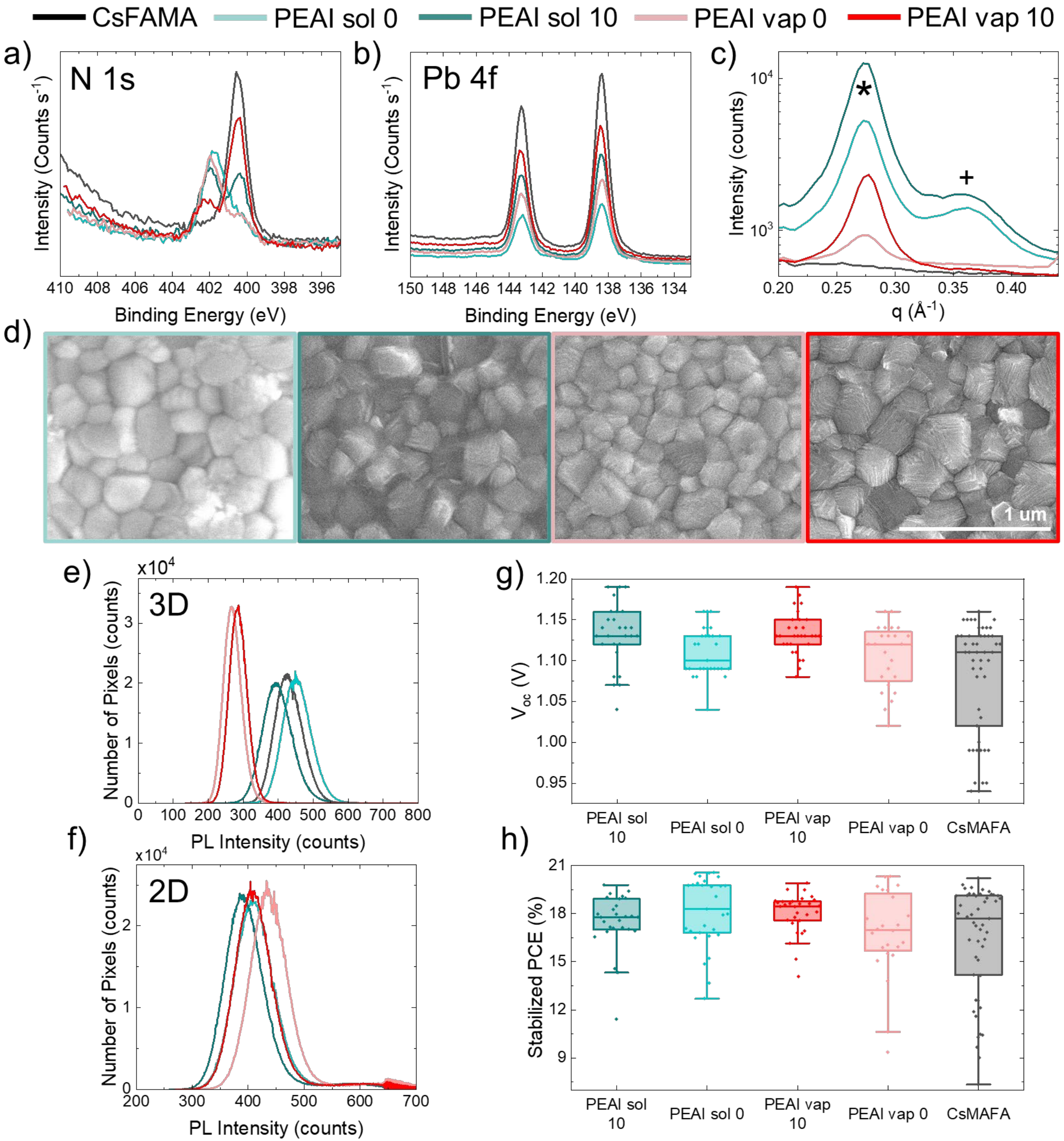
CsMAFA (Ref) CsMAFA+PEAI CsMAFA+PEAI +40 min anneal



Prof. Carlos Silva

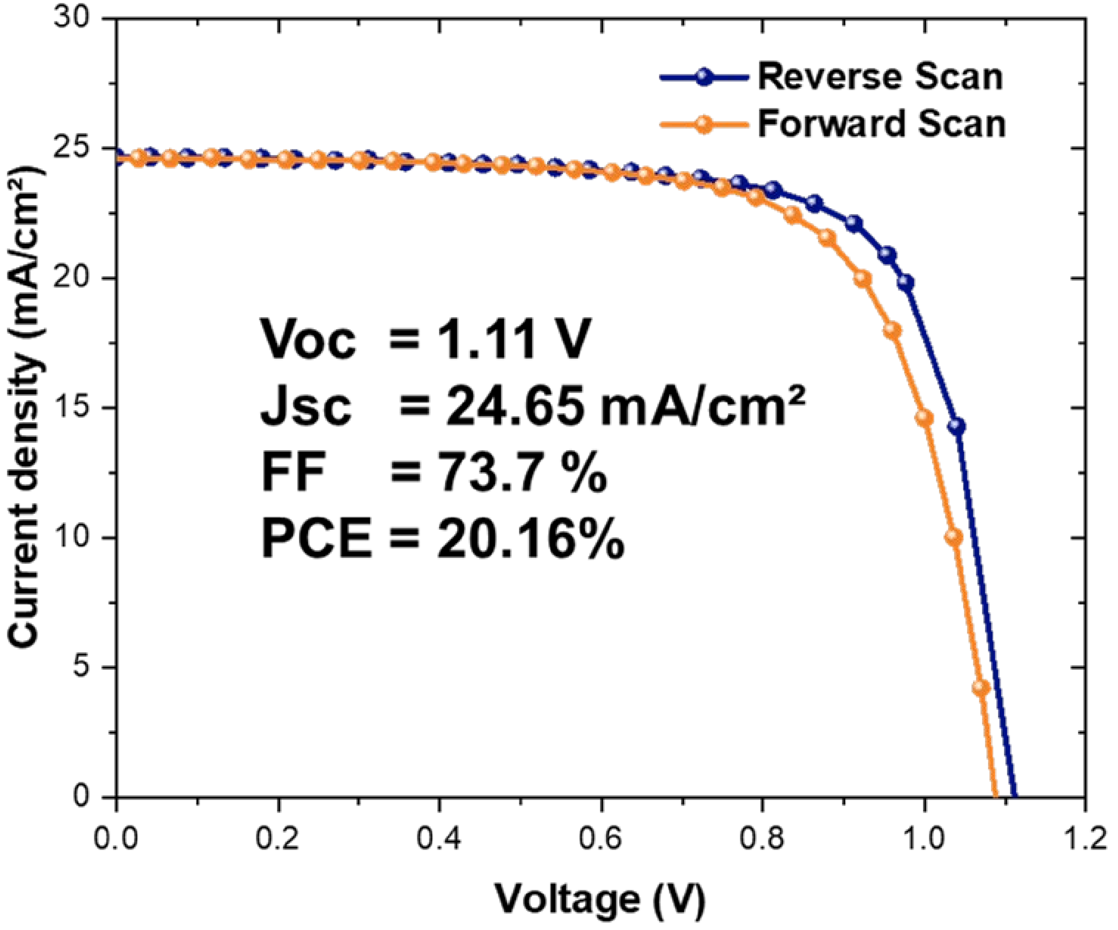
Esteban Rojas

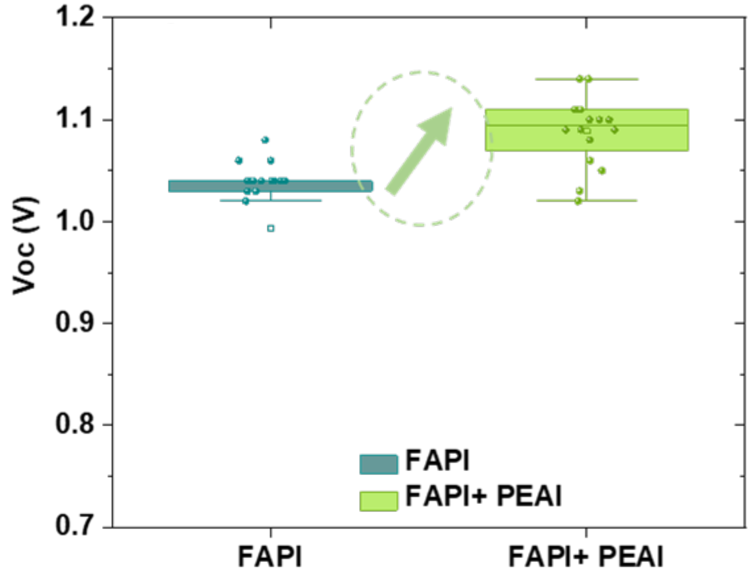
Perini, C. A. R., Correa-Baena, J.-P. et al. (2021). Preventing bulky cation diffusion in lead halide perovskite solar cells. https://doi.org/10.33774/CHEMRXIV-2021-197PF</div>

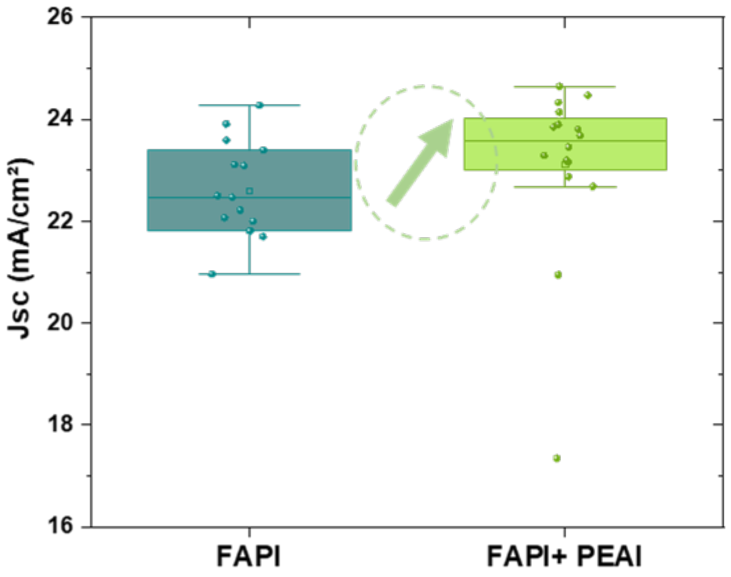


CsFAMA
PEAI sol 0
PEAI sol 10
PEAI vap 0
PEAI vap 10
a)
N 1s
Intensity (Counts s^{-1})
Binding Energy (eV)
b)
Pb 4f
Intensity (Counts s^{-1})
Binding Energy (eV)
c)
Intensity (counts)
q (Å^{-1})
d)
1 um
e)
3D
Number of Pixels (counts)
PL Intensity (counts)
f)
2D
Number of Pixels (counts)
PL Intensity (counts)
g)
V_{oc} (V)
PEAI sol 10
PEAI sol 0
PEAI vap 10
PEAI vap 0
CsMAFA
h)
Stabilized PCE (%)
PEAI sol 10
PEAI sol 0
PEAI vap 10
PEAI vap 0
CsMAFA

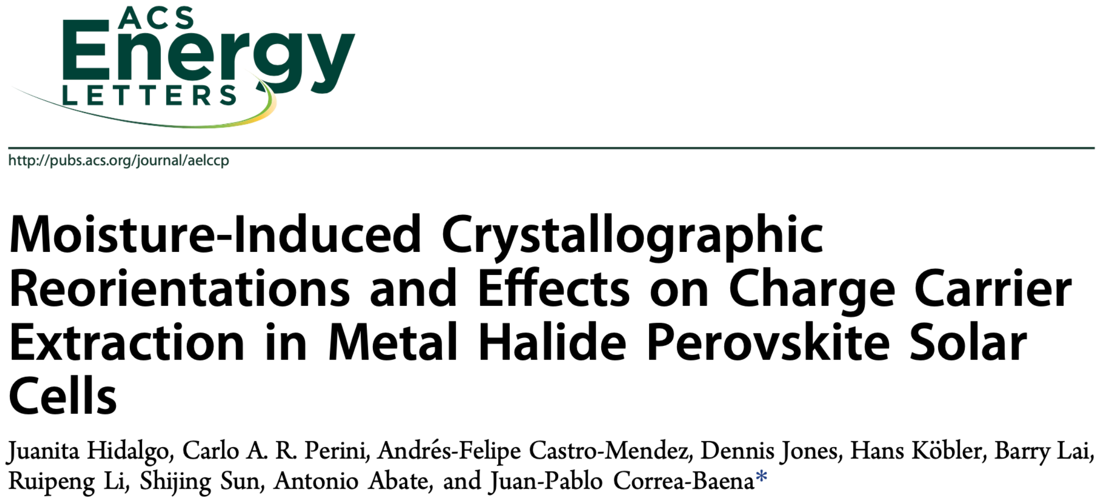
EFFECTS ON DEVICE PERFORMANCE: PURE FAPI



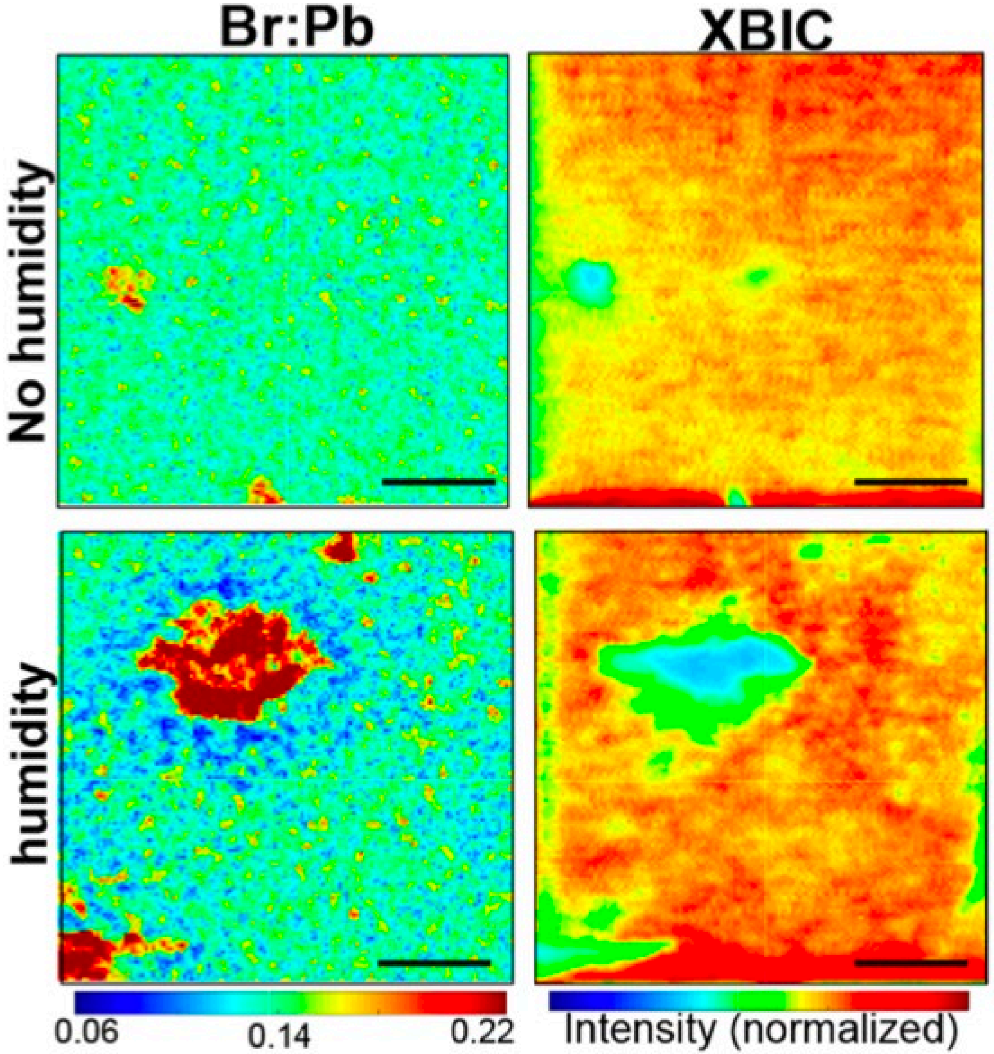




Humidity-Induced Chemical-Electronic Changes



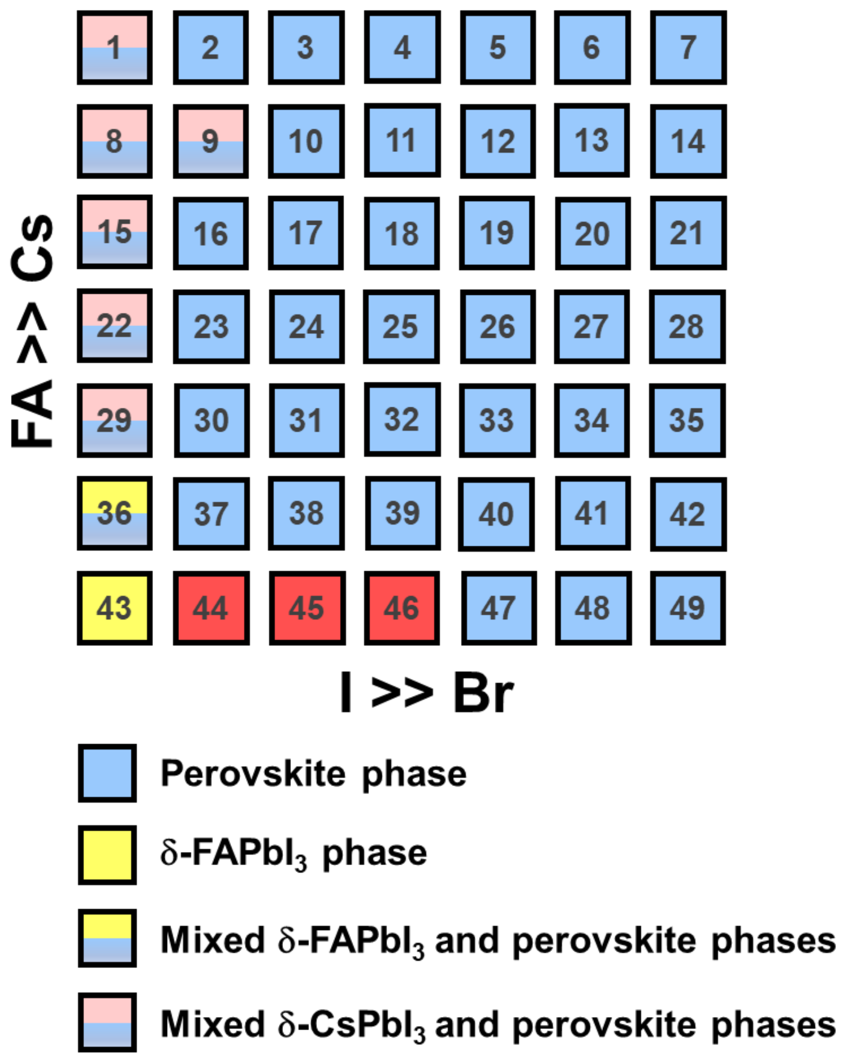
Juanita Hidalgo



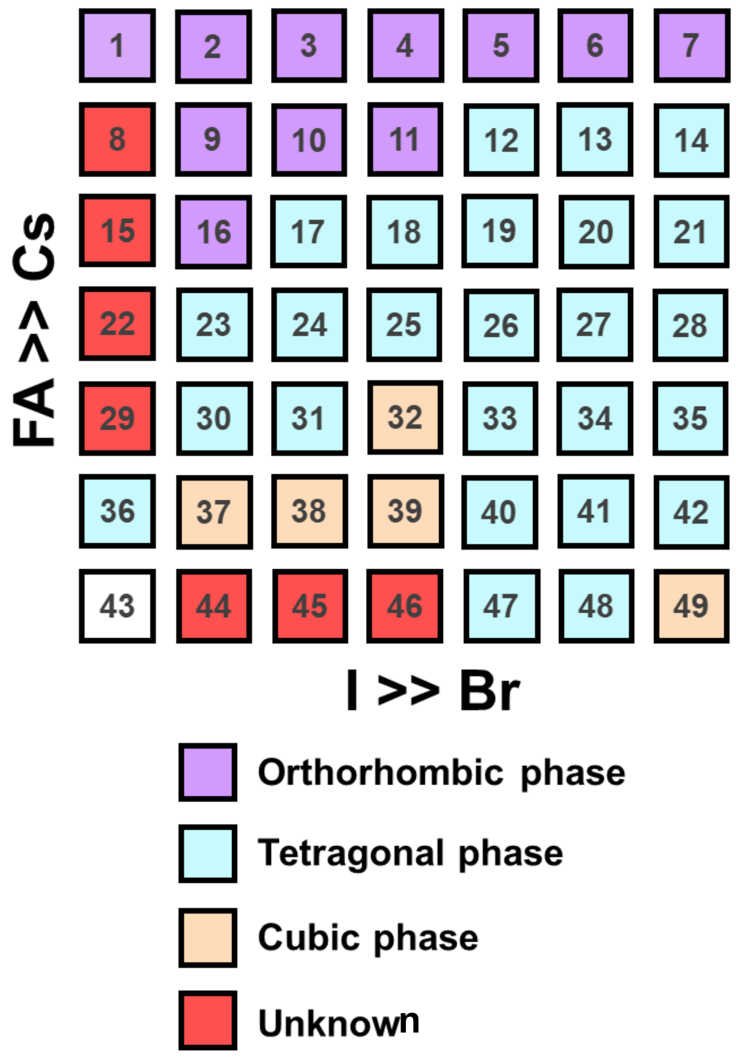
Hidalgo, Correa-Baena, et al. ACS Energy Lett. 2020, 5, 3526−3534

CRYSTALLOGRAPHIC PROPERTIES

The presence of perovskite phases

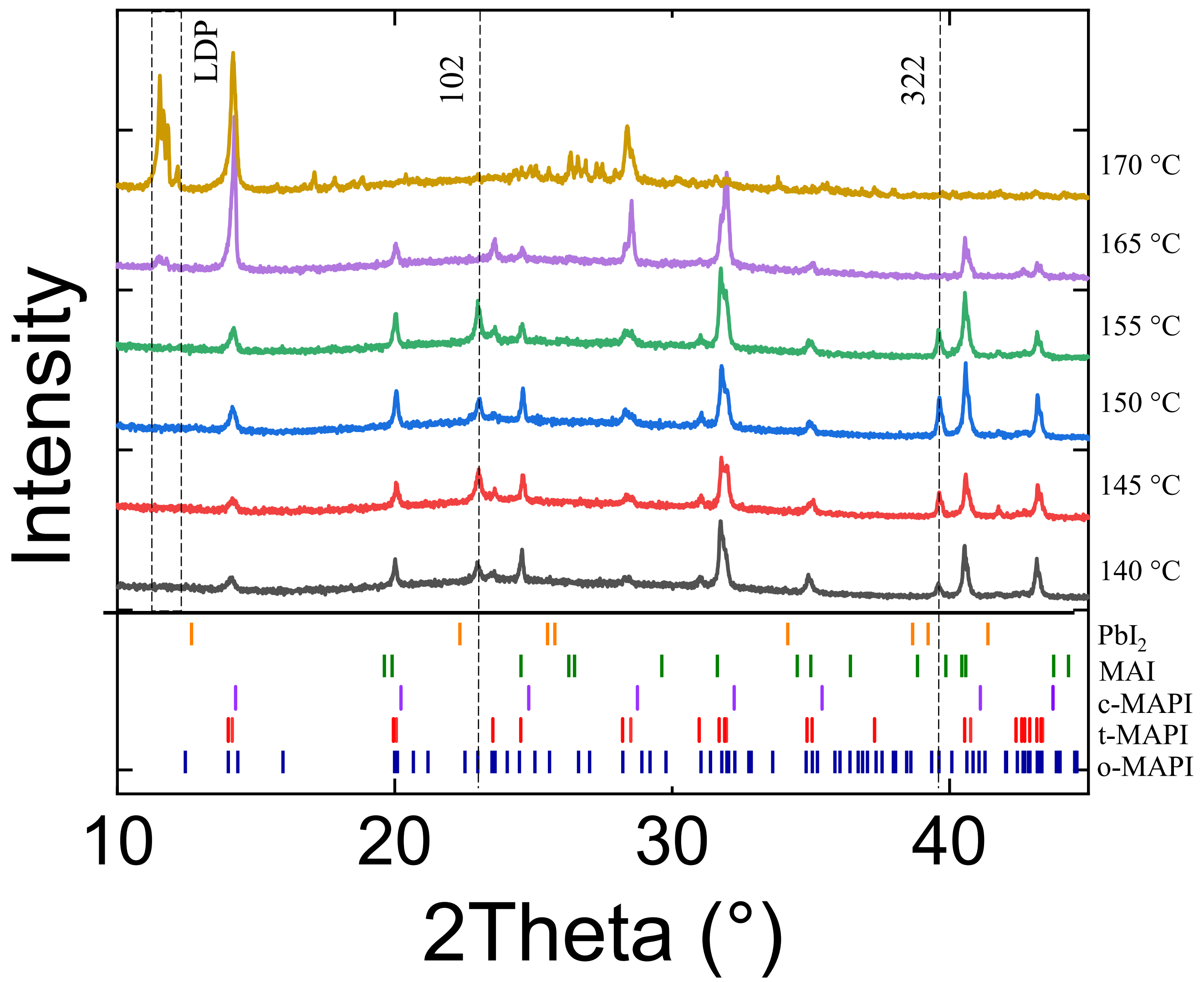


The presence of crystal symmetry for perovskite phases



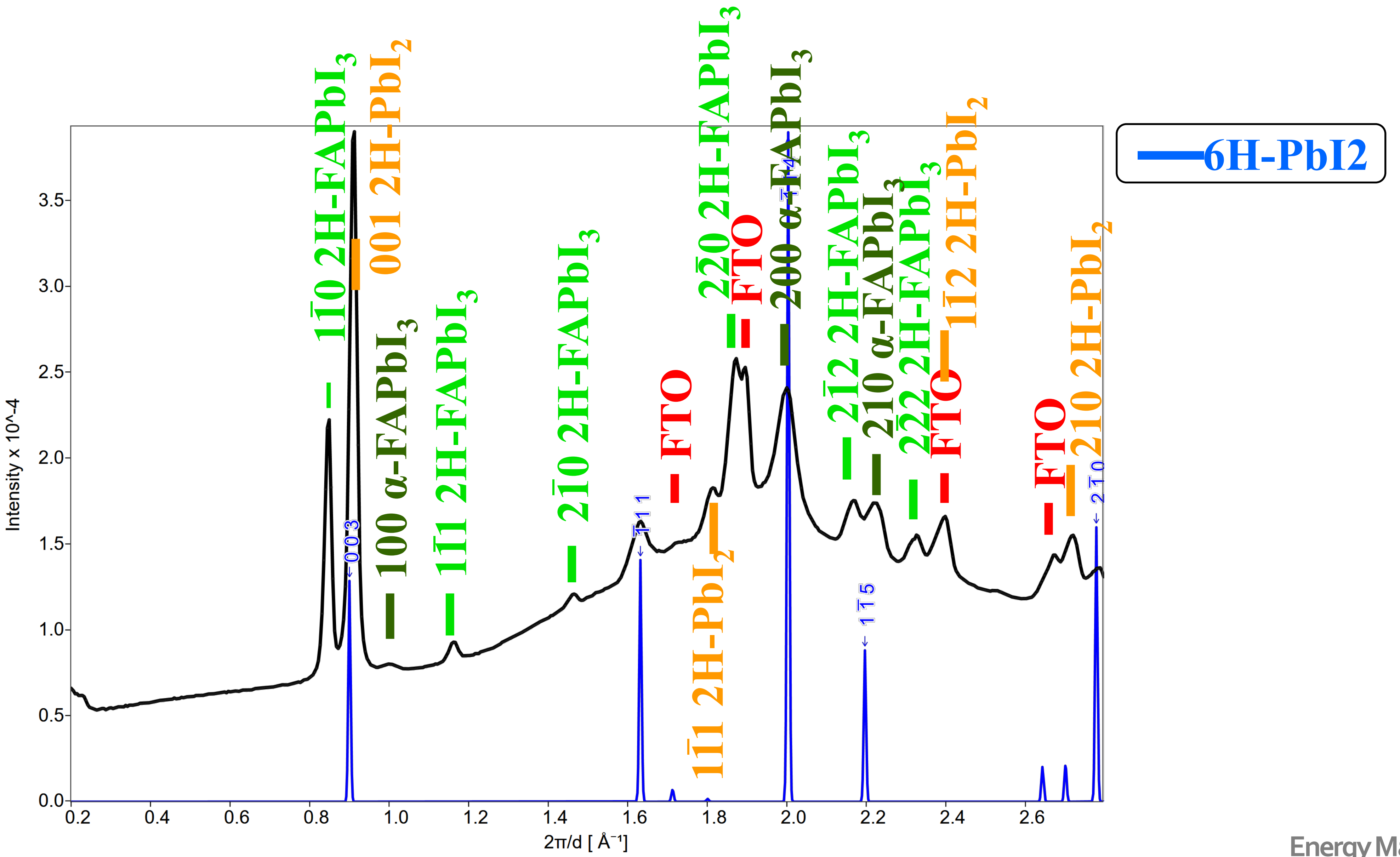
An, Y. , Correa-Baena, J. P. et al. *EES* 2021, 14(12), 6638–6654.

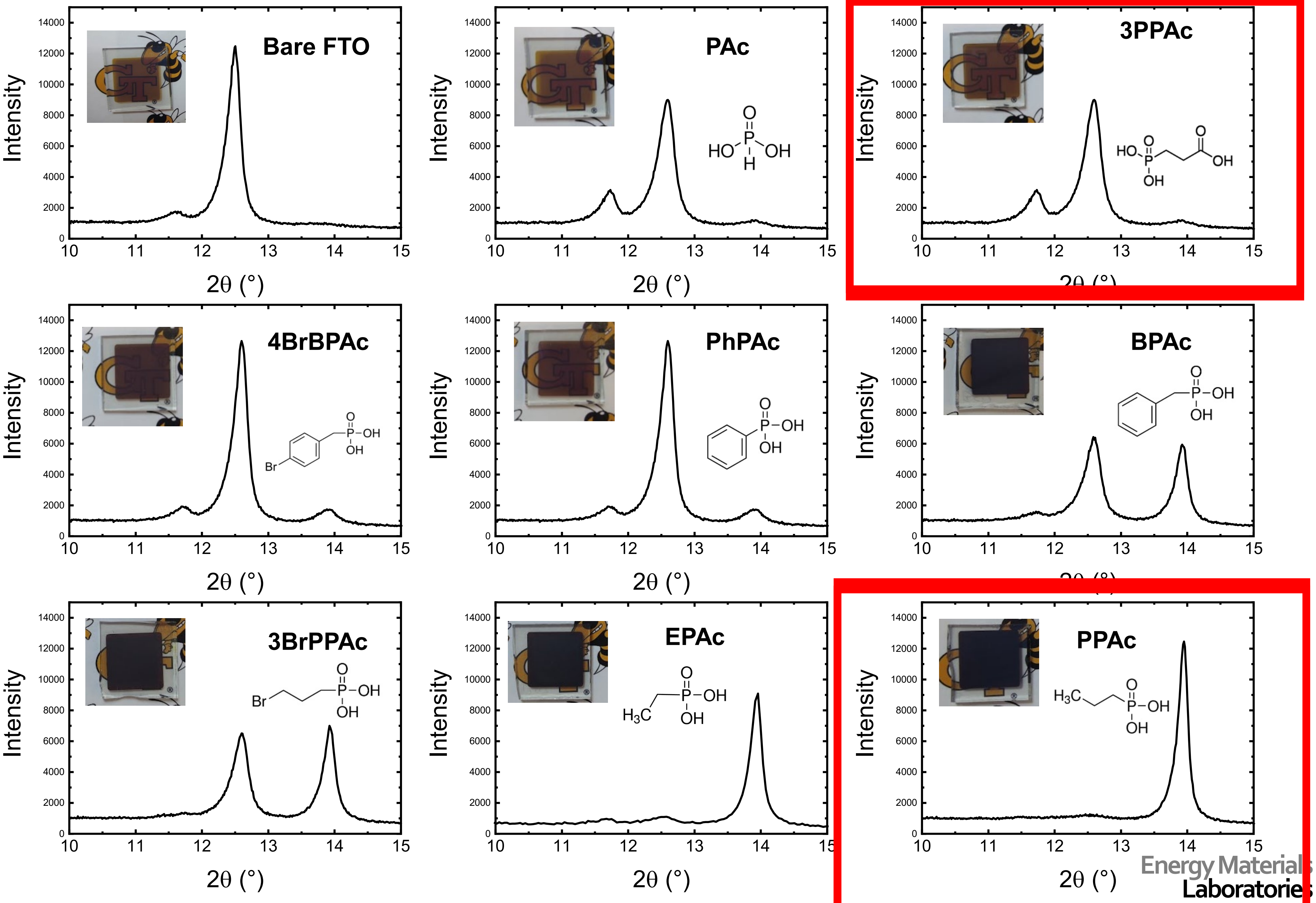
SECONDARY PHASES IN THIN FILMS



- **Under 140 °C:** Only peaks of PbI_2 in XRD
- **140 °C – 155 °C:** Secondary phase present
- **165 °C – 170 °C :** Low dimensional non-perovskite phase present

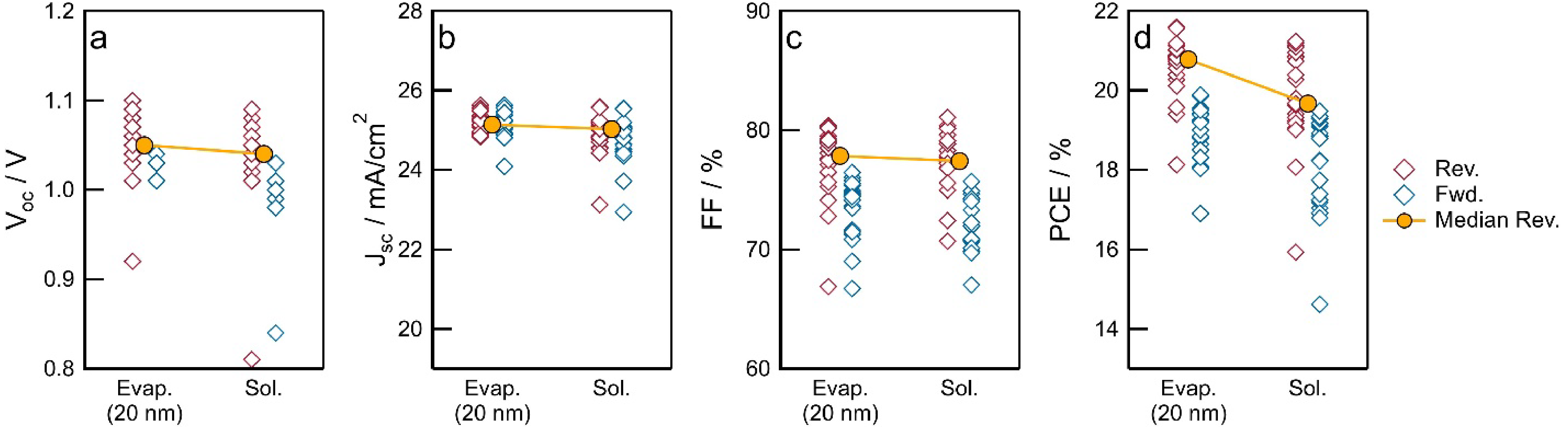
IDENTIFYING SECONDARY PHASES IN FAPI PEROVSKITE





Energy Materials Laboratories

[redacted]



Comparison of photovoltaic performance (a) Voc, (b) Jsc, (c) FF and (d) PCE of solar cells passivated with optimized co-evaporated RP layer (20 nm) ad solution-processed RP layer.