Halide perovskites - a game-changer for photovoltaics?

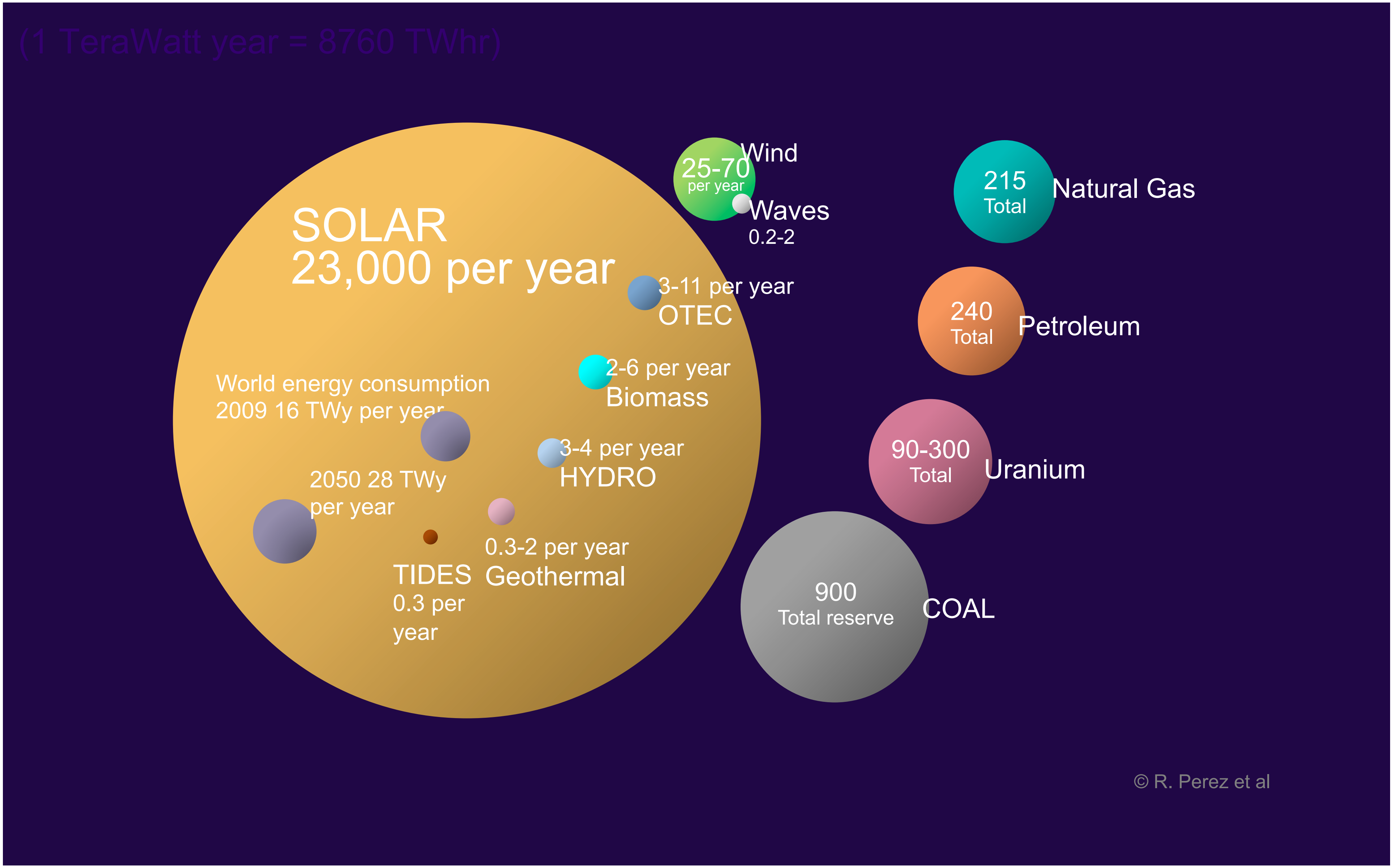
Giles Eperon
Marie Curie Fellow
Ginger Lab
Department of Chemistry
University of Washington
Seattle, WA
USA

eperon@uw.edu

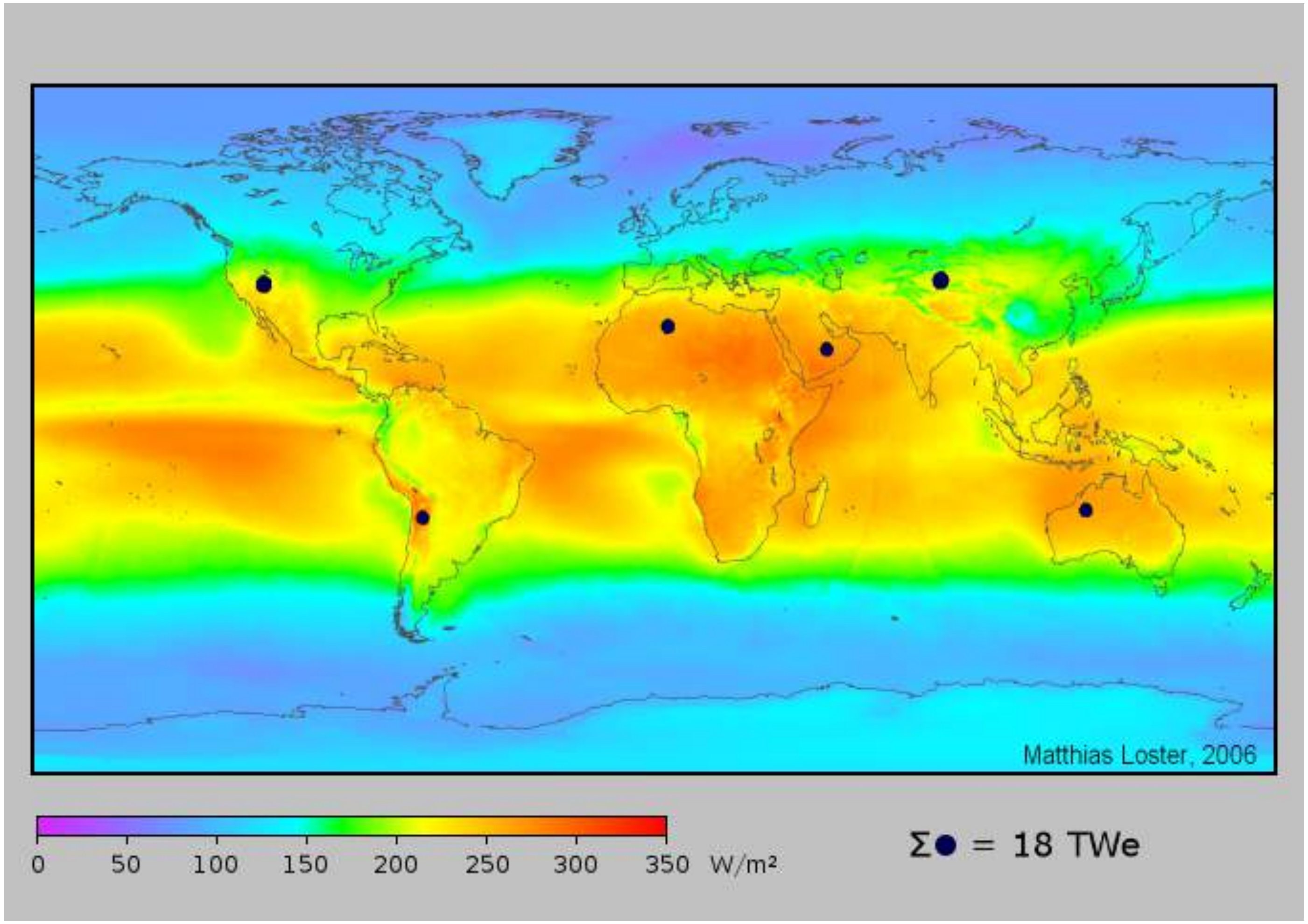
UNIVERSITY *of* WASHINGTON

SOLAR POWER - OVERVIEW

World Energy Resources TW years



How much solar PV do we need?

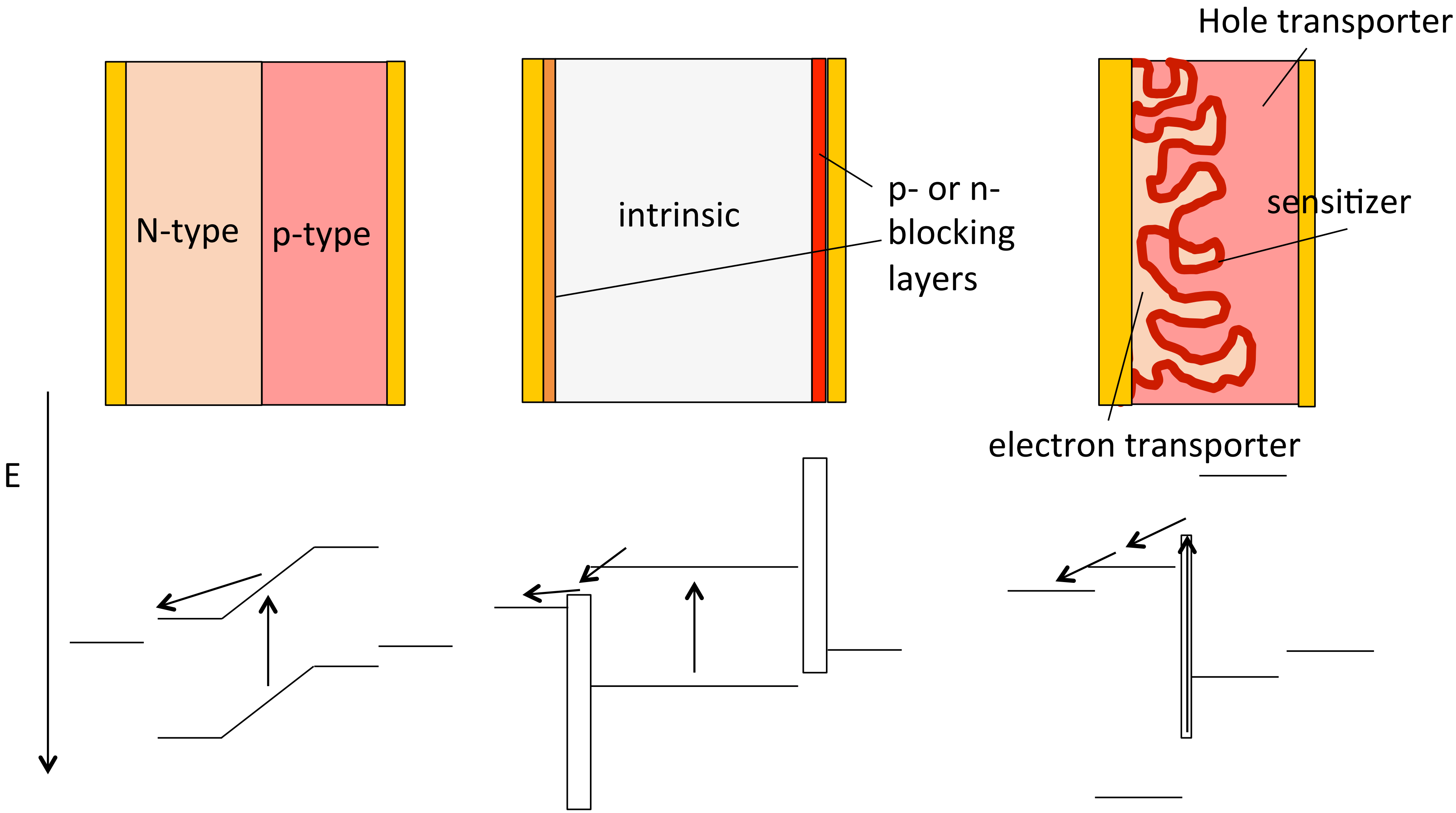


●
Area required at 8% efficiency

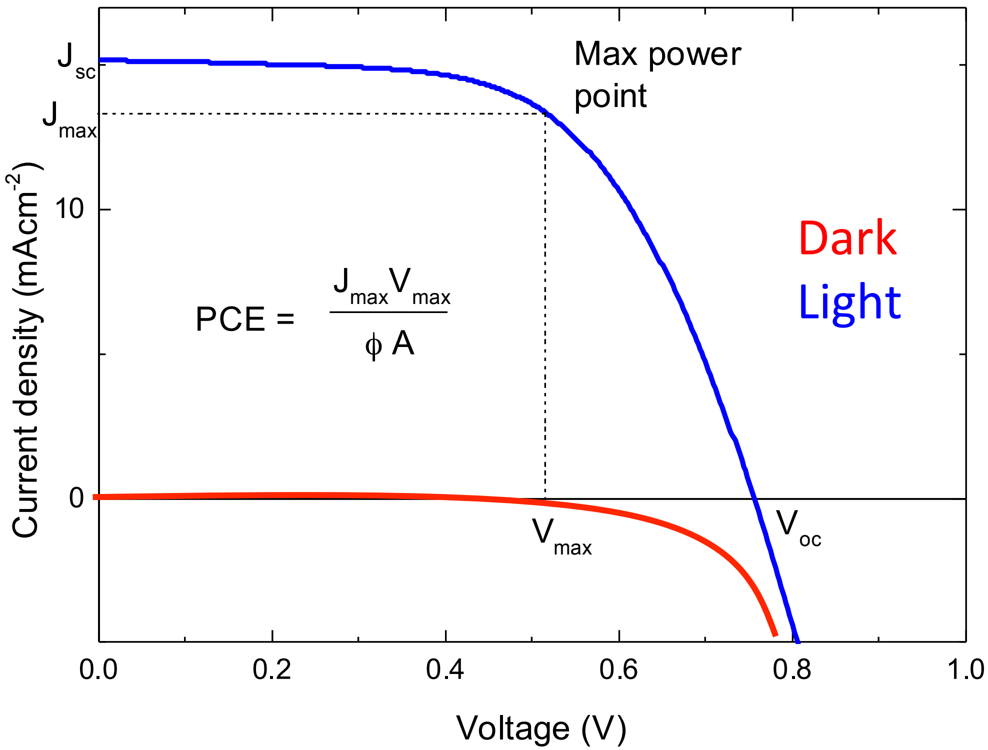
http://www.ez2c.de/ml/solar_land_area/

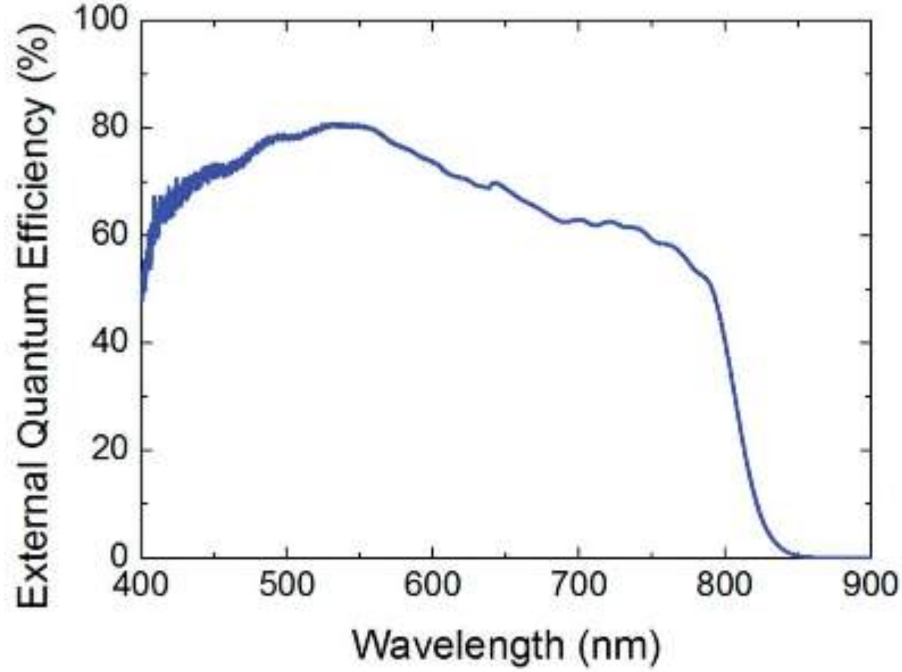
Solar cell basics – types of solar cell

A light absorbing material connected to an external circuit in an asymmetrical manner, allowing physical separation of photoexcited charge carriers to generate current and voltage.



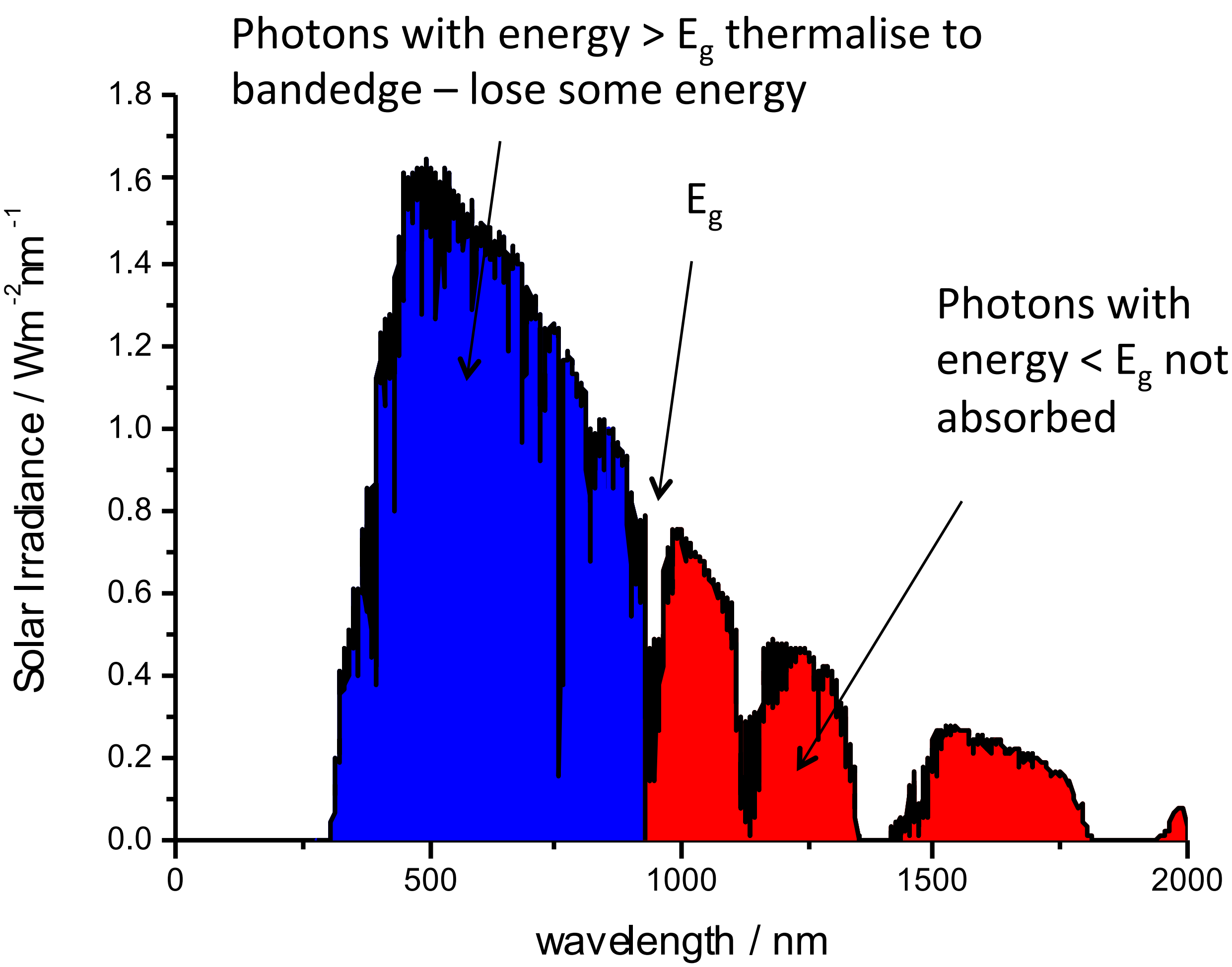
Solar cell operation





Φ = incident light intensity, A = cell area

Choice of material

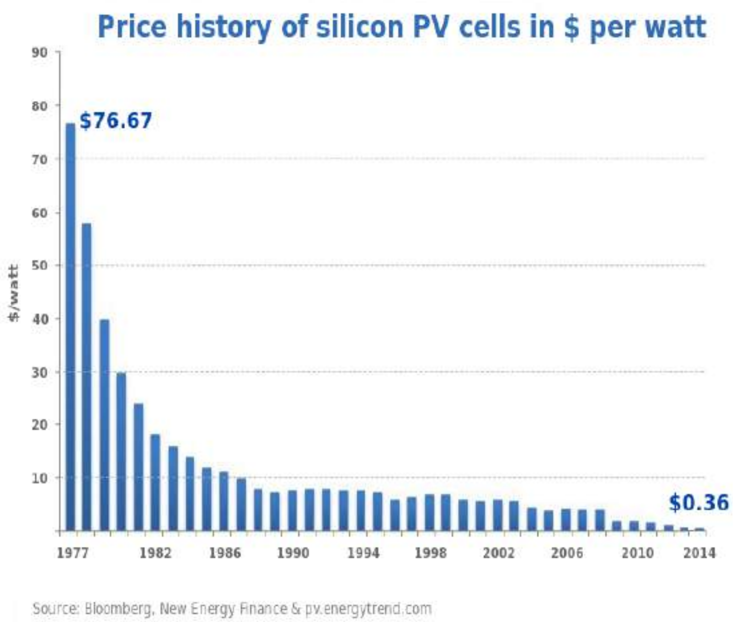


Trade-offs in thermalisation and absorption mean E_g of ~1.1-1.4eV optimum.
PCE of up to 33% achievable (in single layer) with this bandgap.

Silicon PV – Dominant Technology

In 2001 electricity produced from Si PV was around 20 times as expensive as that from burning fossil fuels.

Now, cheapest power in some areas.



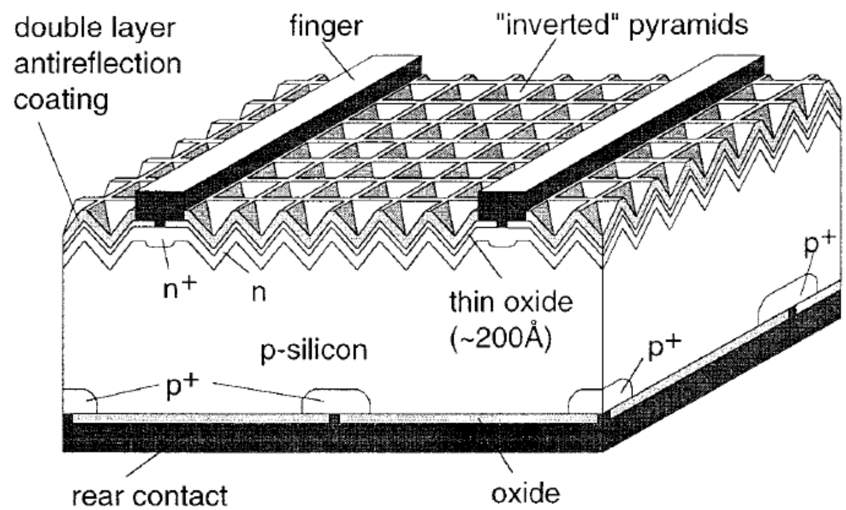
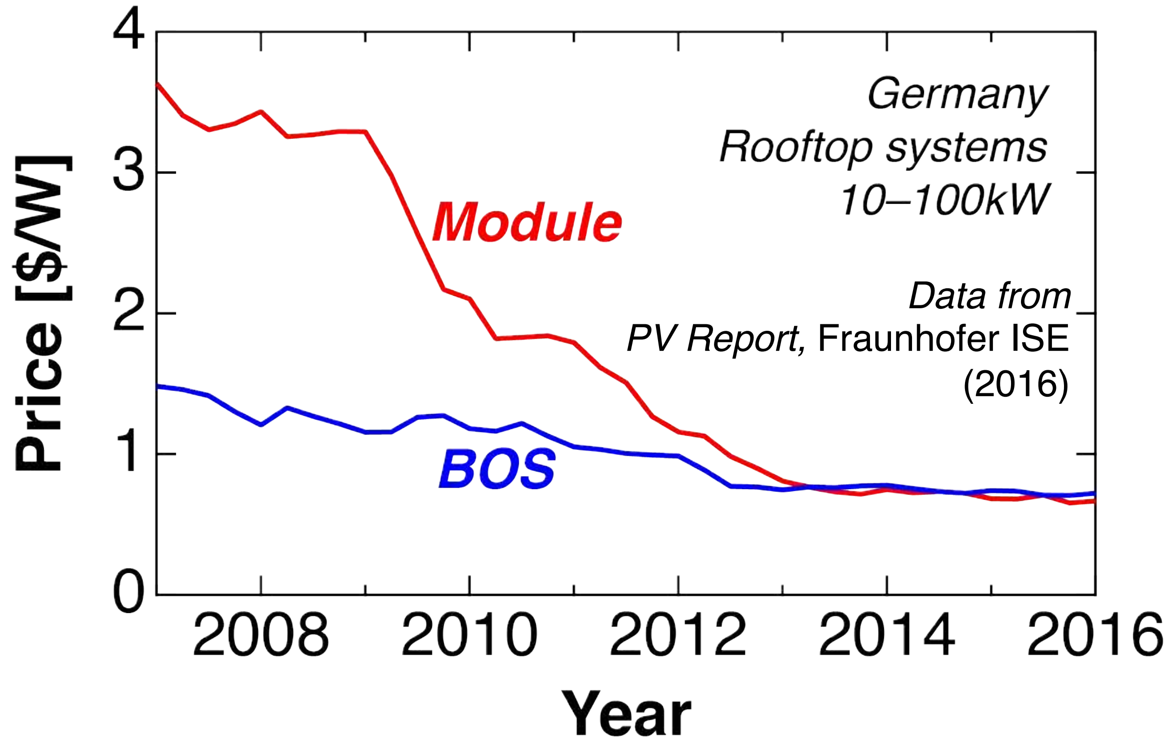


Figure 1. PERL (passivated emitter, rear locally-diffused) cell structure

Silicon may not be enough in the future

- **New factories very expensive**
- **Non-module costs** (Balance of Systems, BOS)



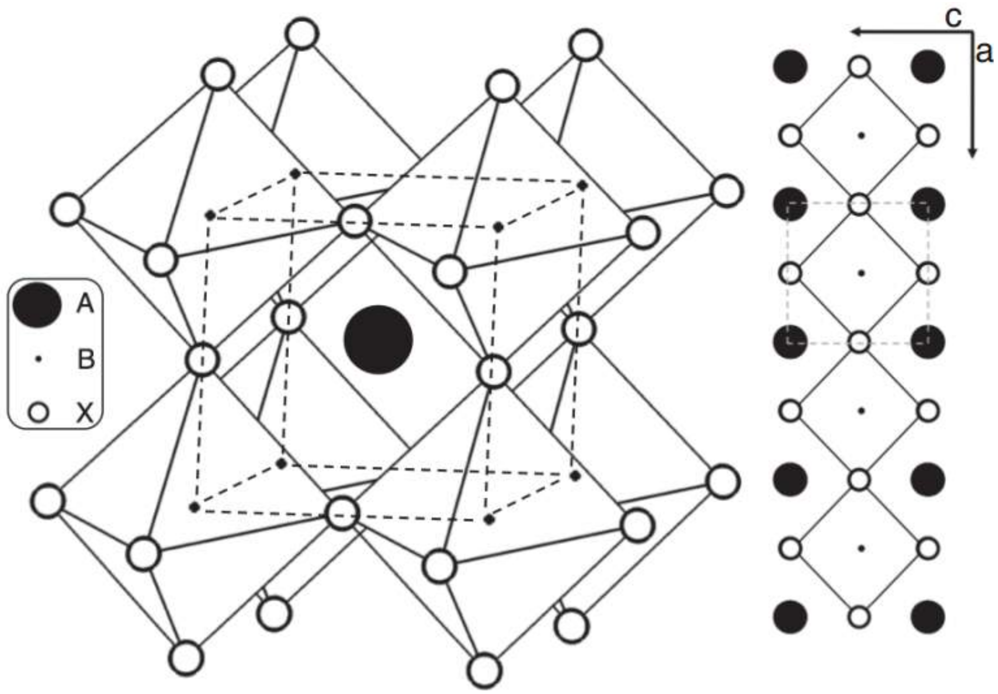
Best way to decrease installation cost per Watt is to make module more efficient – but Si reaching max efficiencies.

Need something that can be scaled fast, cheap, and has potential for higher efficiencies.

THE DEVELOPMENT OF PEROVSKITE PHOTOVOLTAICS

Enter perovskites

All materials with the same crystal structure as $CaTiO_3$, namely **ABX_3**, are termed perovskites.



1892: 1st paper on halide perovskites

Über die Cäsium- und Kalium-Bleihalogenide.

Von

H. L. Wells.[1]

Als Fortsetzung der in diesem Laboratorium[2] begonnenen Arbeit über Doppelhalogenide ist von den Herren G. F. Campbell, P. T. Walden und A. P. Wheeler eine Untersuchung über die Cäsium-Bleisalze unternommen worden. Diese Herren haben die Untersuchung mit vielem Eifer und Geschick durchgeführt, und es macht mir Freude, ihnen meinen Dank auszusprechen. Sie haben die Existenz folgender Salze konstatiert:

Cs_4PbCl_6	Cs_4PbBr_6	—
$CsPbCl_3$	$CsPbBr_3$[3]	$CsPbJ_3$
$CsPb_2Cl_5$	$CsPb_2Br_5$	—

Sheffield Scientific School, New Haven, Conn., Oktober 1892.

Structure deduced 1959:

Kongelige Danske Videnskabernes Selskab, Matematisk-Fysike Meddelelser (1959) 32, p1-p17

Author: **Moller, C.K.**

Title: The structure of cesium plumbo iodide Cs Pb I3

1978: Hybrid Pb and Sn halide perovskites

$CH_3NH_3PbX_3$, ein Pb(II)-System mit kubischer Perowskitstruktur

$CH_3NH_3PbX_3$, a Pb(II)-System with Cubic Perovskite Structure

Dieter Weber
Institut für Anorganische Chemie der Universität Stuttgart

Z. Naturforsch. **33 b,** 1443–1445 (1978); eingegangen am 21. August 1978

Synthesis, X-ray

$CH_3NH_3PbX_3$ (X = Cl, Br, I) has the cubic perovskite structure with the unit cell parameters a = 5,68 Å (X = Cl), a = 5,92 Å (X = Br) and a = 6,27 Å (X = I). With exception of $CH_3NH_3PbCl_3$ the compounds show intense colour, but there is no significant conductivity under normal conditions. The properties of the system are explained by a "p-resonance-bonding". The synthesis is described.

$CH_3NH_3SnBr_xI_{3-x}$ (x = 0–3), ein Sn(II)-System mit kubischer Perowskitstruktur

$CH_3NH_3SnBr_xI_{3-x}$ (x = 0–3), a Sn(II)-System with Cubic Perovskite Structure

Dieter Weber
Institut für Anorganische Chemie der Universität Stuttgart

Z. Naturforsch. **33 b,** 862–865 (1978); eingegangen am 5. Mai 1978

Synthesis, X-ray, Mössbauer Spectra

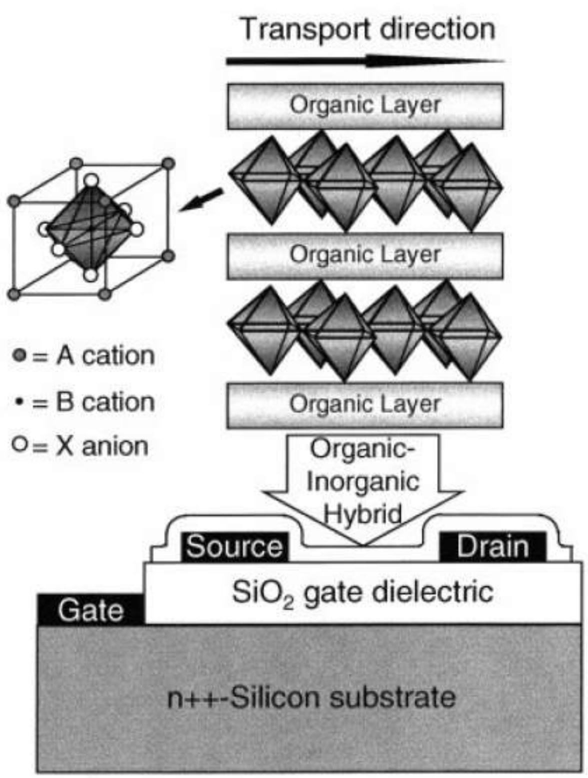
$CH_3NH_3SnBr_xI_{3-x}$ (x = 0–3) has the cubic perovskite structure with the unit cell parameters a = 5.89 Å (x = 3), a = 6.01 Å (x = 2) and a = 6.24 Å (x = 0) and Z = 1. The compounds show intense colour and conducting property. The ^{119}Sn Mössbauer data are consistent with the high symmetry environment of the Sn(II)-ion. A bonding model, using a "p-resonance-bonding", can explain the properties of the cubic system. The synthesis is described.

90s perovskite research

Organic-Inorganic Hybrid Materials as Semiconducting Channels in Thin-Film Field-Effect Transistors

C. R. Kagan, D. B. Mitzi, C. D. Dimitrakopoulos

www.sciencemag.org SCIENCE VOL 286 29 OCTOBER 1999



Chem. Mater. **1998,** *10,* 403–411

Synthesis and Characterization of Organic–Inorganic Perovskite Thin Films Prepared Using a Versatile Two-Step Dipping Technique

Kangning Liang, David B. Mitzi,* and Michael T. Prikas

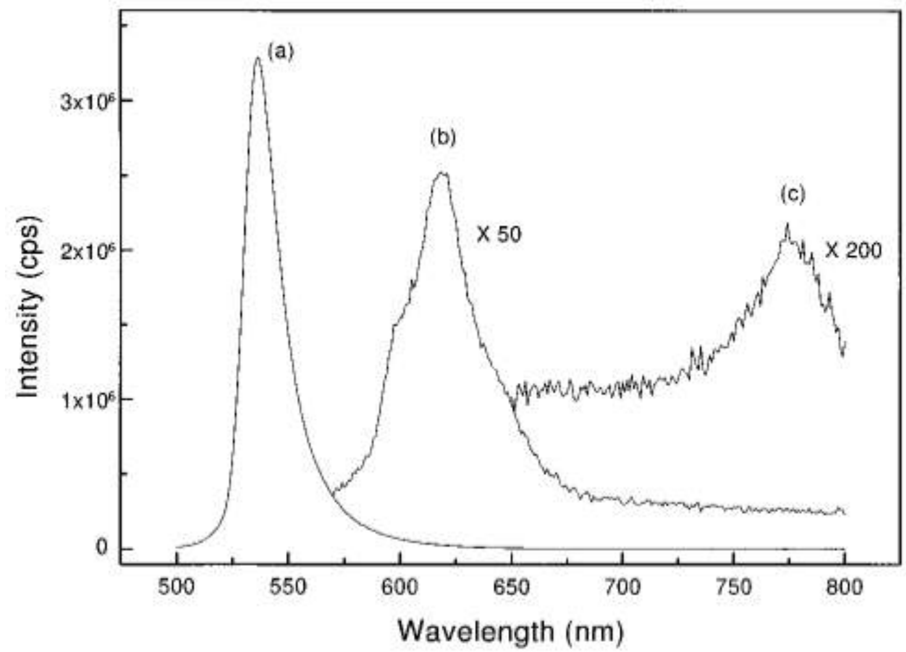


Figure 7. Emission spectra of perovskite thin films prepared using the dipping technique, with an excitation wavelength of 480 nm, for (a) $(C_4H_9NH_3)_2PbI_4$, (b) $(C_4H_9NH_3)_2(CH_3NH_3)Pb_2I_7$, and (c) $CH_3NH_3PbI_3$.

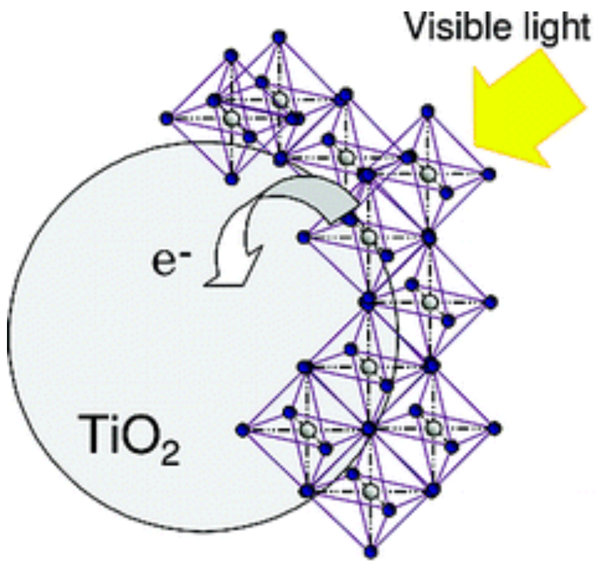
First Solar Cells

Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells

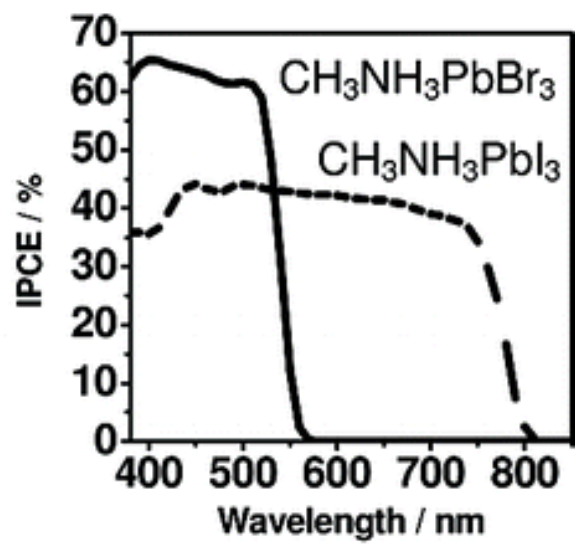
Akihiro Kojima,[†] Kenjiro Teshima,[‡] Yasuo Shirai,[§] and Tsutomu Miyasaka[*,†,‡,∥]

J. AM. CHEM. SOC. 2009, *131*, 6050–6051

Solution-processed sensitizing layer of $MAPbI_3$

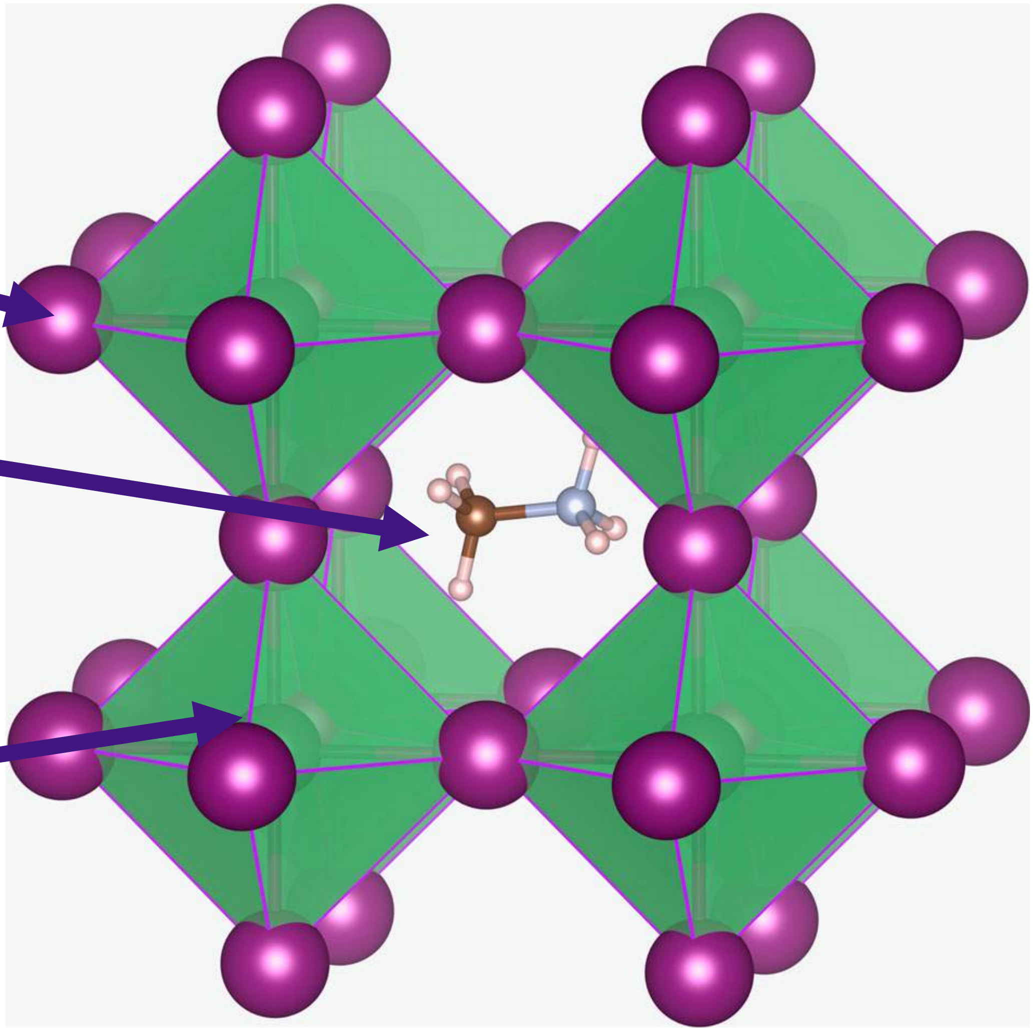


Perovskite nanocrystalline sensitizers



Methylammonium lead iodide

Bandgap 1.6eV



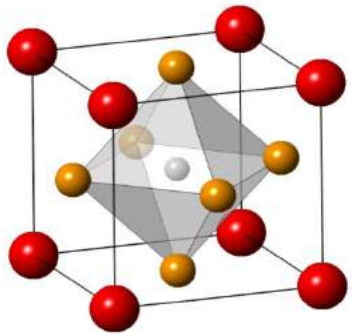
Iodide

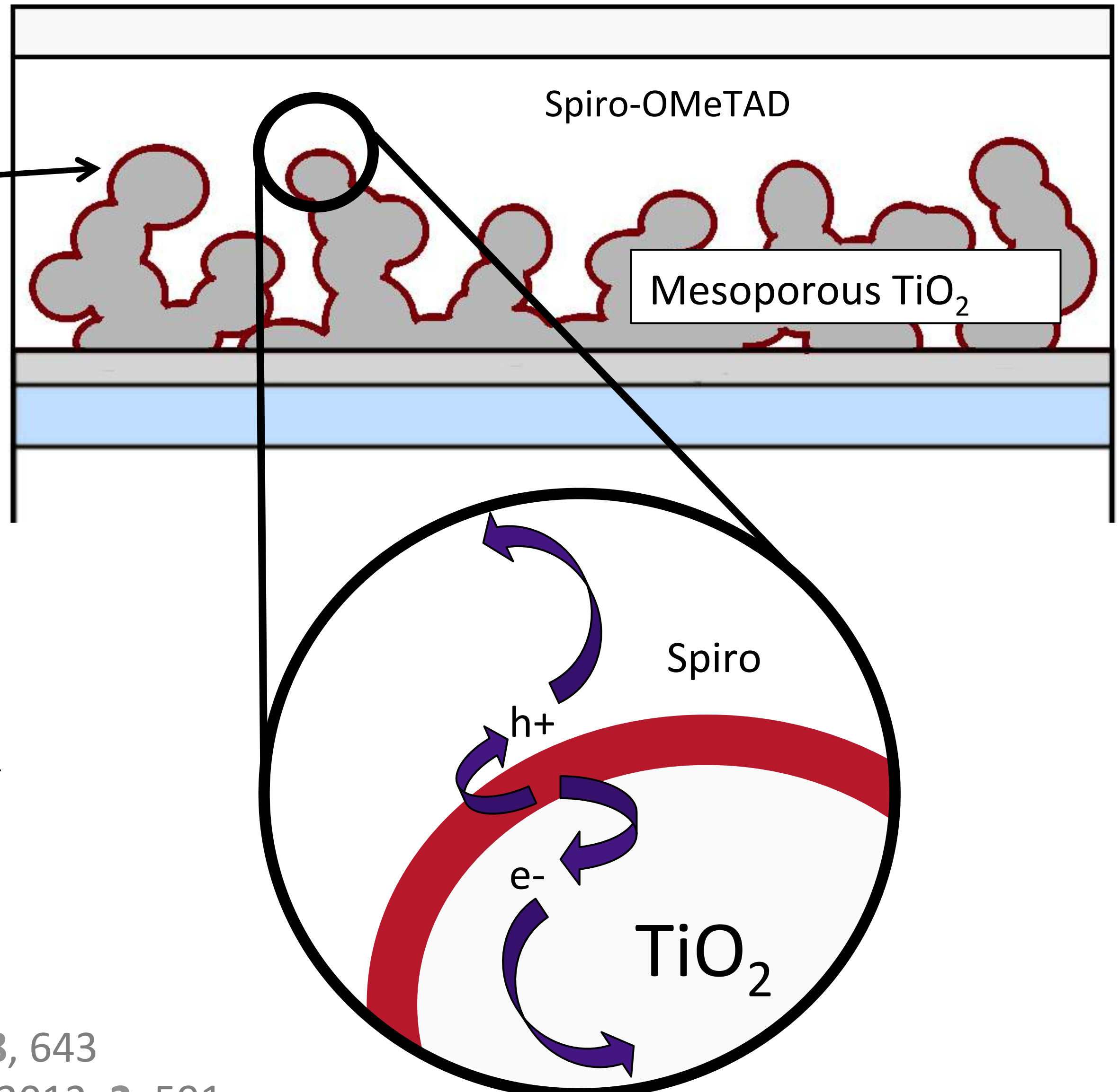
Methylammonium

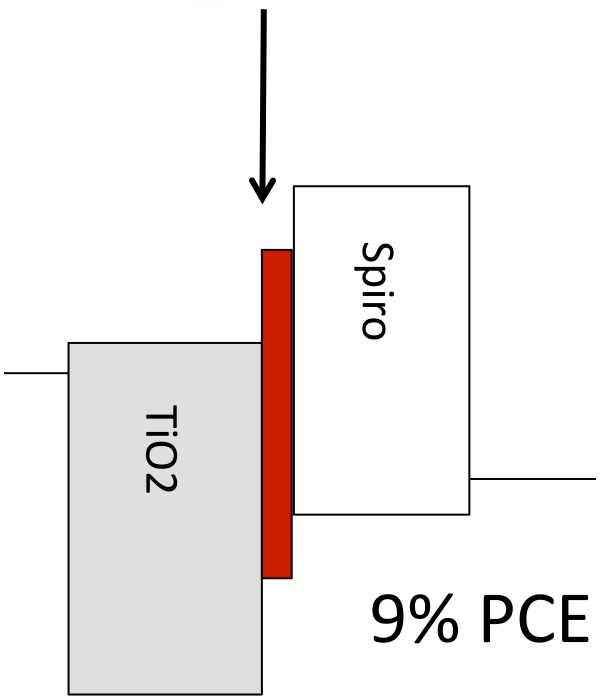
$CH_3NH_3^+$ (MA)

Lead

Solid state hole transporters





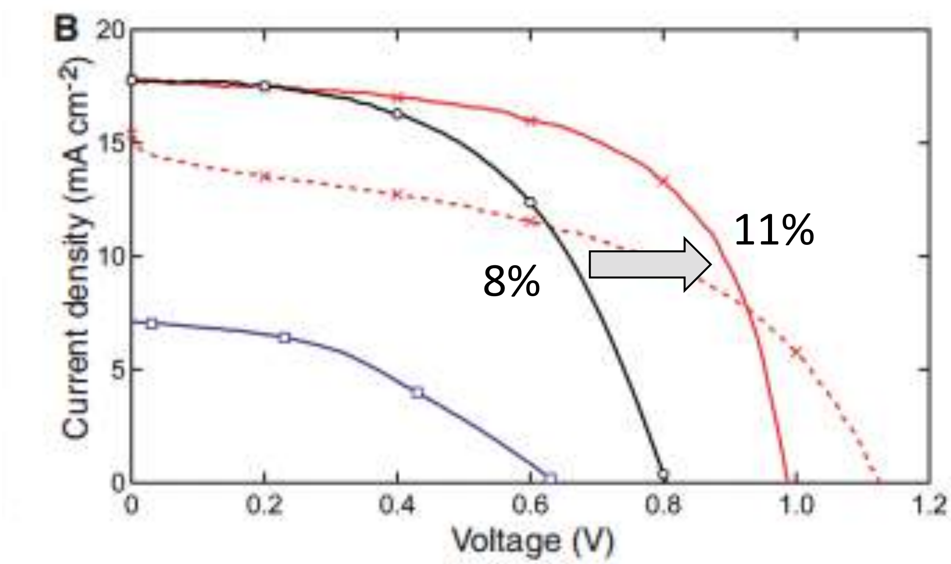


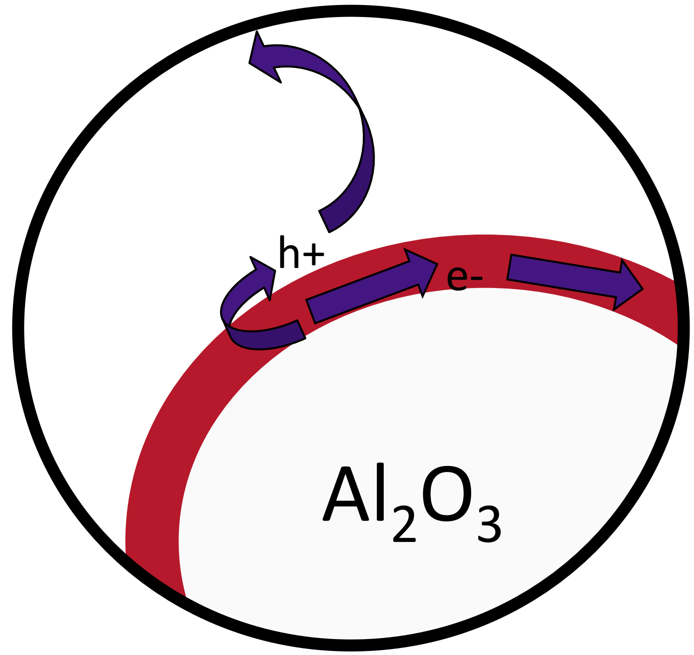
9% PCE

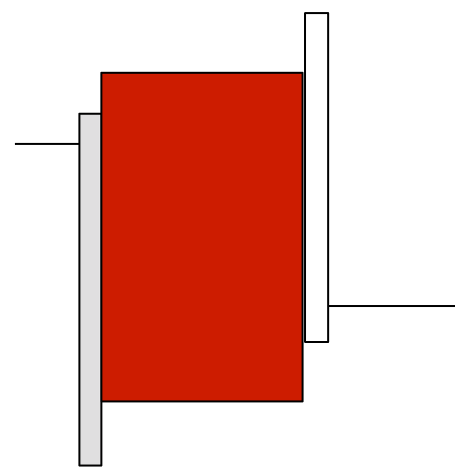
Lee MM et al, *Science* 2012, **338**, 643
Kim H-S et al, *Scientific Reports* 2012, **2**, 591

Transport IN the perovskite

- Found we could replace TiO_2 with inert material (Al_2O_3) and get **more efficient** cells!
- Long-range carrier transport possible within perovskite layer

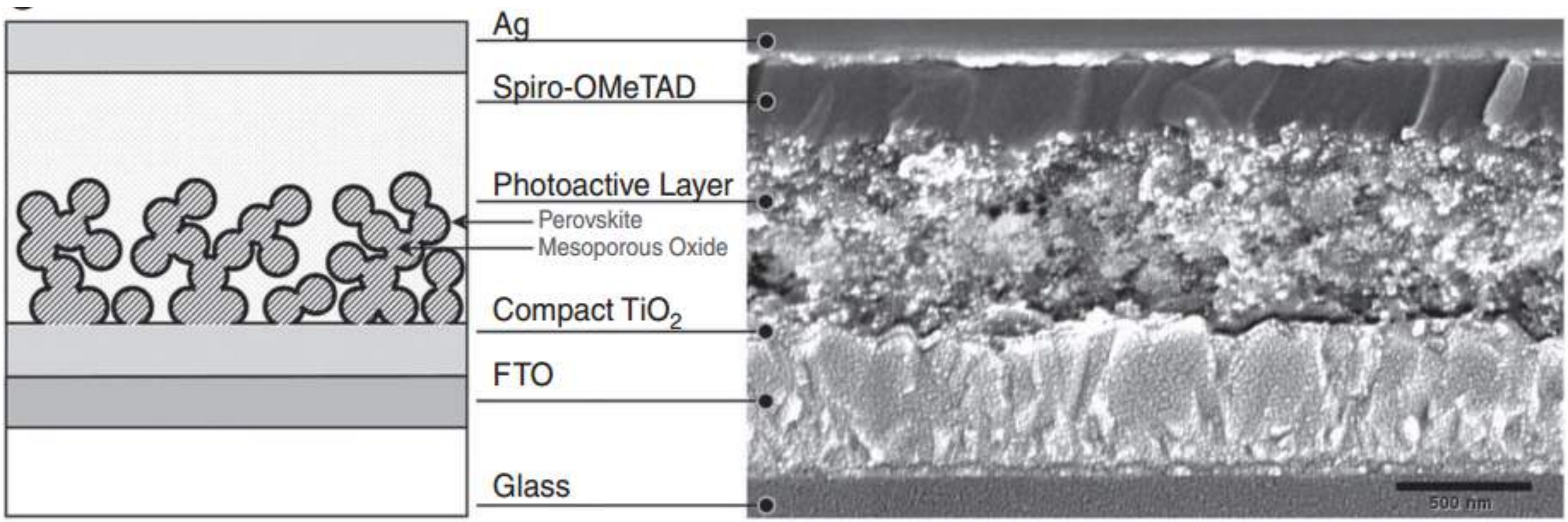




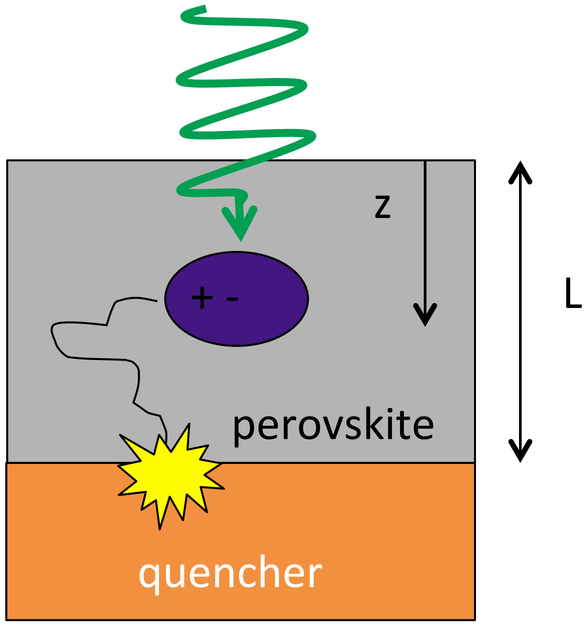


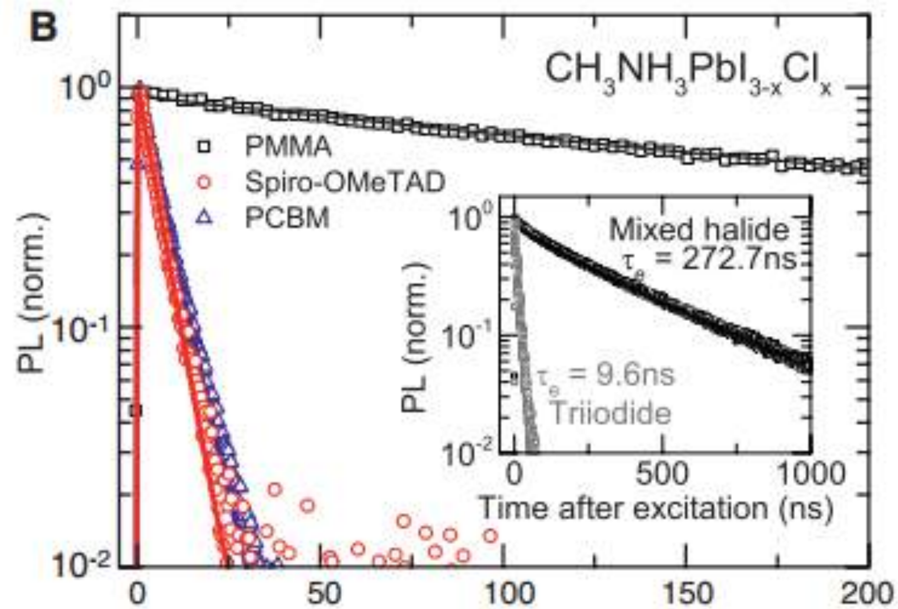
Lee et al, *Science* 2012, **338**, 643
Ball et al, *Energy & Environmental Science* 2013, **6**, 1739

Mesostructured perovskite solar cell



How far can carriers go?





Time (ns)

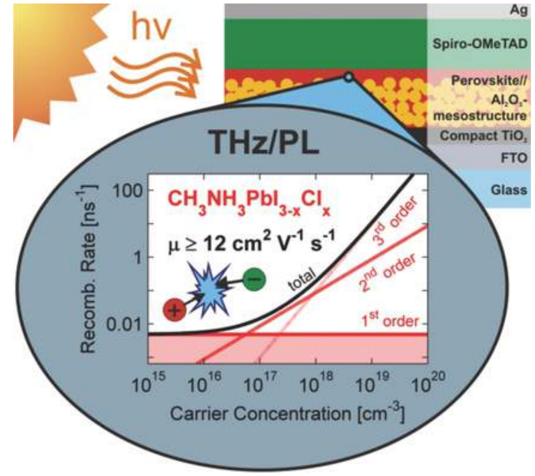
$$\frac{\partial n(z,t)}{\partial t} = D\frac{\partial^2 n(z,t)}{\partial z^2} - k(t)n(z,t)$$

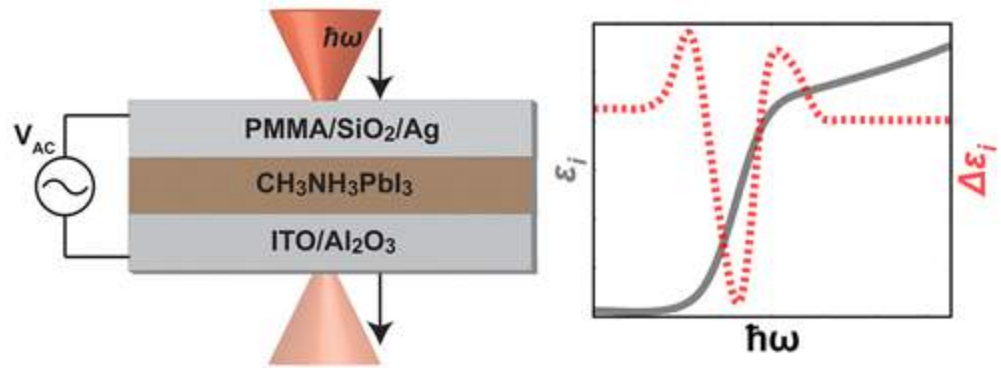
Diffusion length for electrons **and holes** > 1um

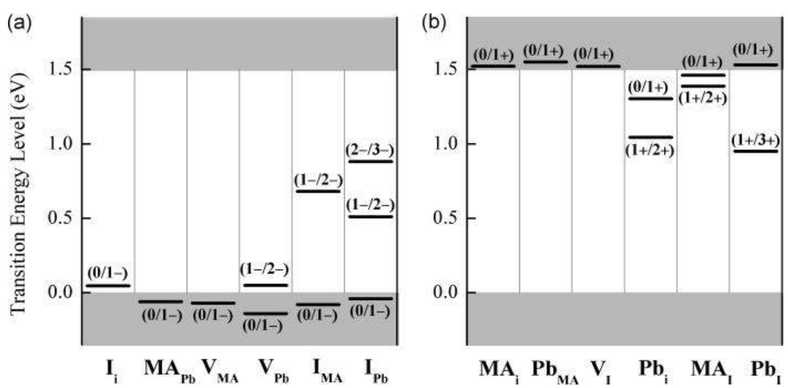
Stranks, Snaith, et al, *Science*, 2013
Dong, Huang, et al, *Science* 2015

Perovskite physical parameters

- Long PL lifetimes – 500ns+
- Mobility – 10-30cm^{2}V^{-1}s^{-1}
- Exciton binding energy – 5-10meV
- PLQE – 30%+
- Defect tolerance



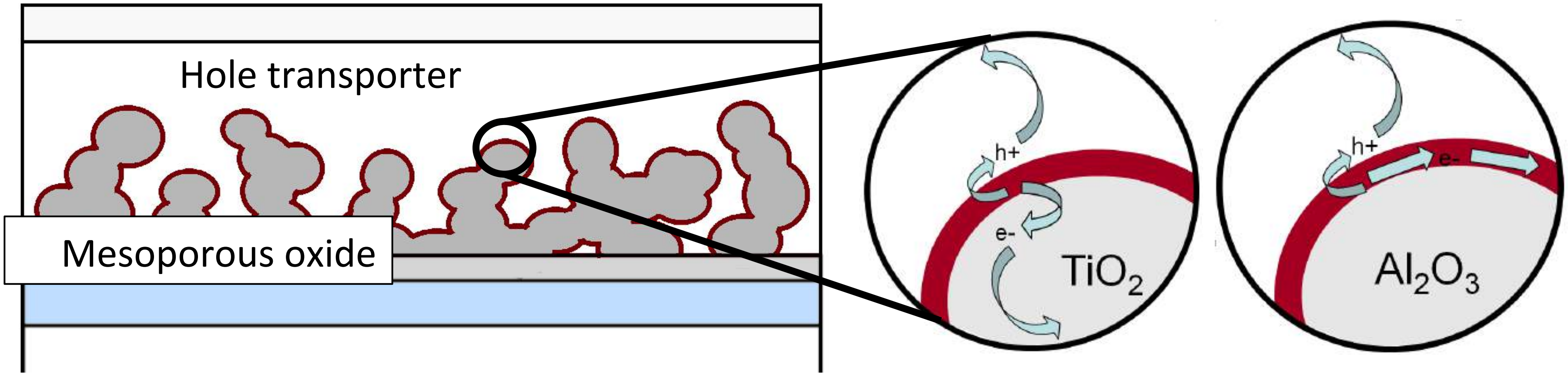




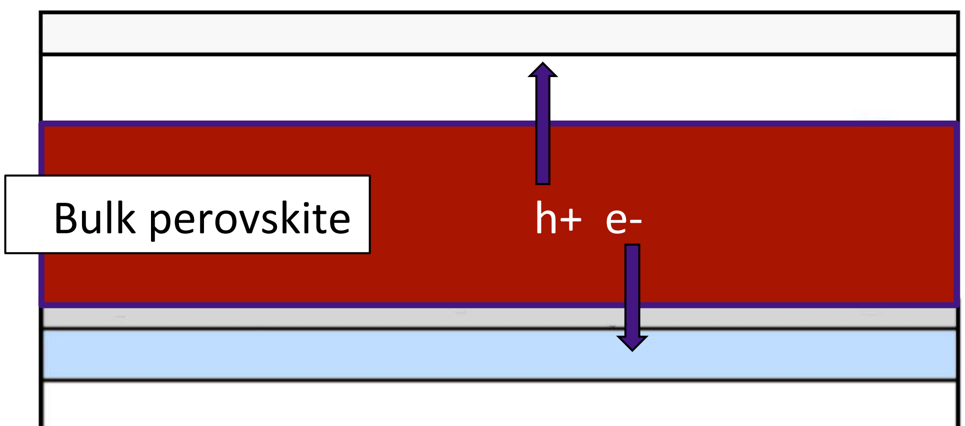
Wehrenfennig et al, Adv Mat 2013; Ziffer et al, ACS Phot. 2016; Deschler et al JPCL 2014; Yin et al APL 2014

What's this mesostructure doing?

- Mesostructured approaches have shown efficiency up to **>15%**

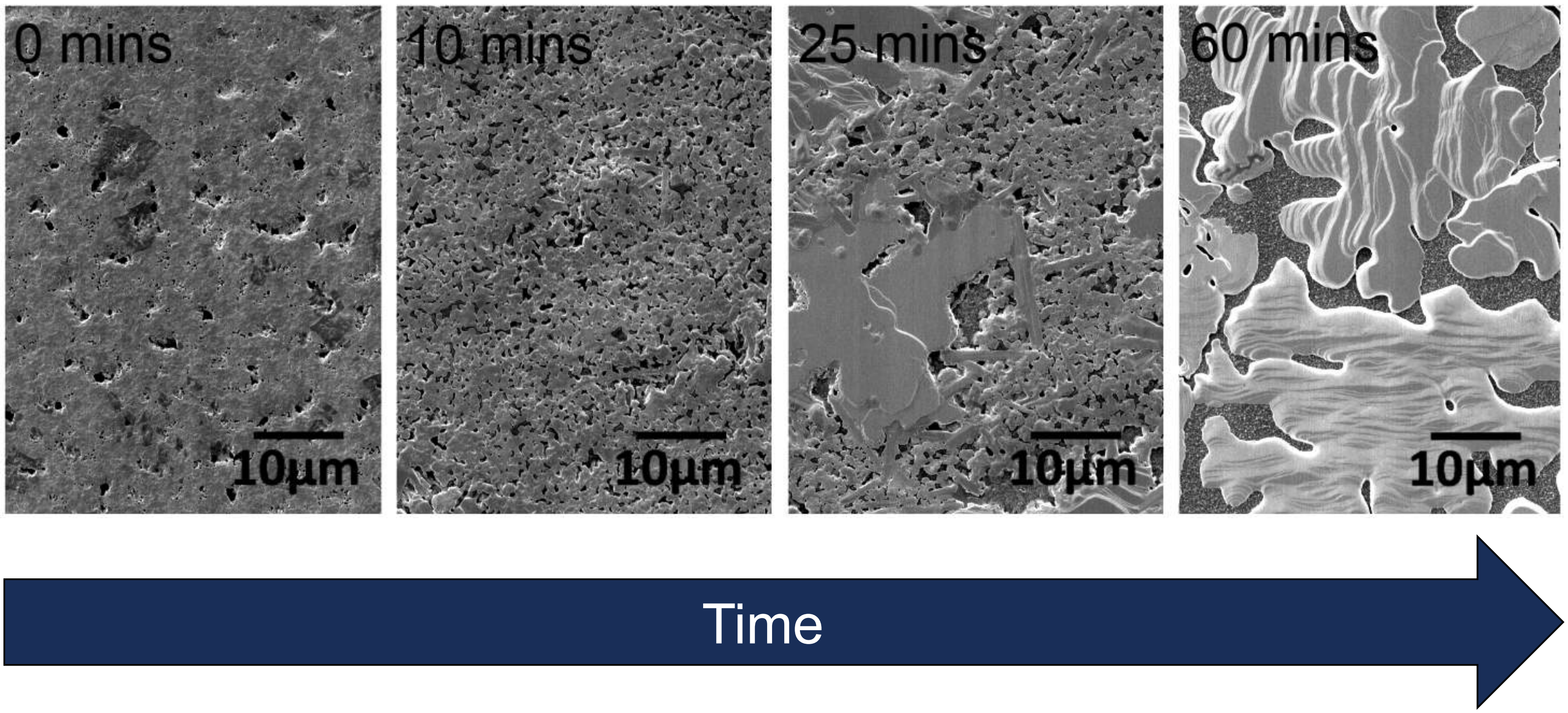


- 'Flat' solution-processed films only up to **5%** efficient so far



Kim H-S et al, *Scientific Reports* 2012
Ball et al, *Energy & Environmental Science* 2013

Dewetting during annealing limited planar junctions

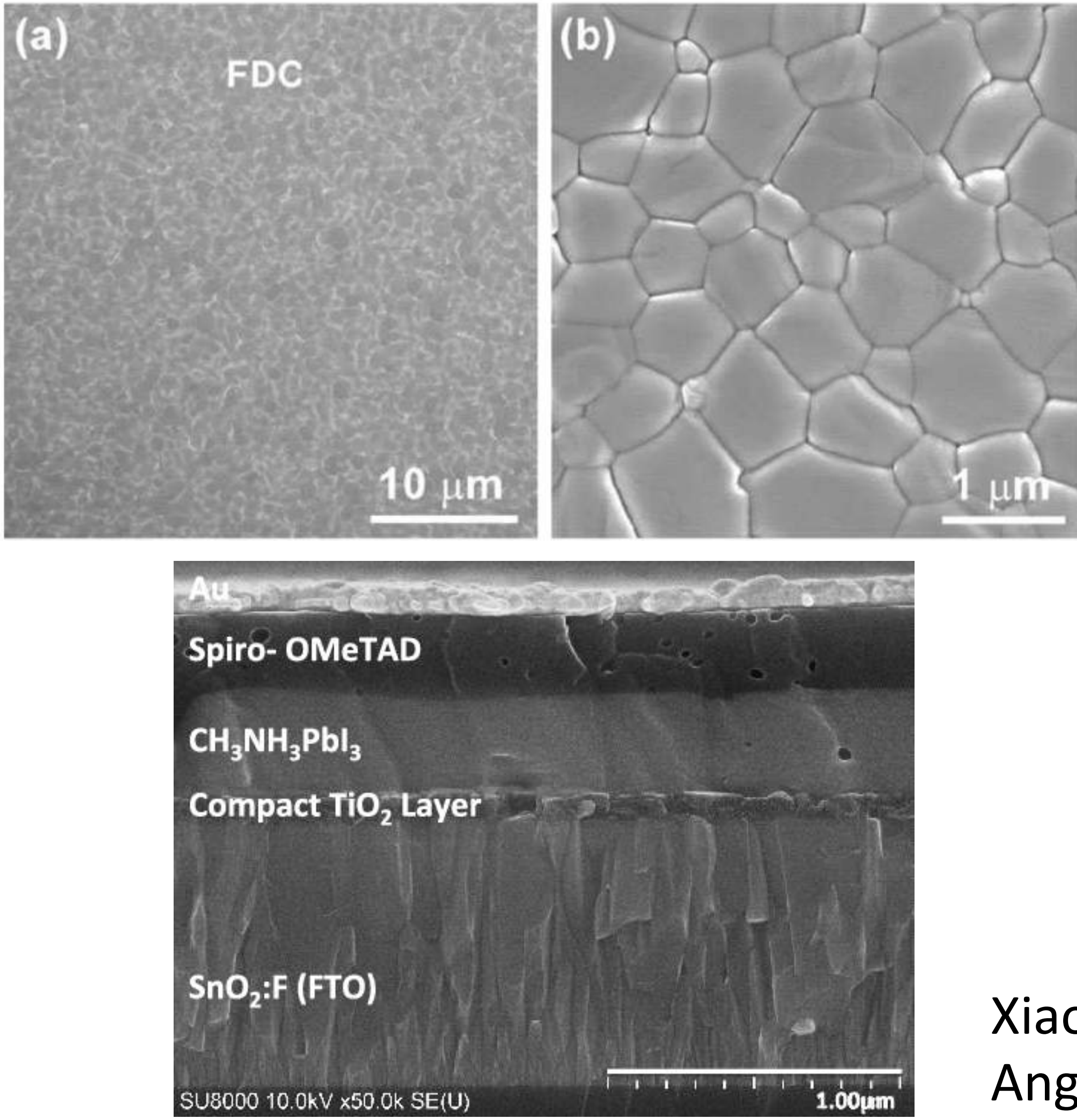


As spin-coated

Final crystallized perovskite

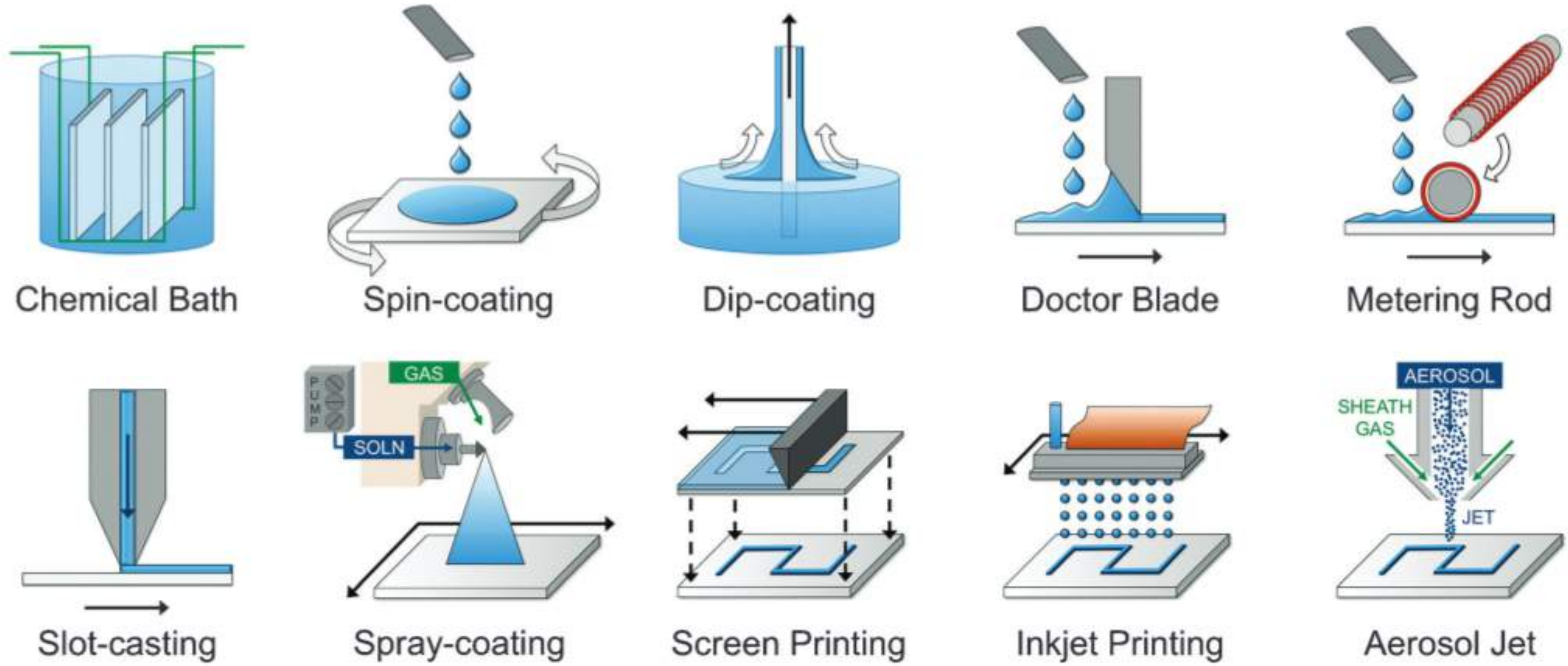
Eperon GE, Snaith HJ et al, *AFM* 2013

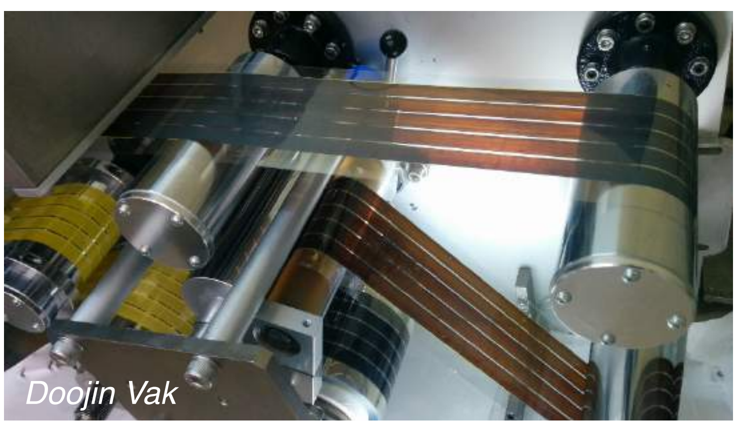
Now, high quality polycrystalline films



Xiao, Spiccia et al, Angewandte 2014

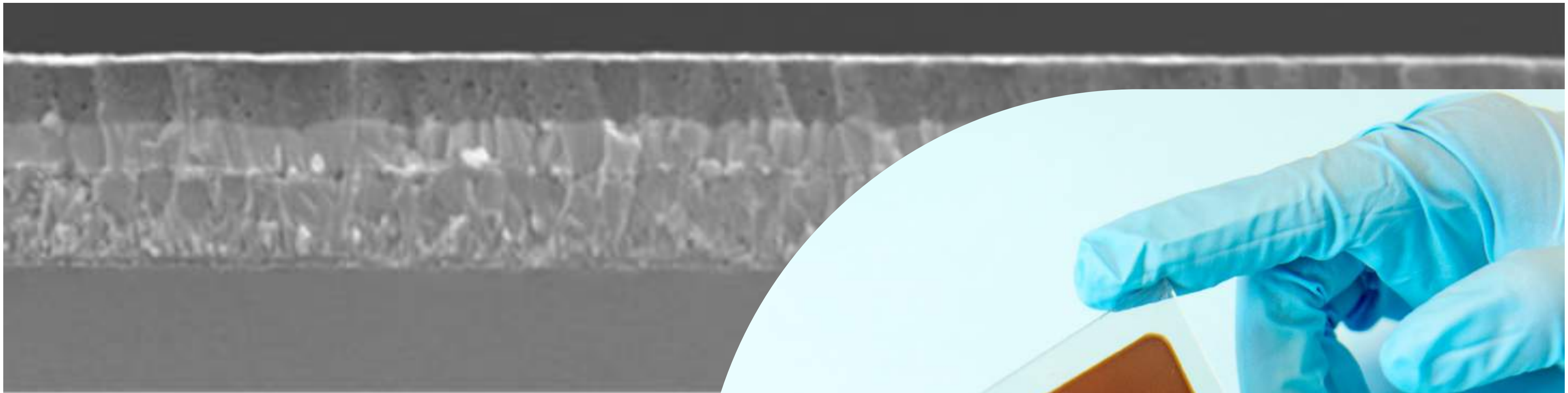
Solution processing options

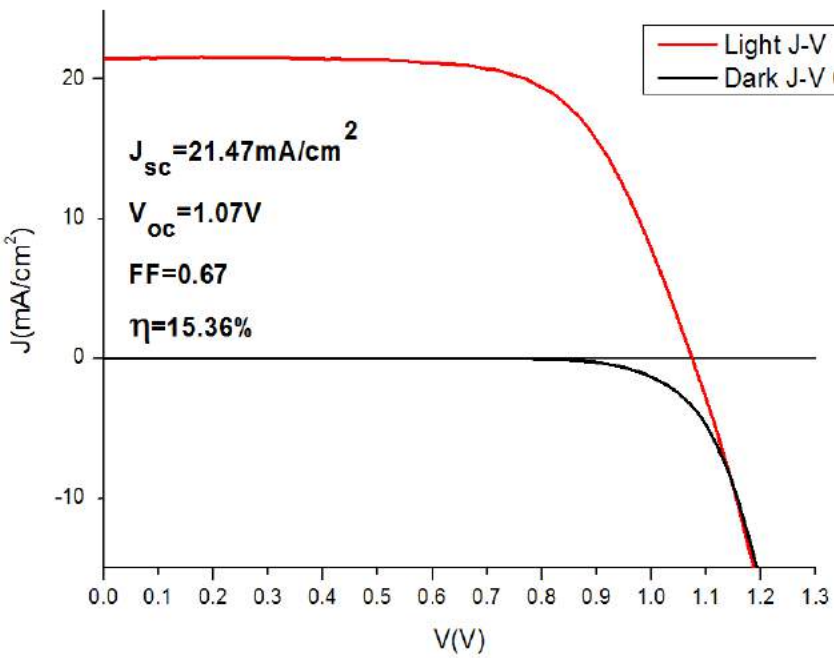


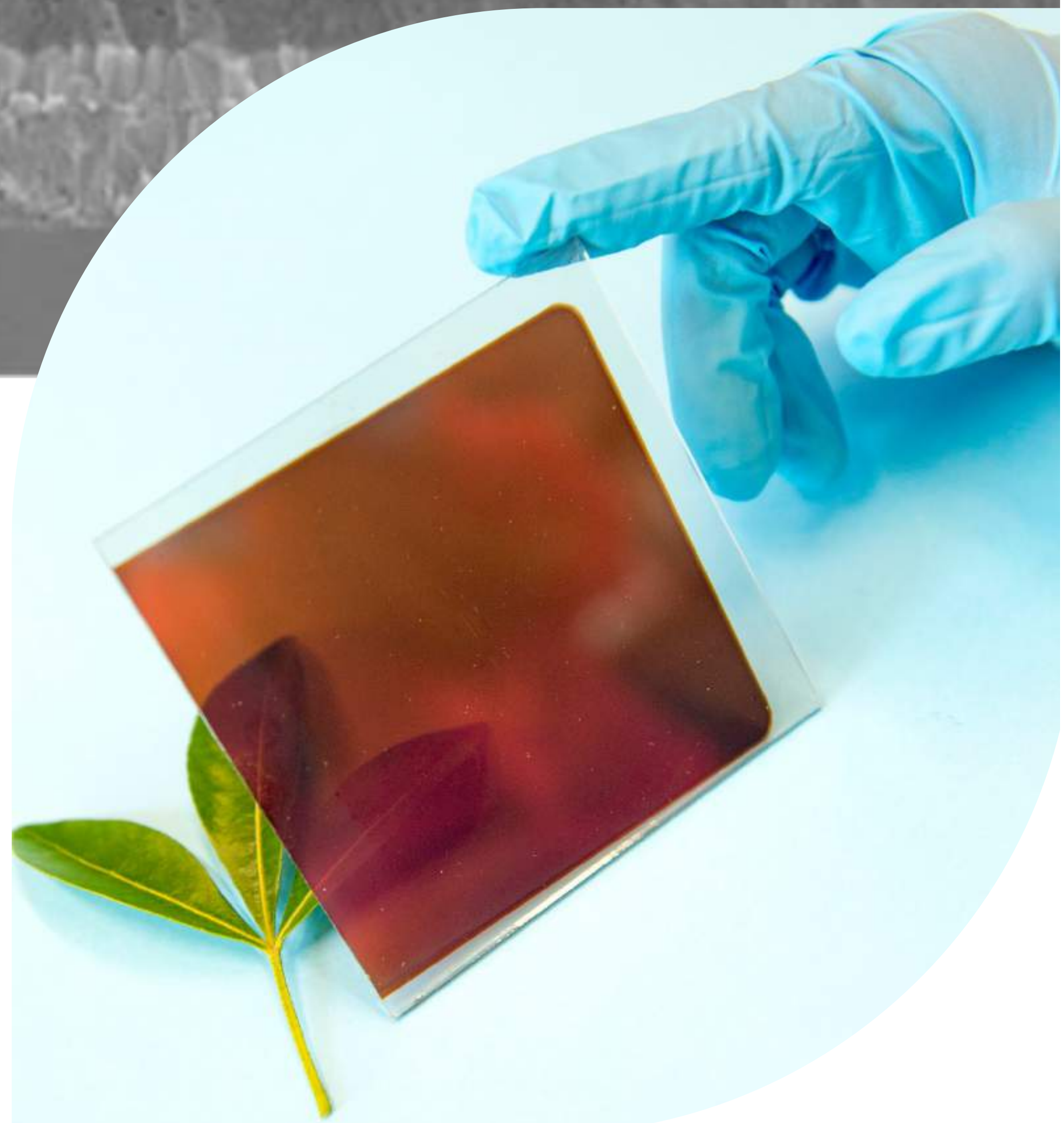


Pasquarelli et al, Chem Soc Rev 2011

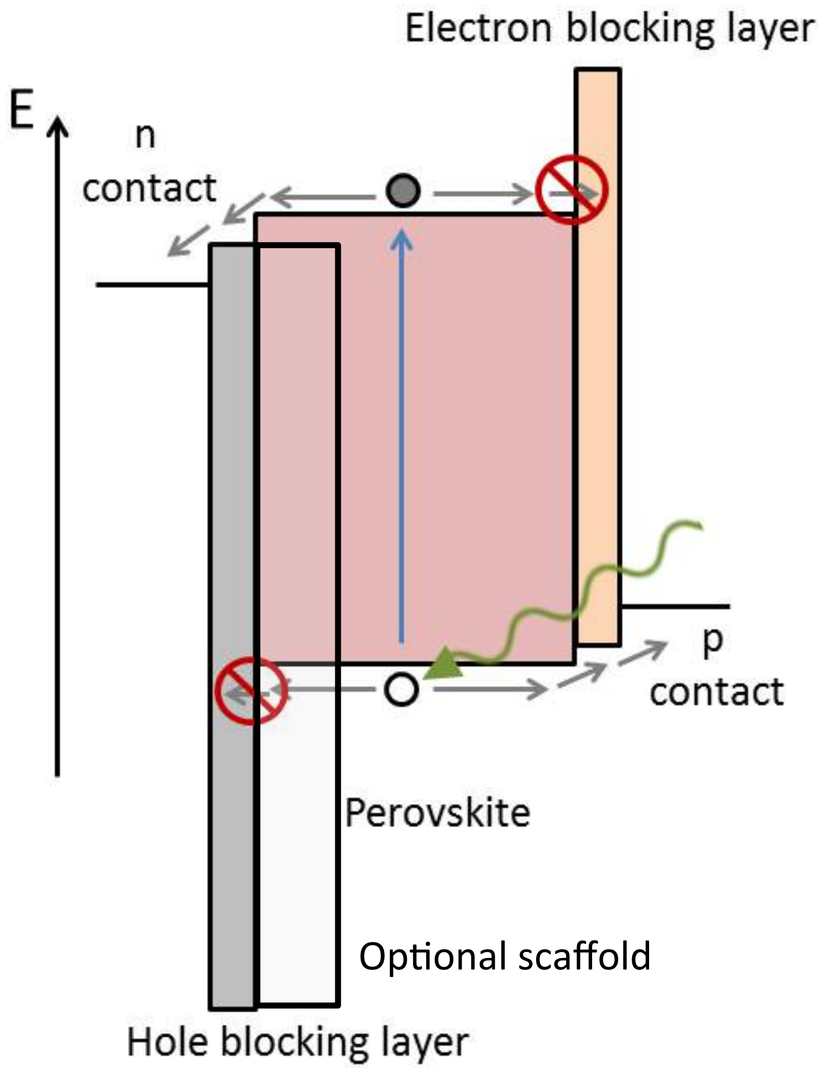
Can also evaporate perovskites







Perovskite solar cells – operation

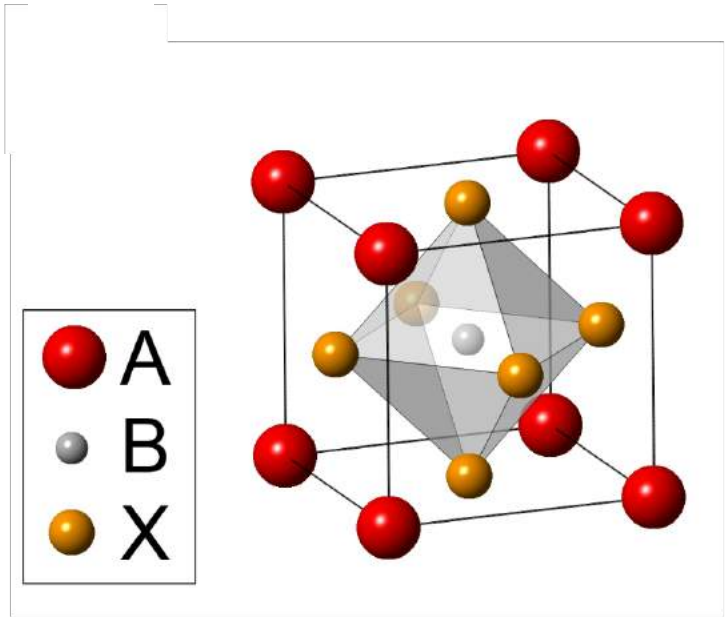


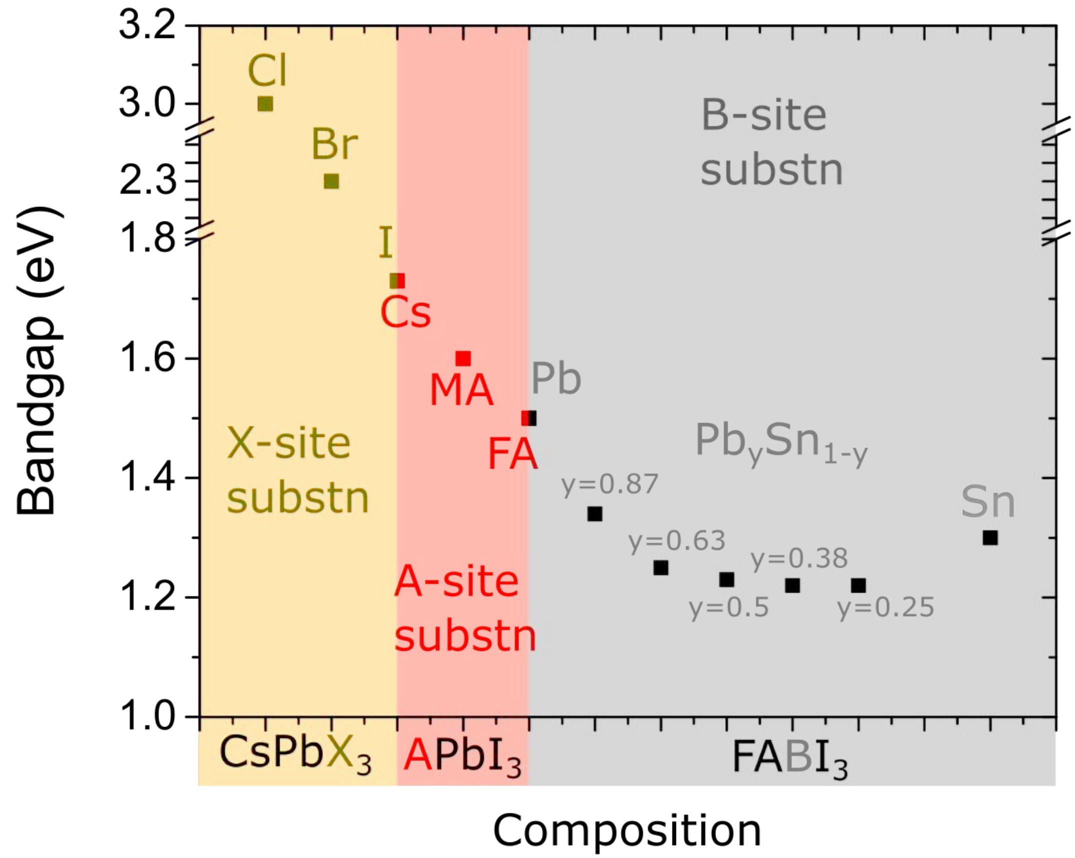
N-type contacts:
- TiO_2, SnO_2, PCBM, C60, PEIE, polyTPD

P-type contacts
- Spiro-OMeTAD, NiO_x, V_2O_5 PEDOT:PSS, CuSCN, CuI, MoO_x, P3HT…

Miyata et al, Nat Phys 2015

Tuneable bandgaps allow more ideal materials





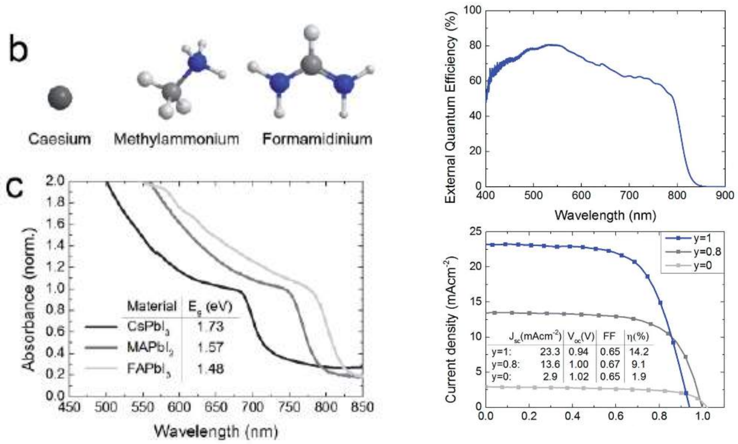
Bandgap tuneable smoothly between 1.2 and 3.0eV

More advances continually made…

Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells†

Energy Environ. Sci., 2014, **7**, 982–988 | **983**

Giles E. Eperon, Samuel D. Stranks, Christopher Menelaou, Michael B. Johnston, Laura M. Herz and Henry J. Snaith*



LETTERS
PUBLISHED ONLINE: 22 DECEMBER 2013 | DOI: 10.1038/NPHOTON.2013.341
nature photonics

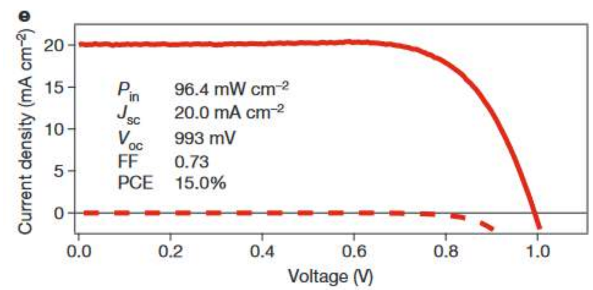
Perovskite solar cells employing organic charge-transport layers

Olga Malinkiewicz[1], Aswani Yella[2], Yong Hui Lee[2], Guillermo Mínguez Espallargas[1], Michael Graetzel[2], Mohammad K. Nazeeruddin[2]* and Henk J. Bolink[1]*

LETTER
doi:10.1038/nature12340

Sequential deposition as a route to high-performance perovskite-sensitized solar cells

Julian Burschka[1]*, Norman Pellet[1,2]*, Soo-Jin Moon[1], Robin Humphry-Baker[1], Peng Gao[1], Mohammad K. Nazeeruddin[1] & Michael Grätzel[1]

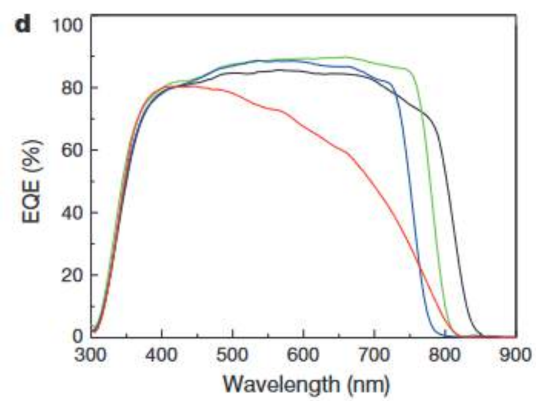


LETTER
doi:10.1038/nature14133

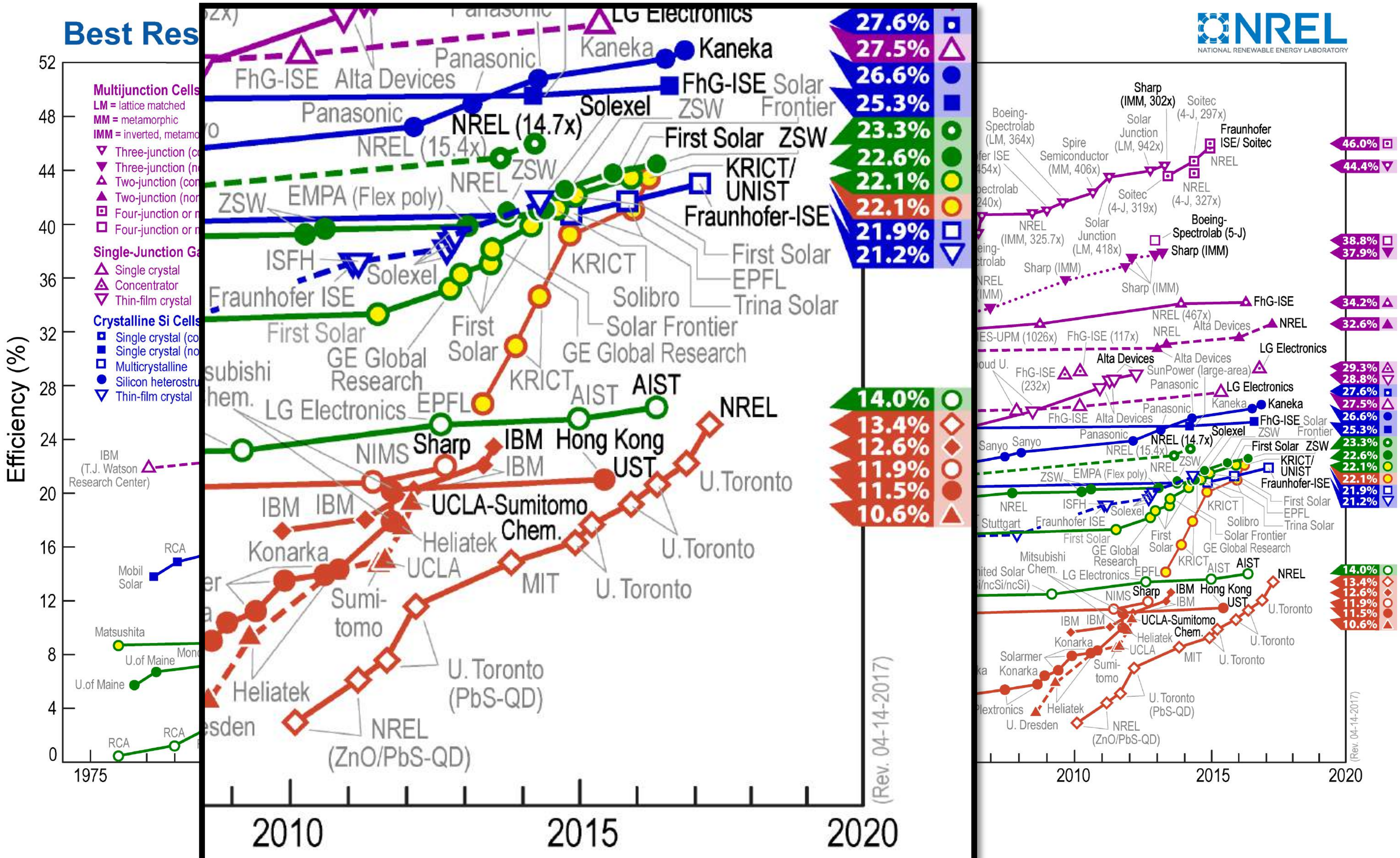
Compositional engineering of perovskite materials for high-performance solar cells

Nam Joong Jeon[1]*, Jun Hong Noh[1]*, Woon Seok Yang[1], Young Chan Kim[1], Seungchan Ryu[1], Jangwon Seo[1] & Sang Il Seok[1,2]

476 | NATURE | VOL 517 | 22 JANUARY 2015

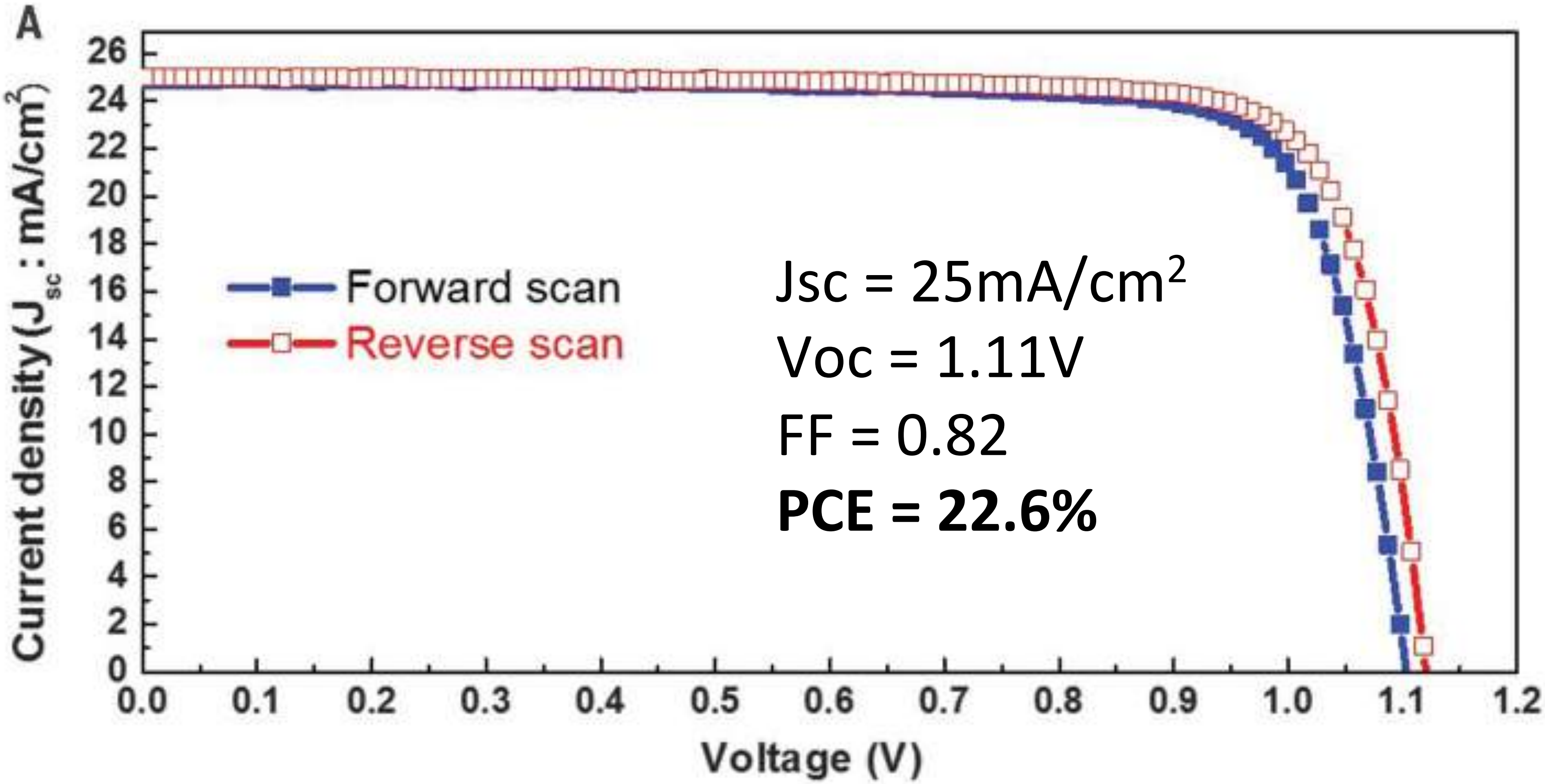


Rapid progress



https://www.nrel.gov/pv/assets/images/efficiency-chart.png

Current-voltage characteristics



J_{sc} = 25mA/cm^2

V_{oc} = 1.11V

FF = 0.82

PCE = 22.6%

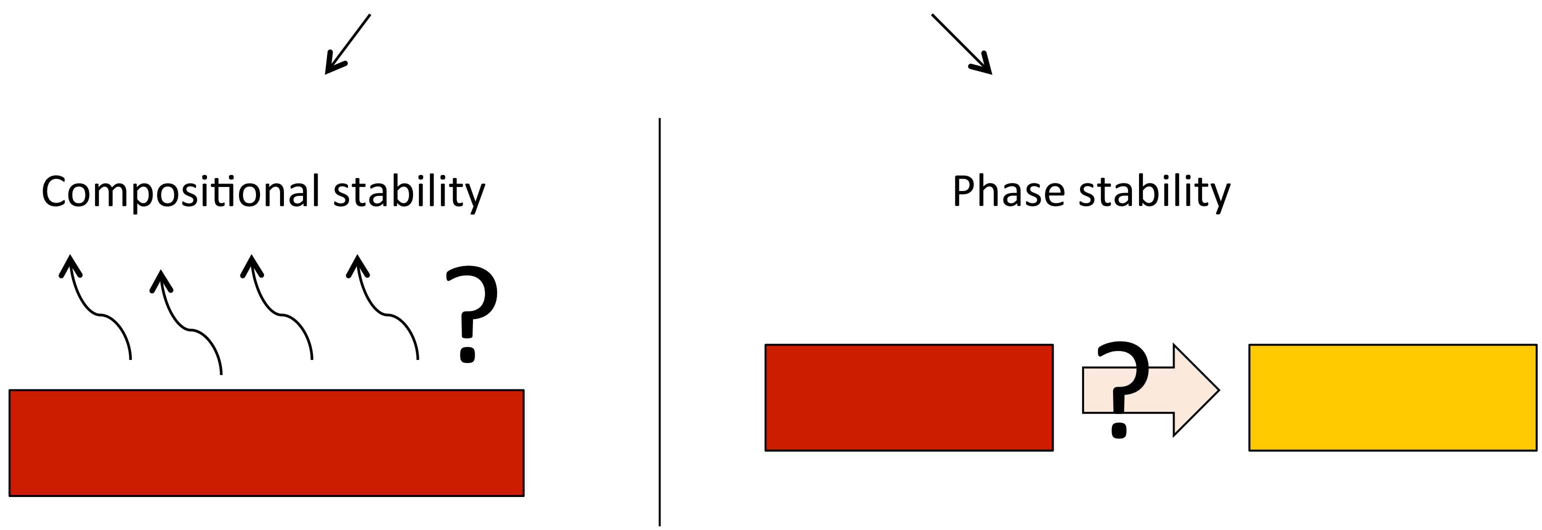
$FAPbI_3$ perovskite

Seok et al, Science 2017

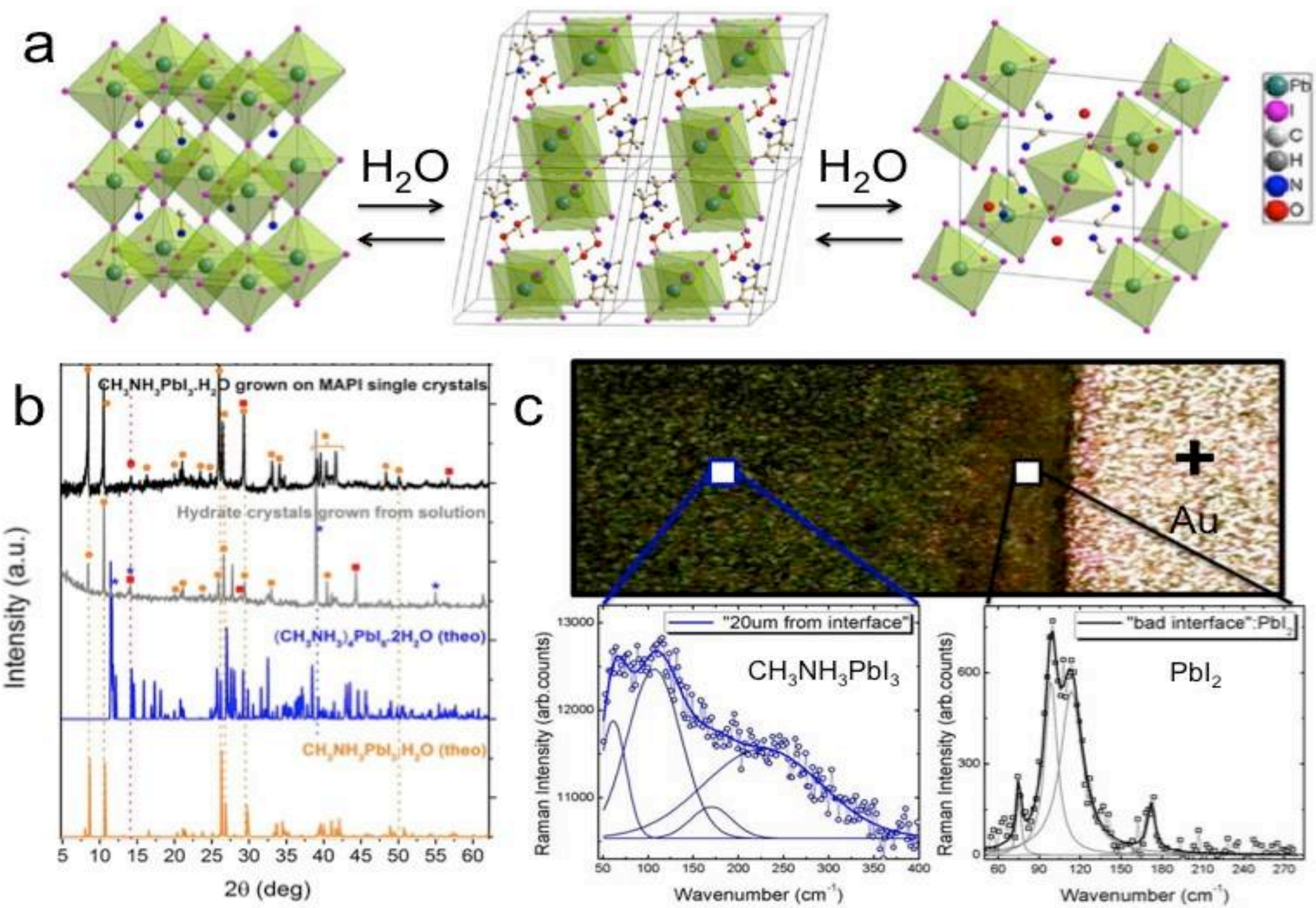
ARE PEROVSKITES ‘STABLE’?

Stability

- **Stability to ambient atmosphere**
- **Biasing stability**
- **Optical stability**
- **Thermal stability: need -40^{o}C to 85^{o}C cycling stability for international IEC standards**

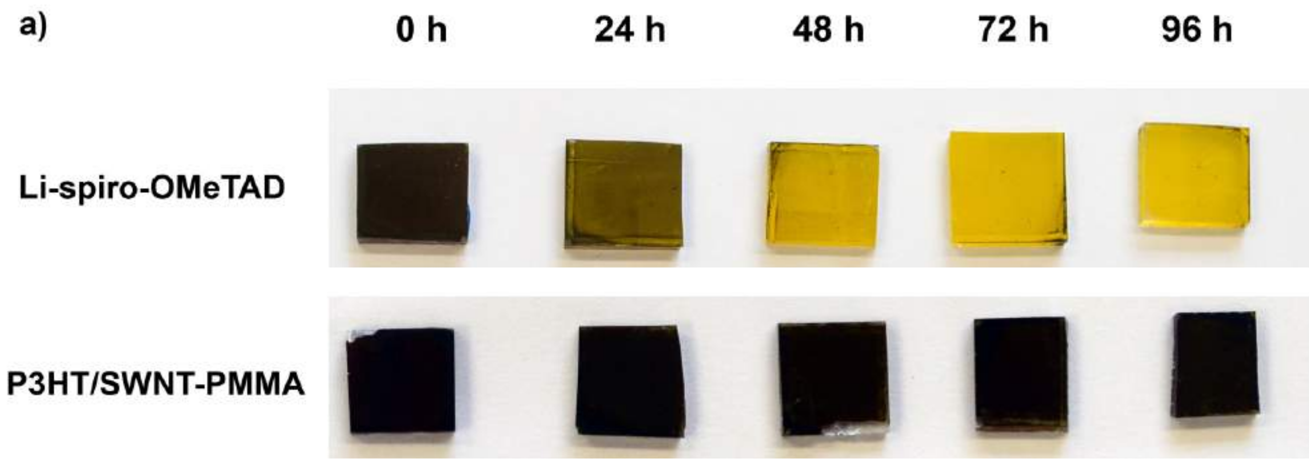


Ambient Sensitivity - moisture



A. Leguy, …… T. Bein, J. Nelson, P. Docampo, P. R. F. Barnes, *Chem. Mater.* **2015**

Ambient atmosphere stability

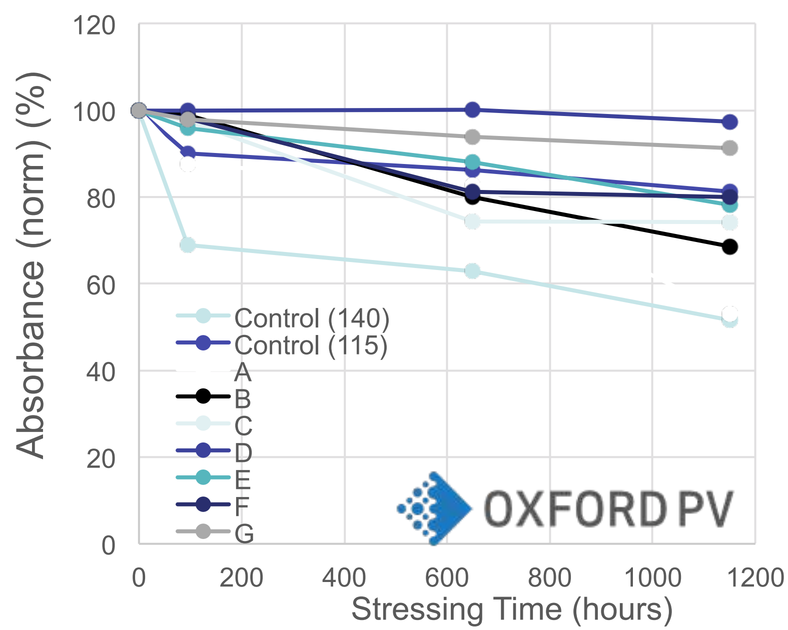


Solution 1:

Employ a top charge transporter which protects the perovskite

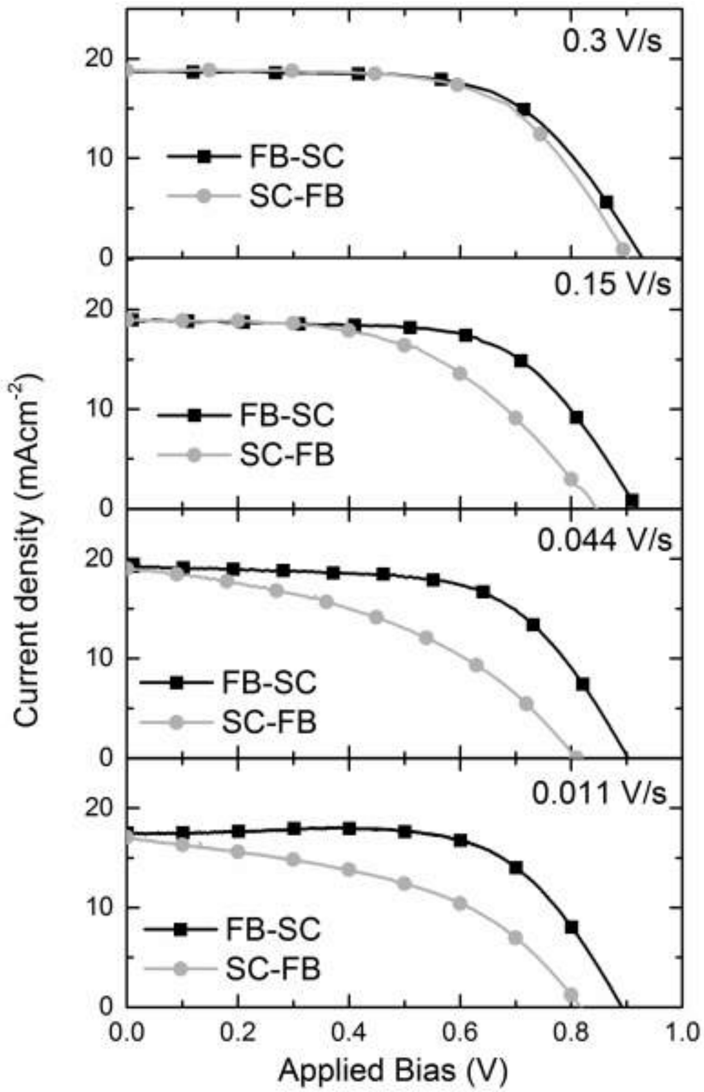
Solution 2:
Encapsulate the devices well

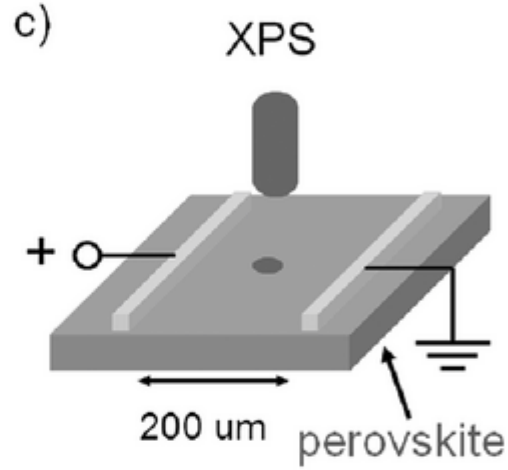
Encapsulation selection using 1000hr 85^{o}C/85% baseline

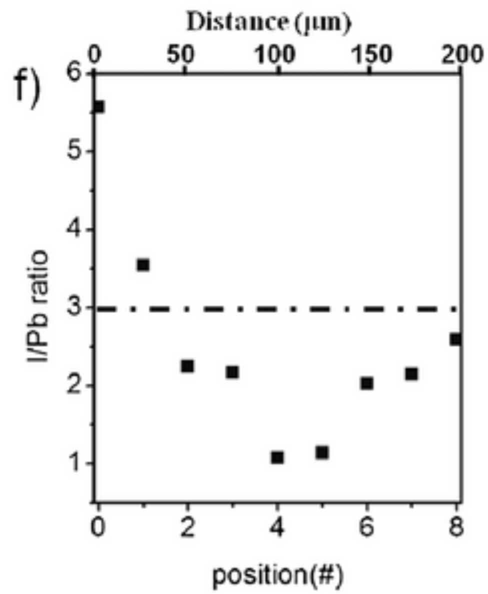


Habisreutinger et al, Nano Lett 2014

Electrical stability – ion motion





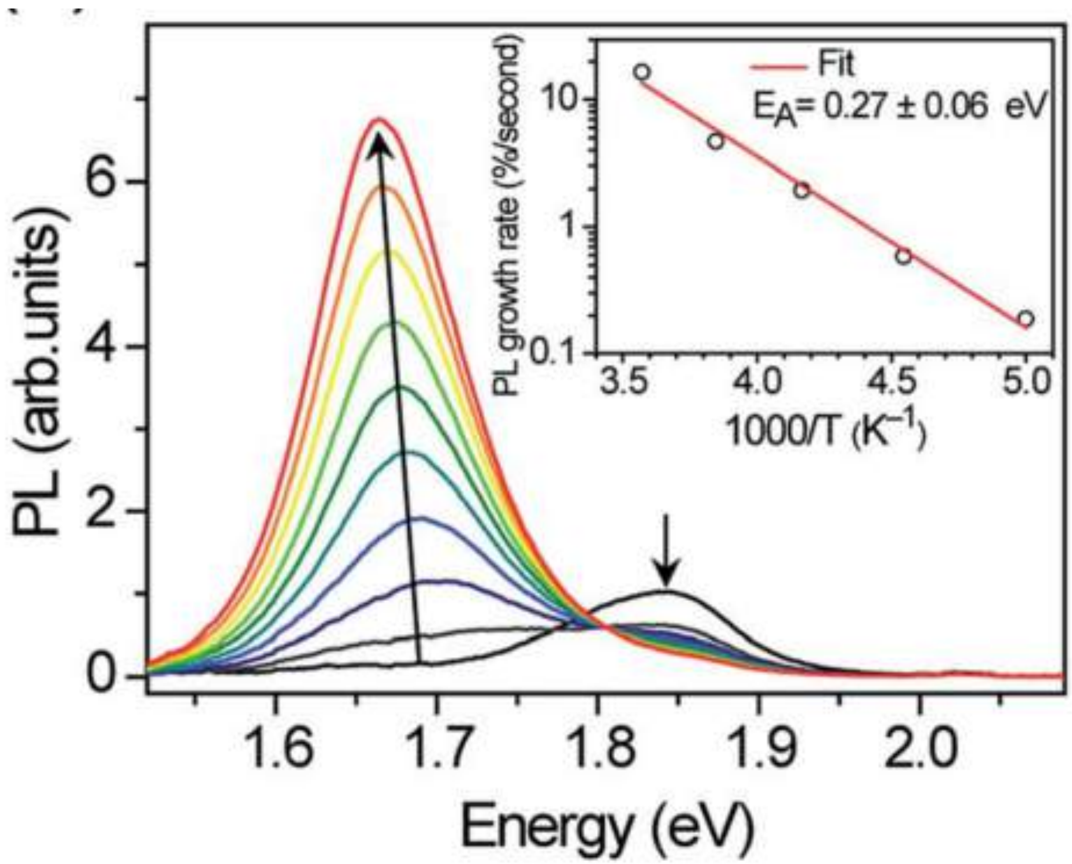


E_A ~ 0.23eV for iodide ion movement

Is this facile movement of lattice constituents problematic?

Li et al, Adv mat 2016
Snaith et al, JPCL 2014

Stability under light – halide segregation

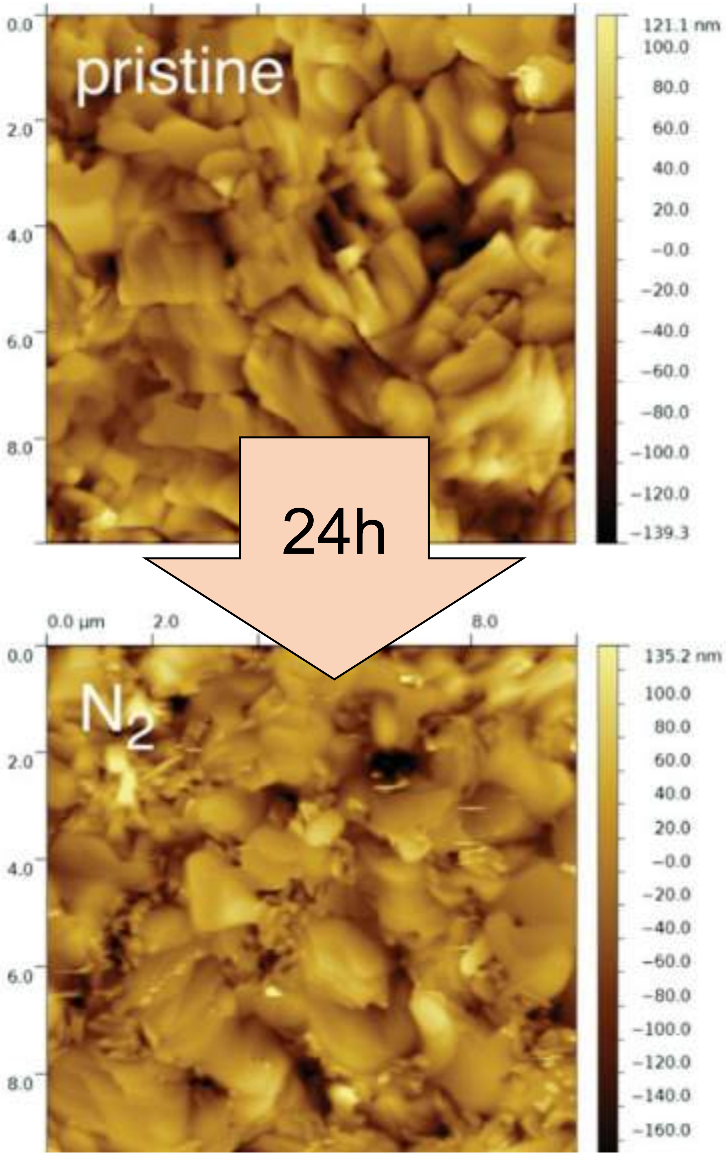


Mixed halides shown to have strong PL shifts under illumination, corresponding to halide segregation.

Will critically limit voltage to the lowest value of bandgap

Hoke et al, Chem Sci, 2014

Thermal stability: MA critically unstable at 85ºC

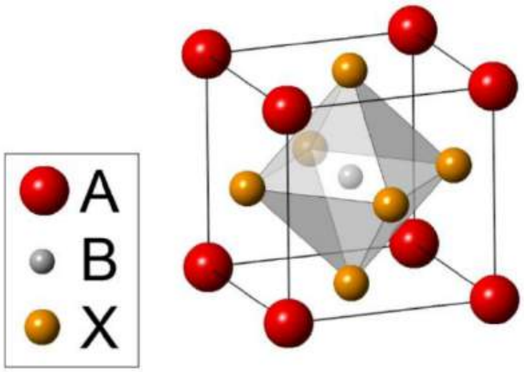


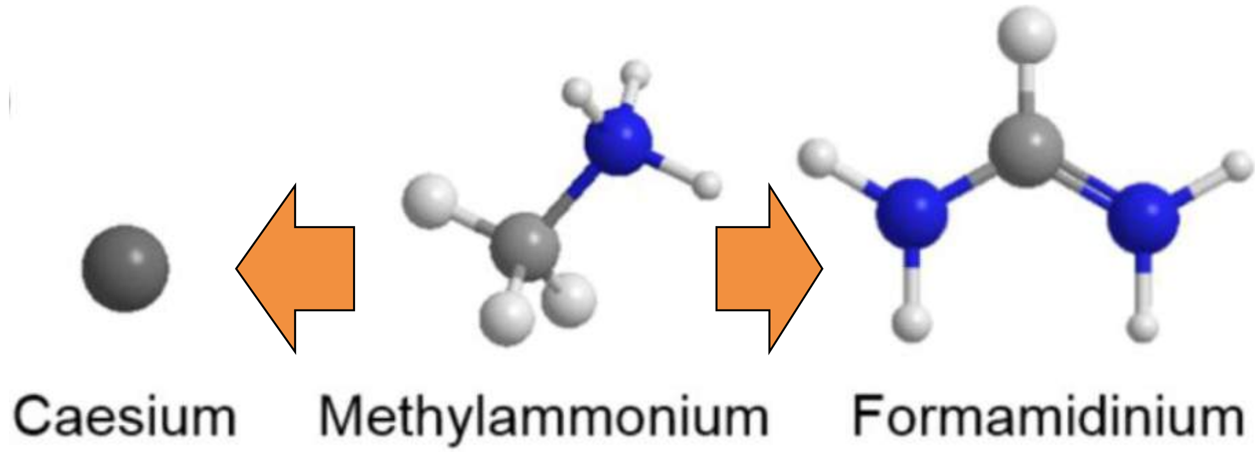
From Conings et al, Adv En. Mat, 2015

Even under pure N_2, MA lost at 85ºC!

How can we avoid this?

Replace MA…?

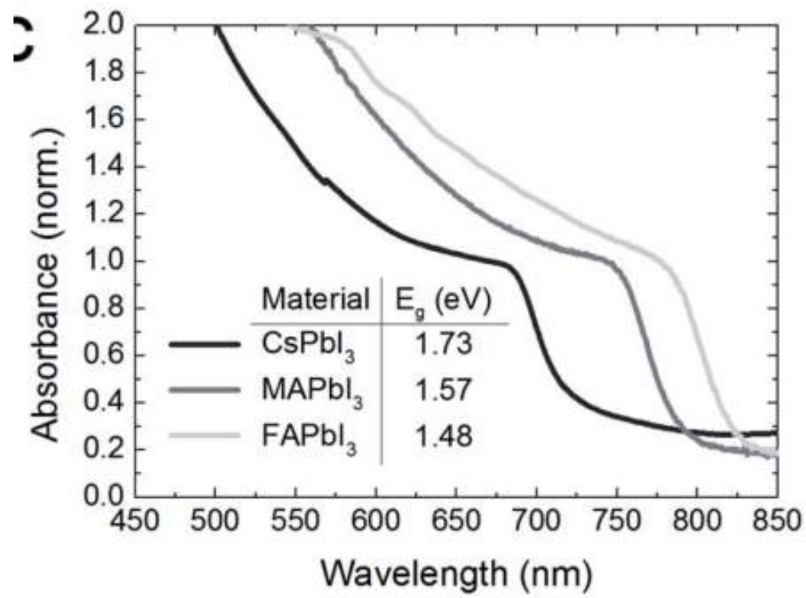




$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_x)}$$

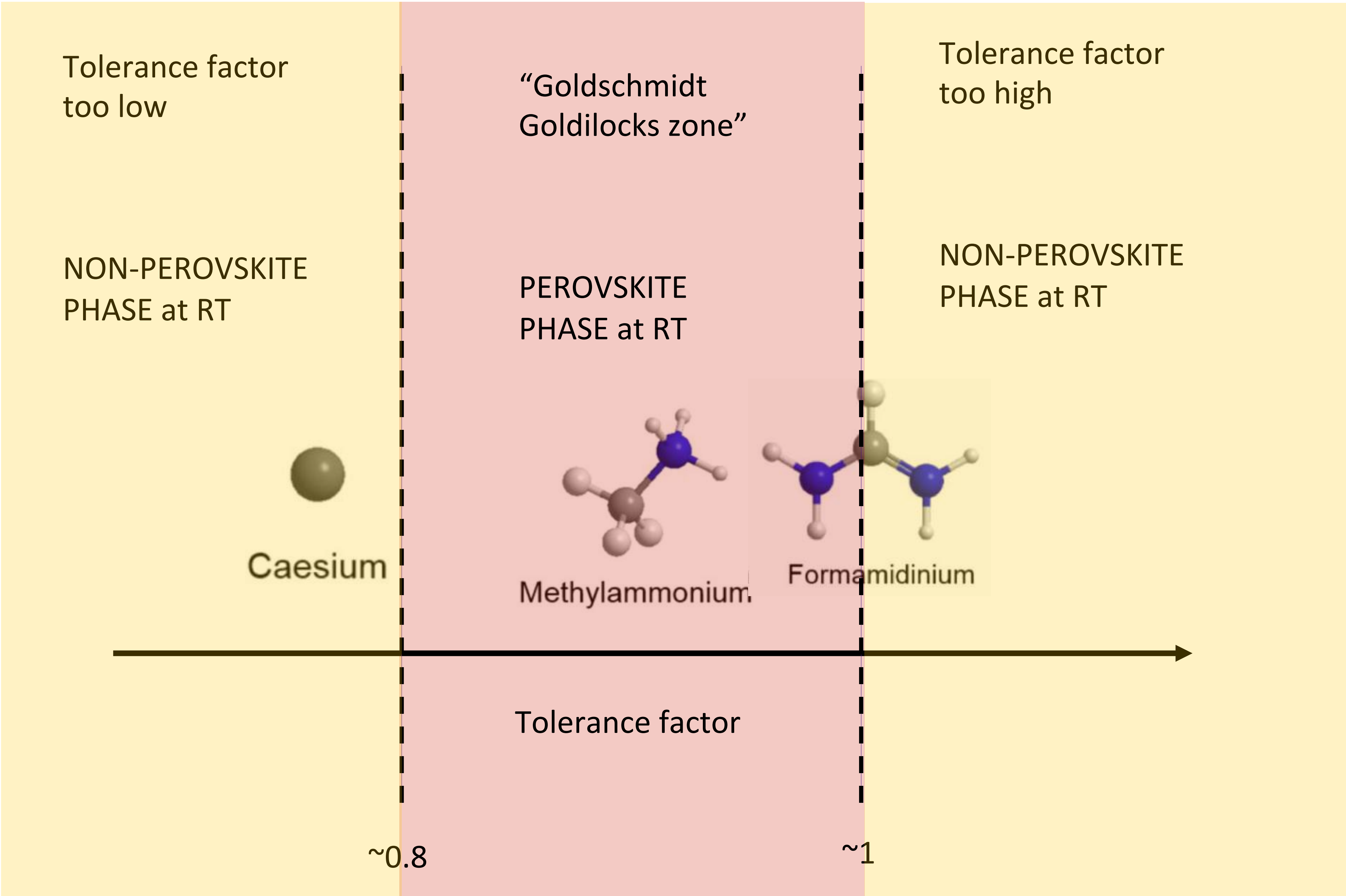
r_A, r_B, r_X correspond to the ionic radii of the 3 components

Tolerance factor between ~ 0.8 and 1.0 allow cubic perovskite at room temp.

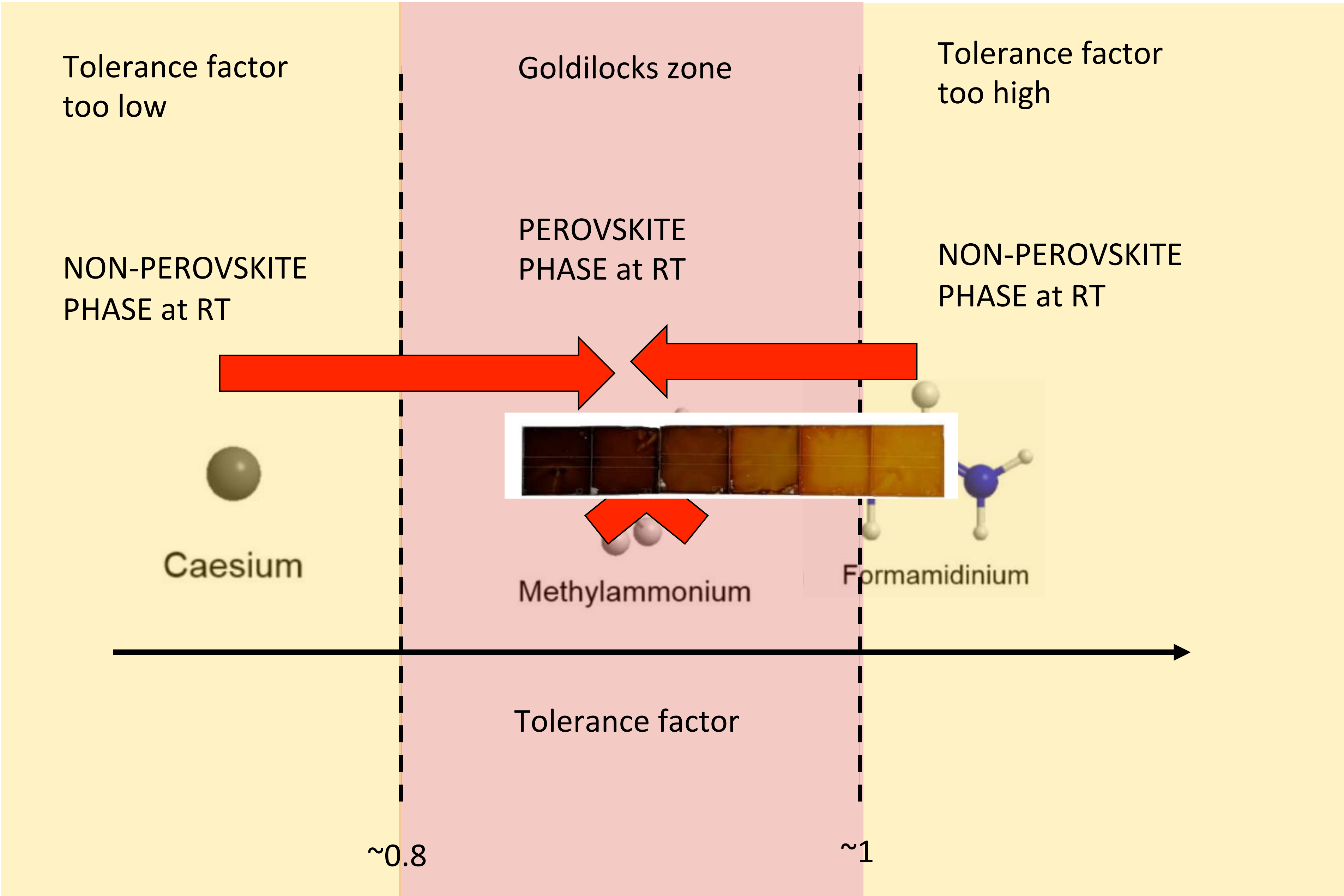


Eperon et al, EES, 2014

Tolerance factor and preferred phase ($APbI_3$)

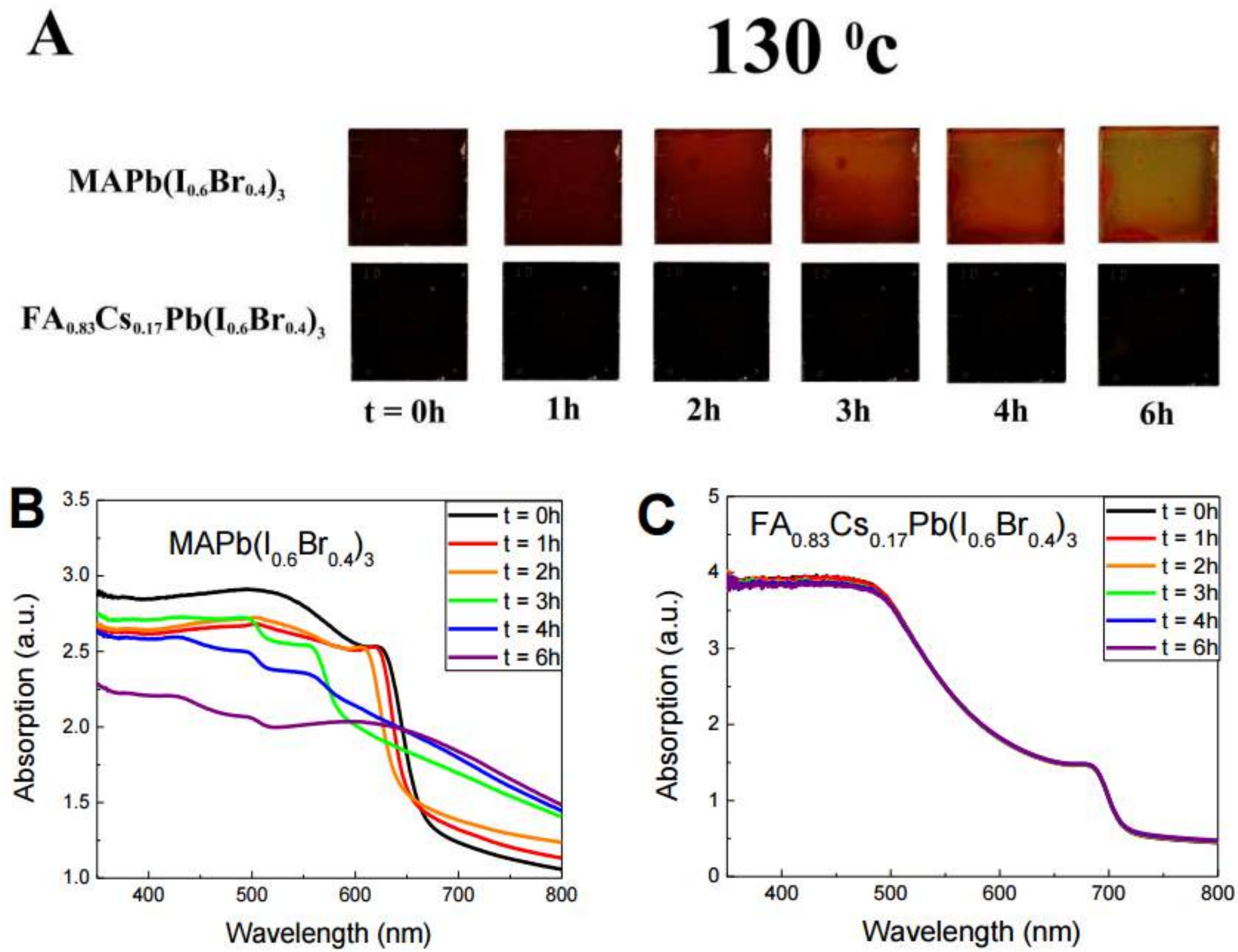


Tune cation



Tolerance factor
too low
Goldilocks zone
Tolerance factor
too high
NON-PEROVSKITE
PHASE at RT
PEROVSKITE
PHASE at RT
NON-PEROVSKITE
PHASE at RT
Caesium
Methylammonium
Formamidinium
Tolerance factor
~0.8
~1

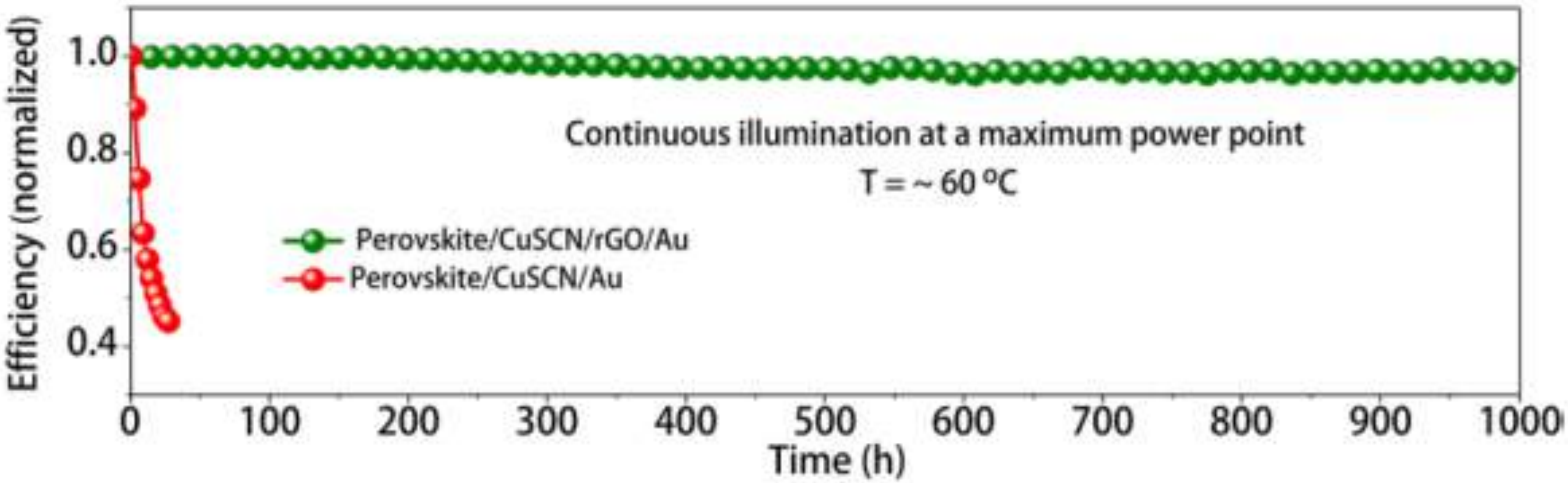
FA-Cs Pb X3



Li et al, Chem Mat 2016

Stability today

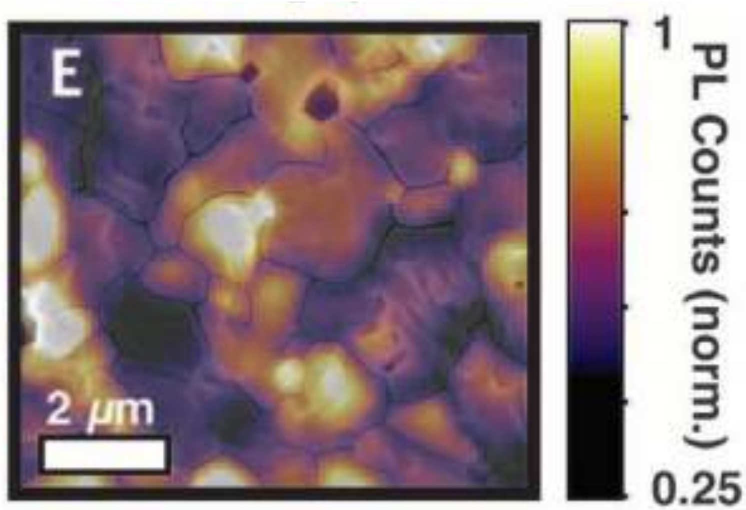
Unencapsulated performance



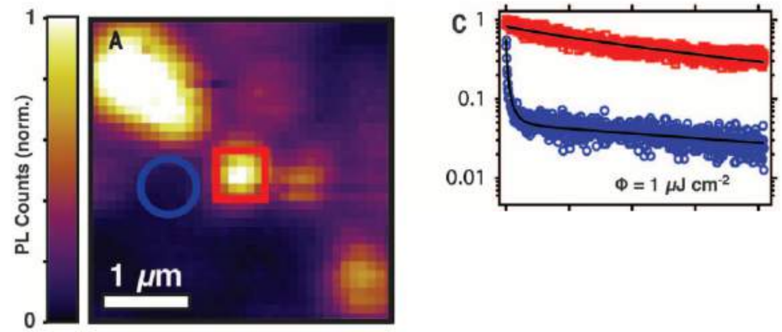
Arora et al, Science 2017

CURRENT HOT TOPICS IN PEROVSKITE RESEARCH (A.K.A., WHAT I'M WORKING ON NOW)

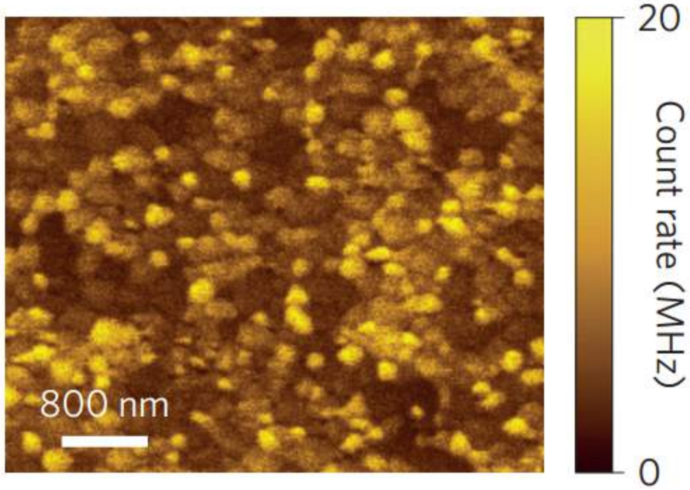
What's currently limiting perovskites?



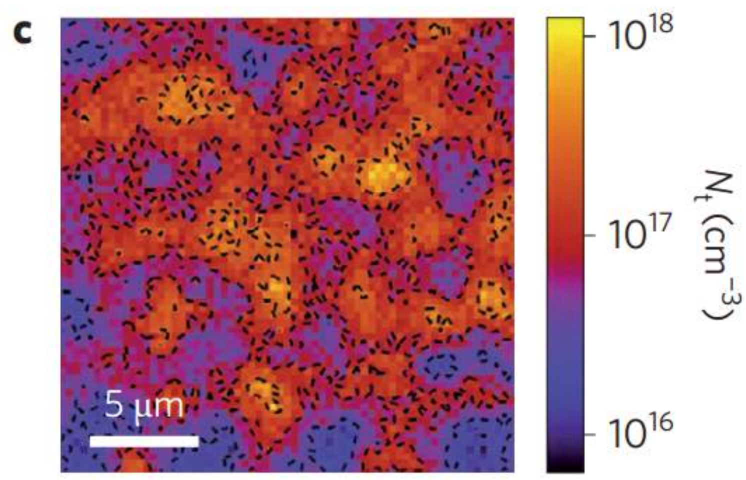
PL intensity and lifetimes



Cathodoluminescence



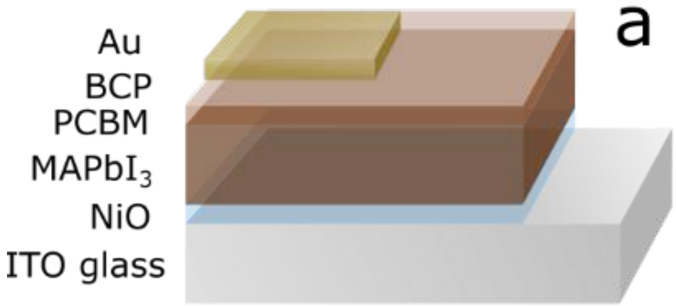
Trap state densities

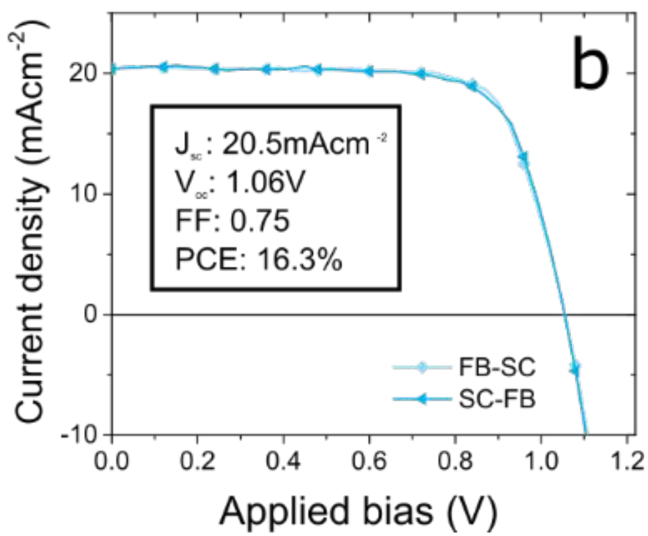


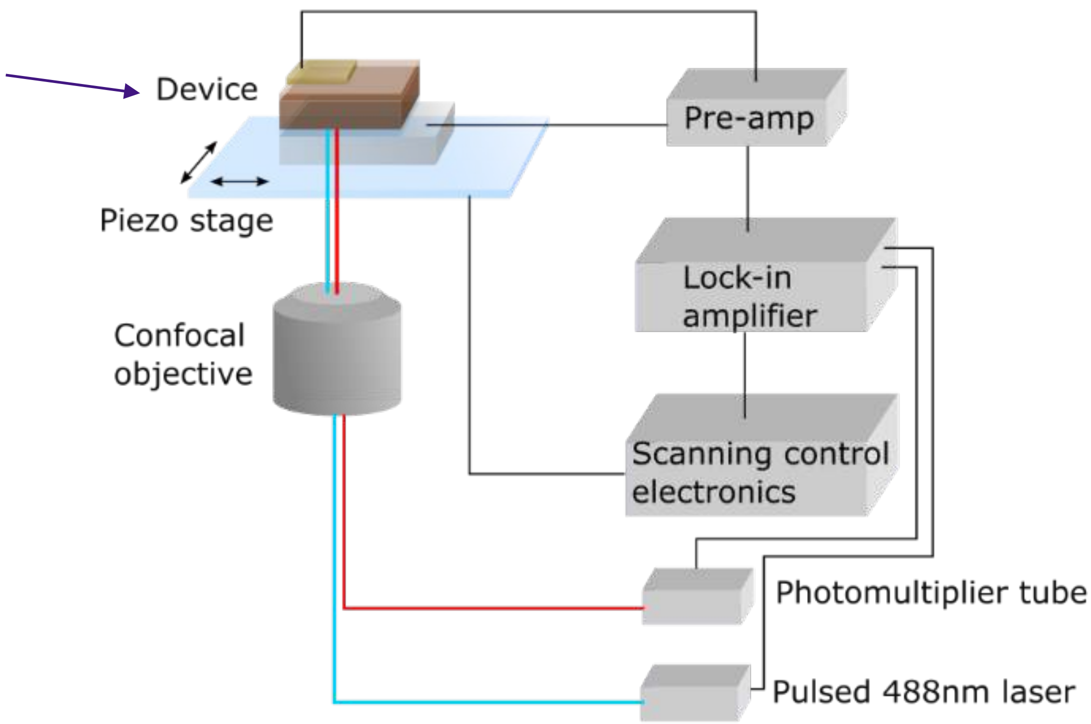
DeQuilettes et al, Science, 2015
Draguta, S. et al. J. Phys. Chem. Lett. 7, 715–721 (2016)
Bischak, C. G., Sanehira, E. M., Precht, J. T., Luther, J. M. & Ginsberg, N. S. Nano Lett. 15, 4799–4807 (2015)

Correlate performance and PL

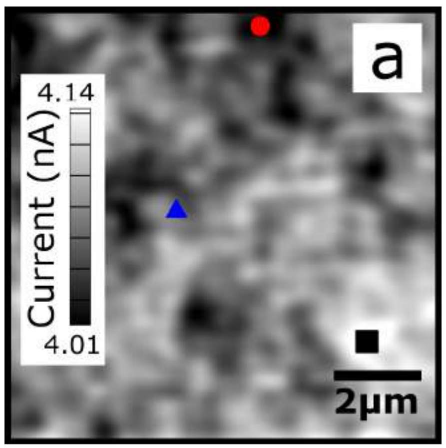
LBIC / LBIV / PL

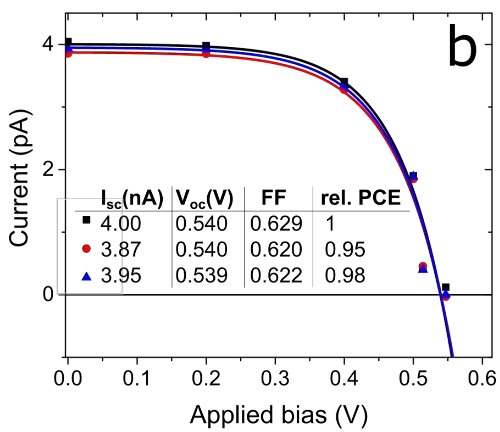


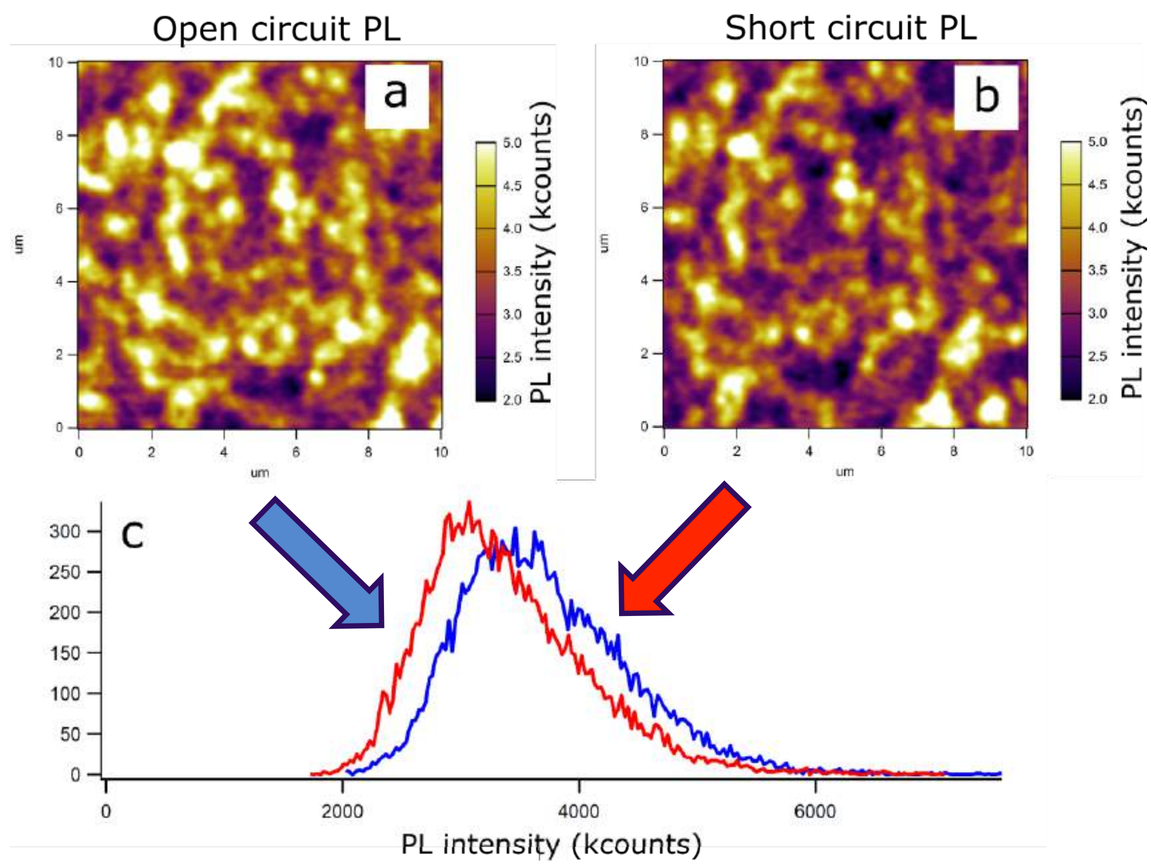




Some extraction heterogeneity, but small impact. Contact limited!

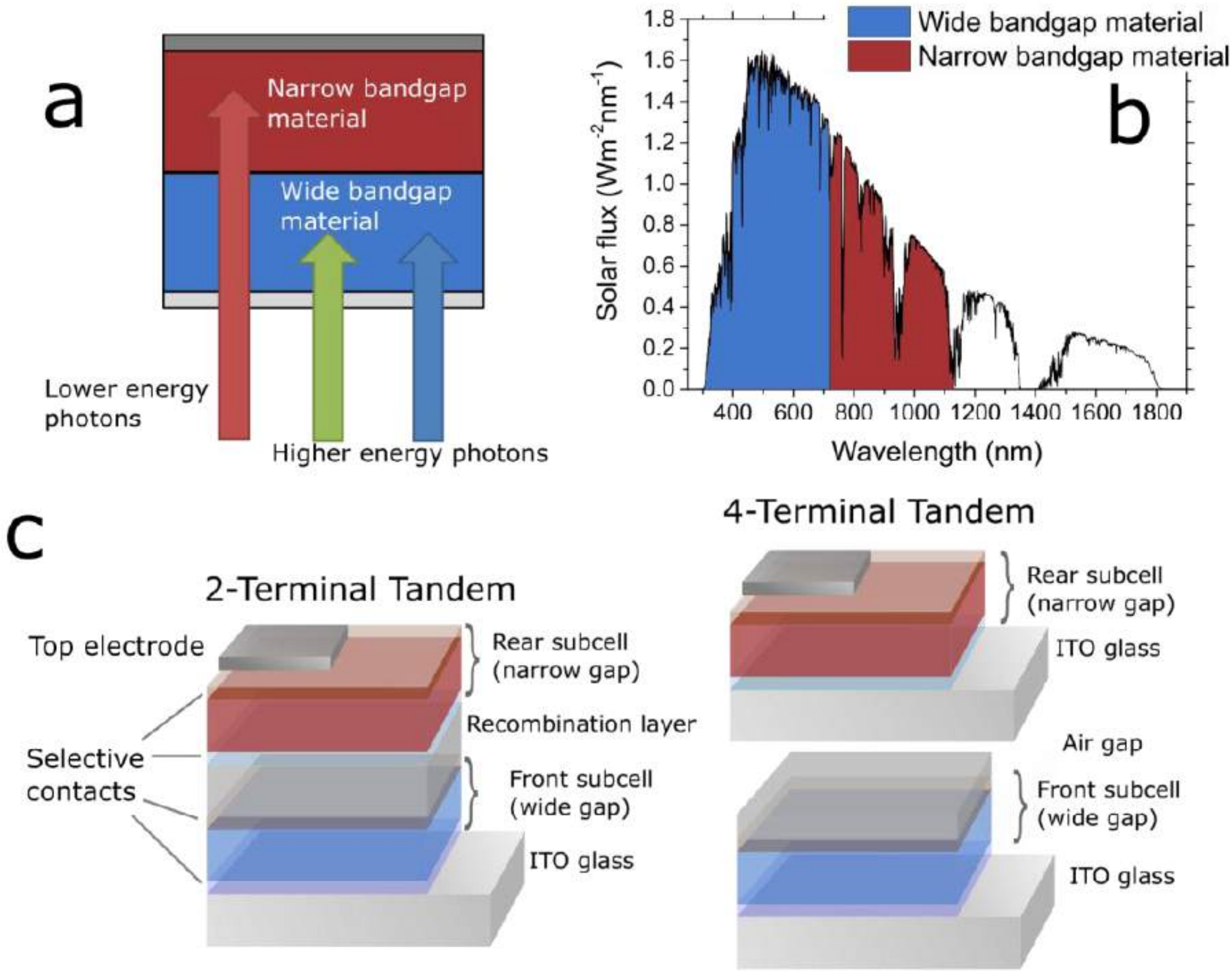




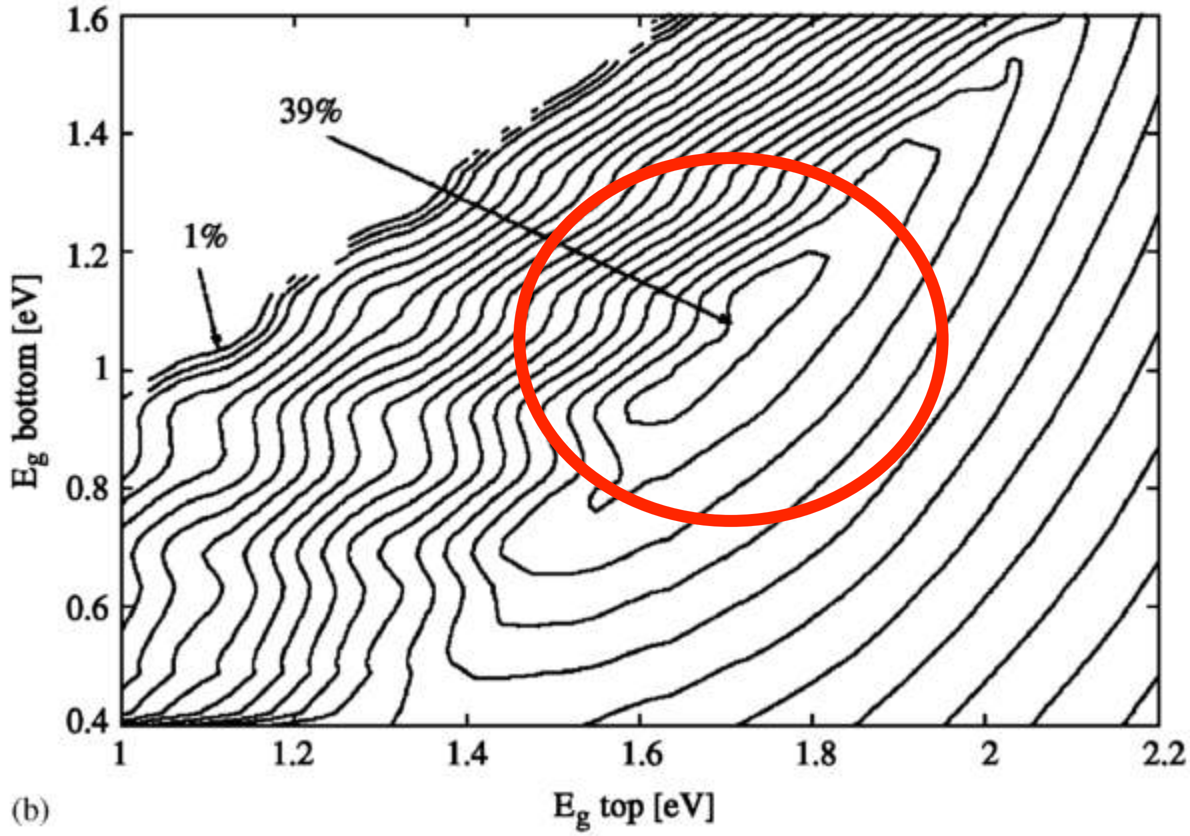


Little difference in PL magnitude implies high non radiative losses at open circuit.

Tandem solar cells

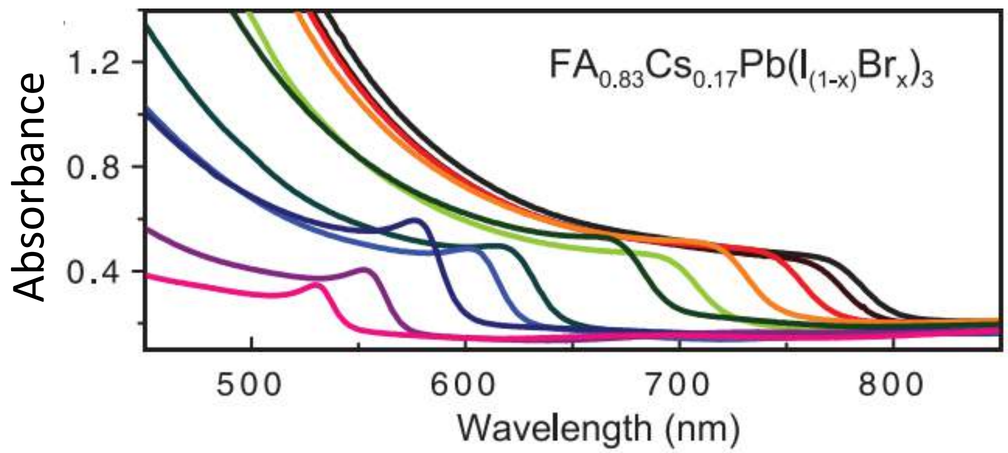


How to make a good tandem?

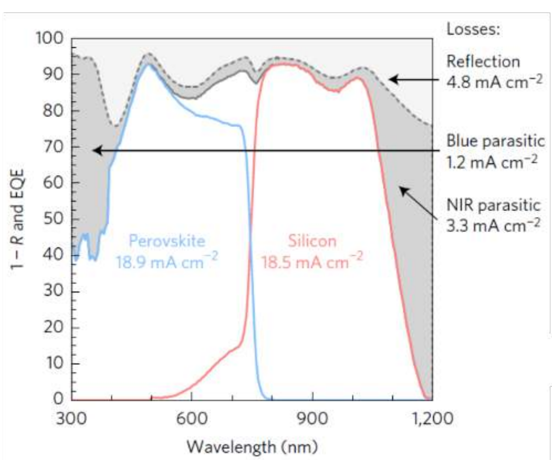


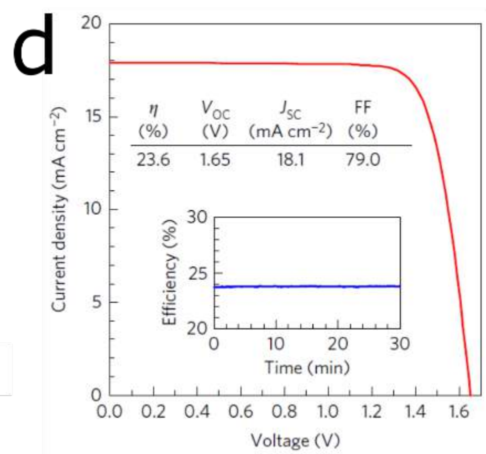
Hoerantner et al, ACS Energy Lett 2017
Meillaud, Miazza et al, Sol. En. Mat. Sol. Cells 2006

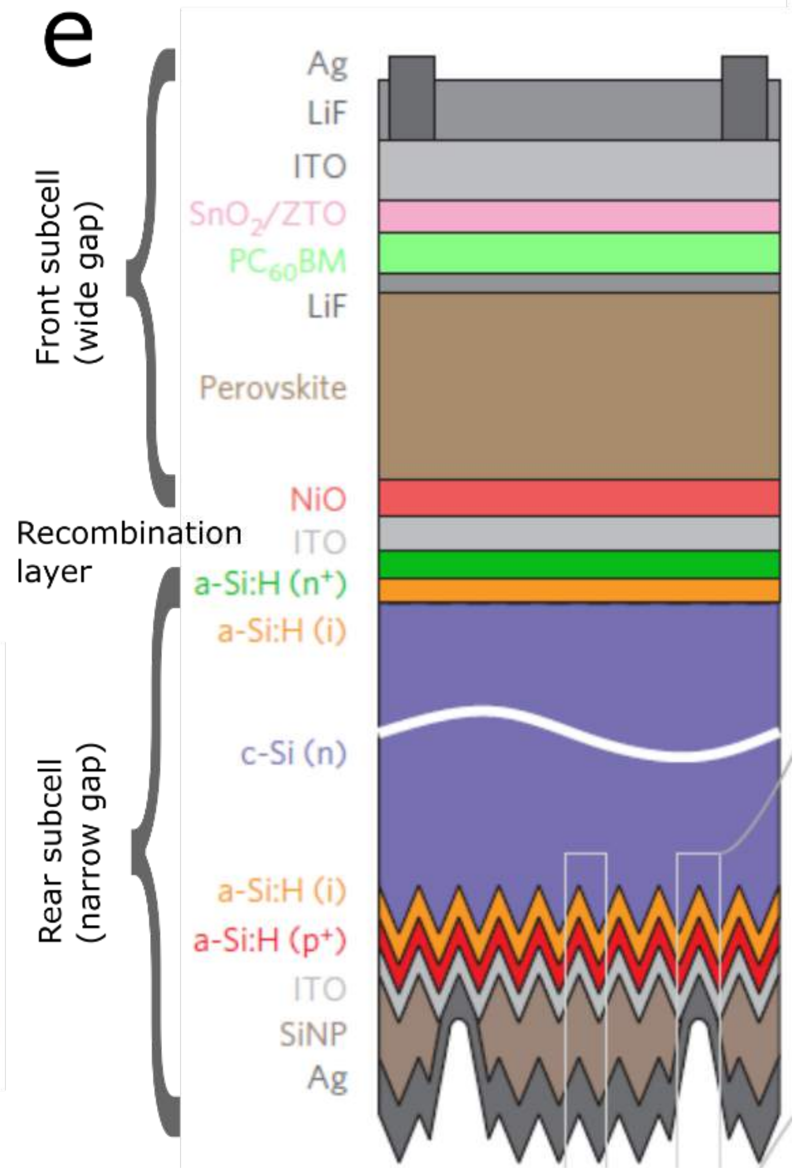
Wide bandgap perovskites for perov-Si tandems



2-terminal

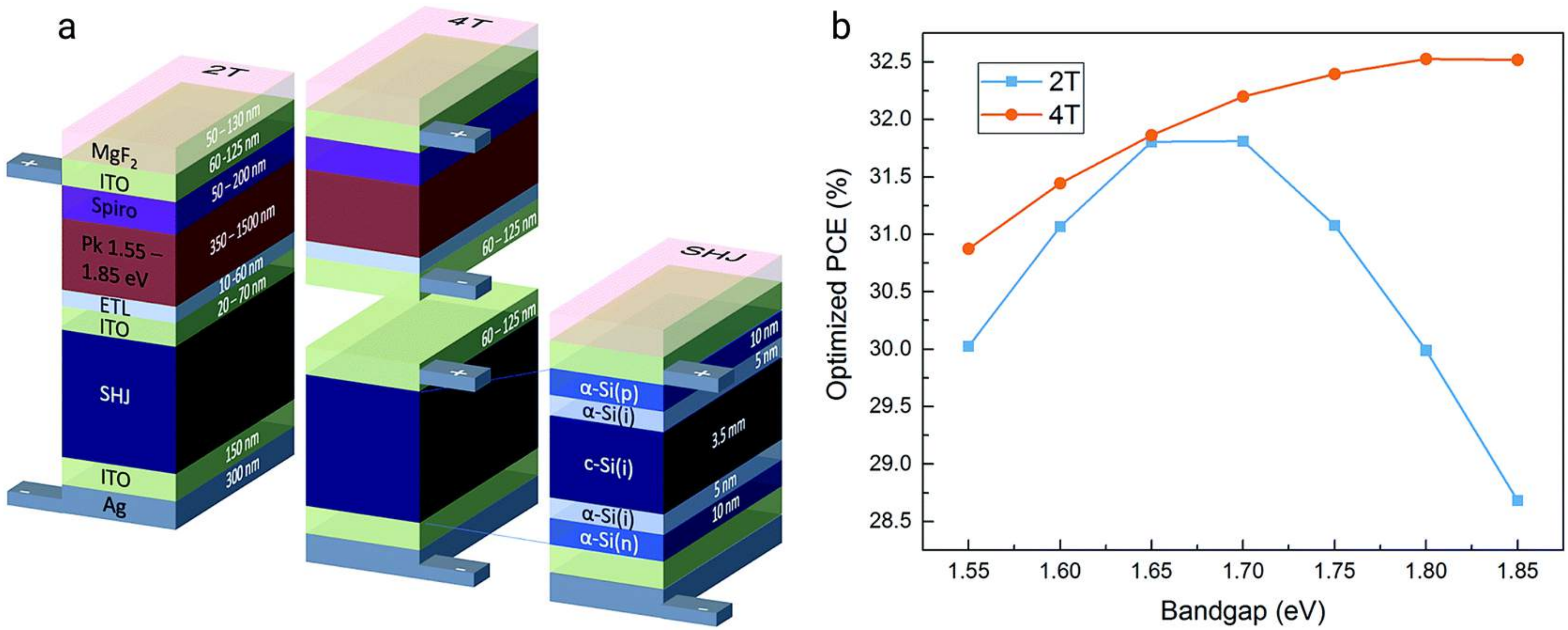


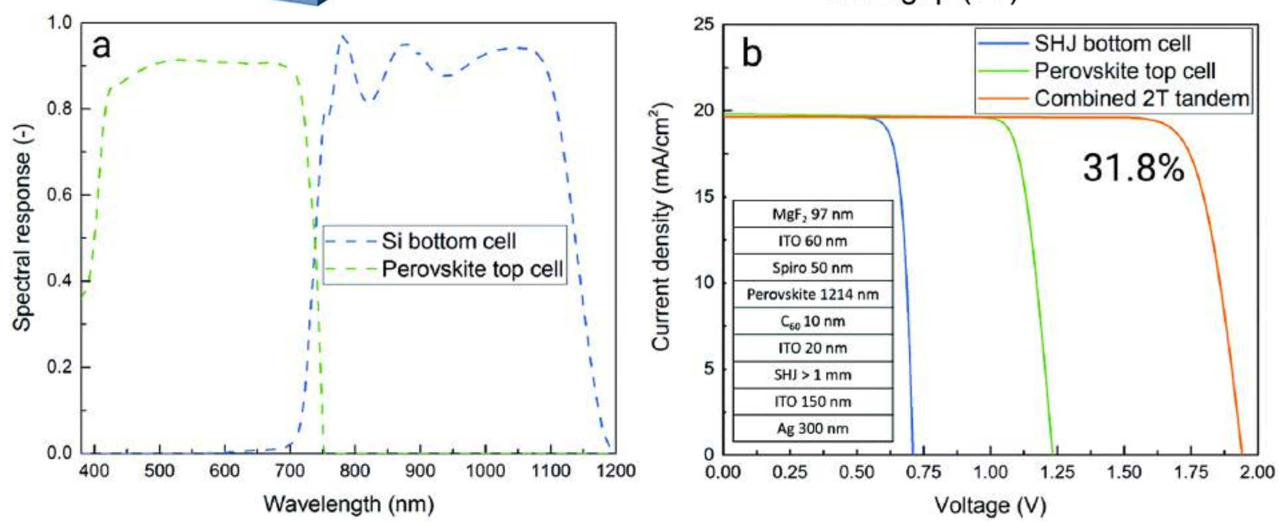




Mcmeekin et al, Science 2015; Bush et al, Nat Energy 2017

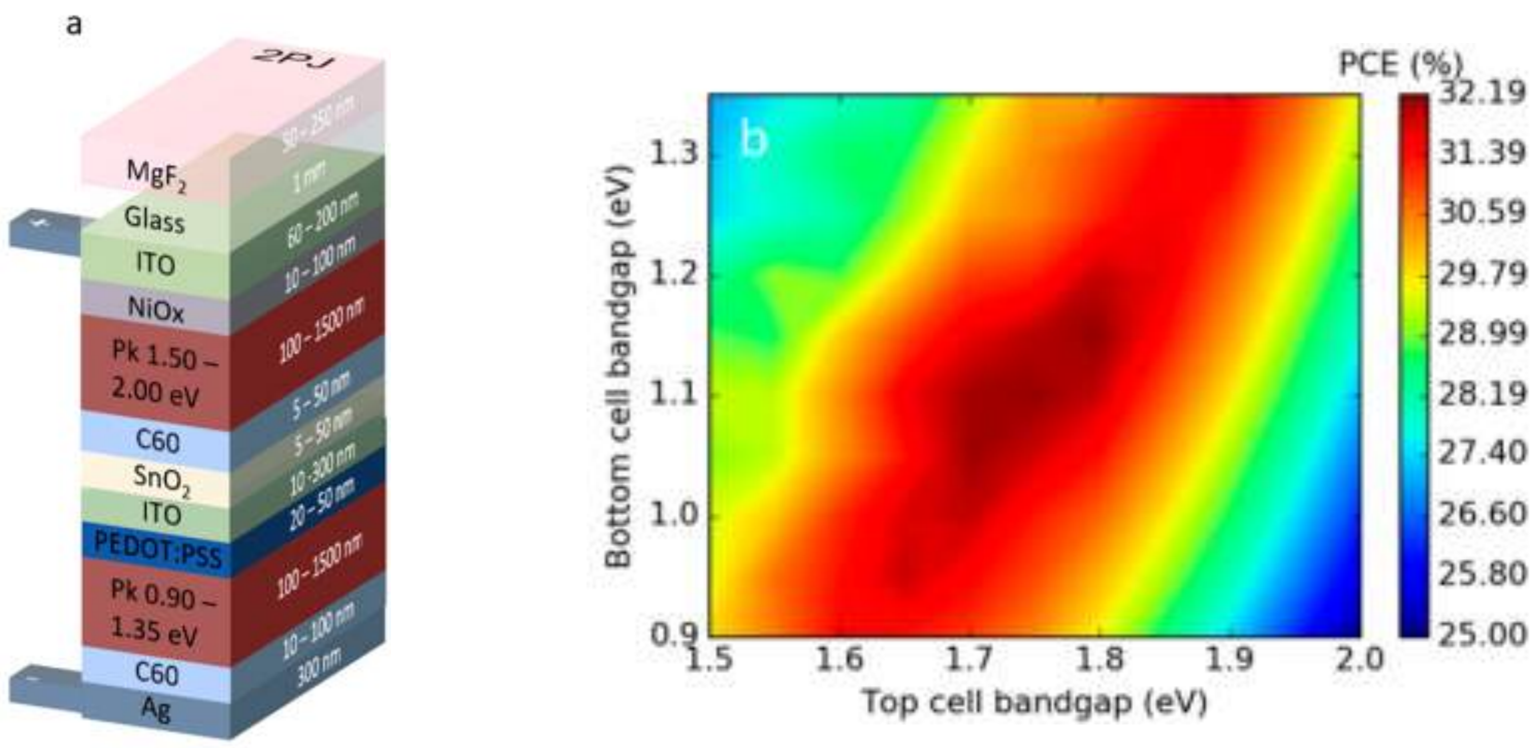
Perovskite-Si tandems – max PCE





Hoerantner et al,
EES 2017

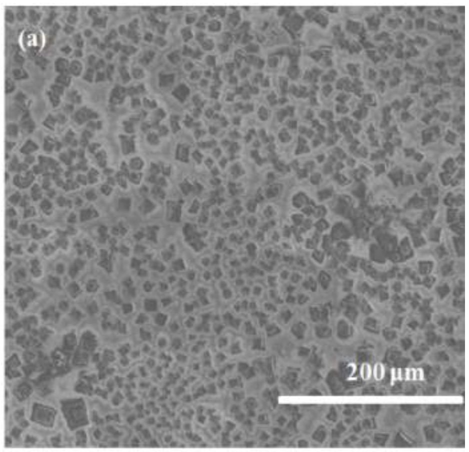
Perovskite-perovskite tandems?



Hoerantner et al, ACS Energy Lett 2017

1.2eV perovskite solar cells?

1:1 MAI:SnI2 in DMF?

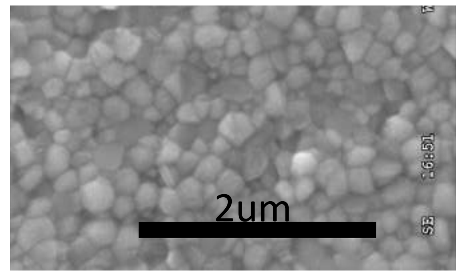


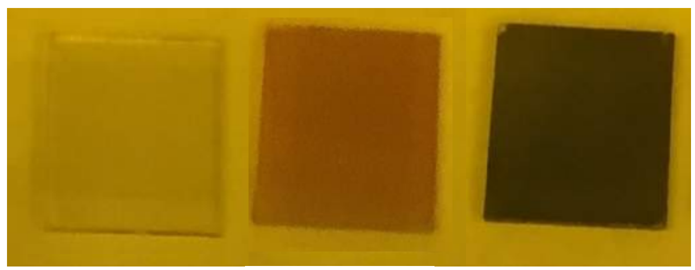
…not so promising morphology.

Tin-based materials crystallise very rapidly, during spin-coating

Noel et al, EES 2014

New deposition technique

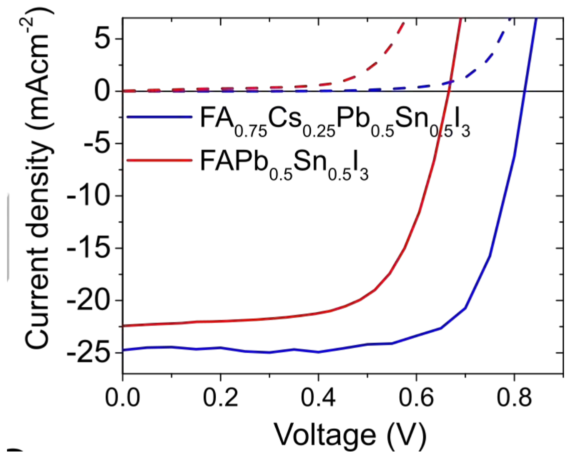


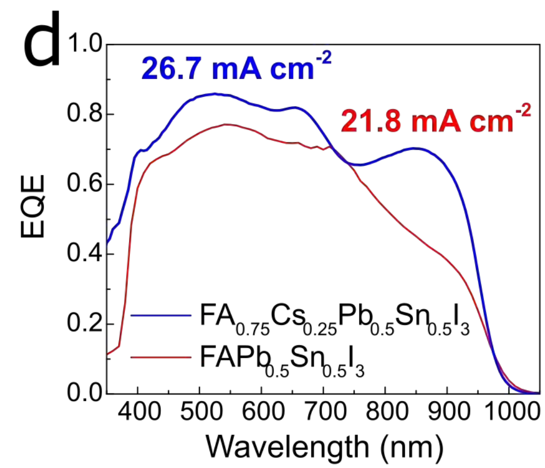


1. After spin-coating

2. After immersion in anisole bath

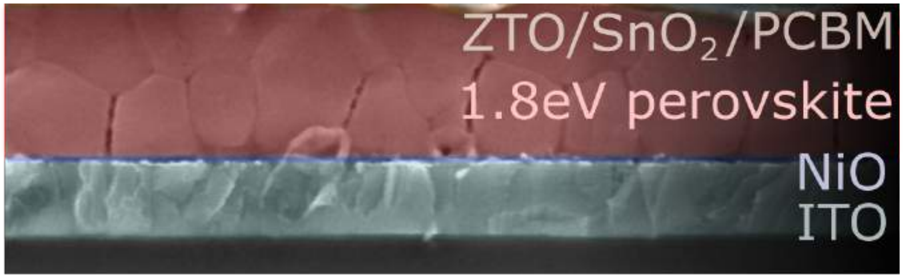
4. After annealing.





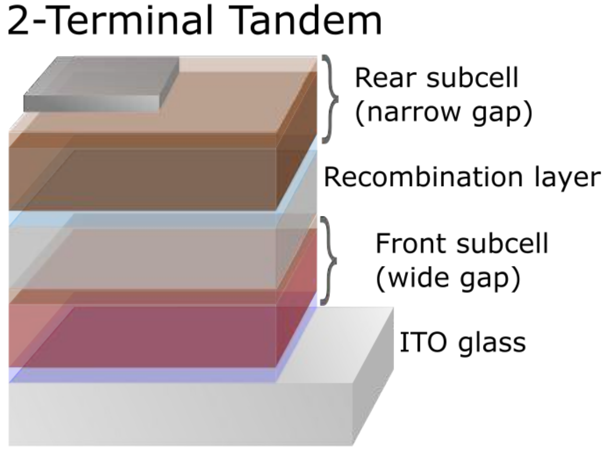
Enabled 18% efficient low gap perovskites

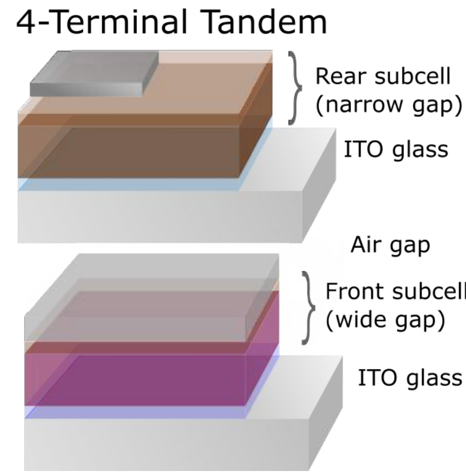
Sputtered ITO interlayer enable 2T tandems

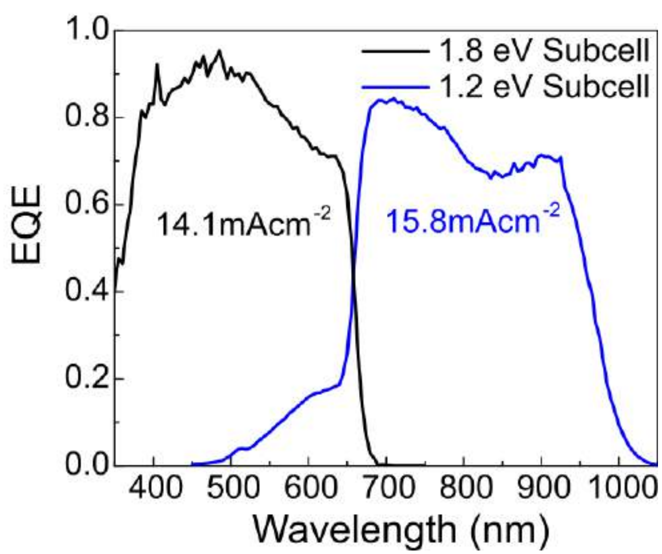


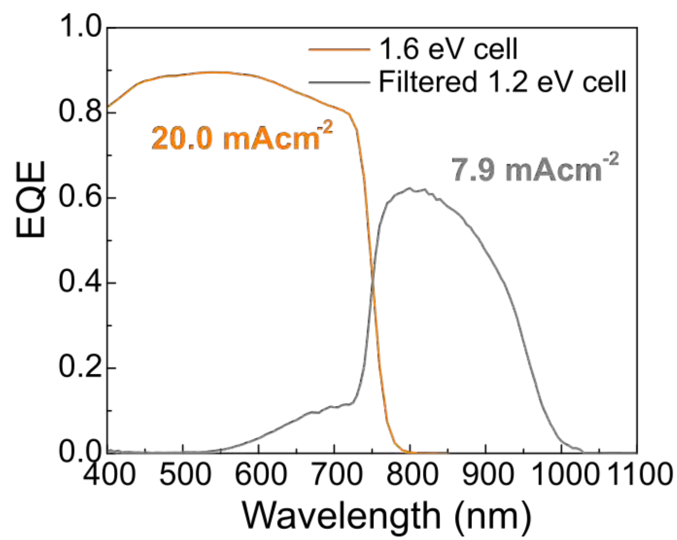
No lattice matching needed!

2T and 4T perovskite tandems - >20%





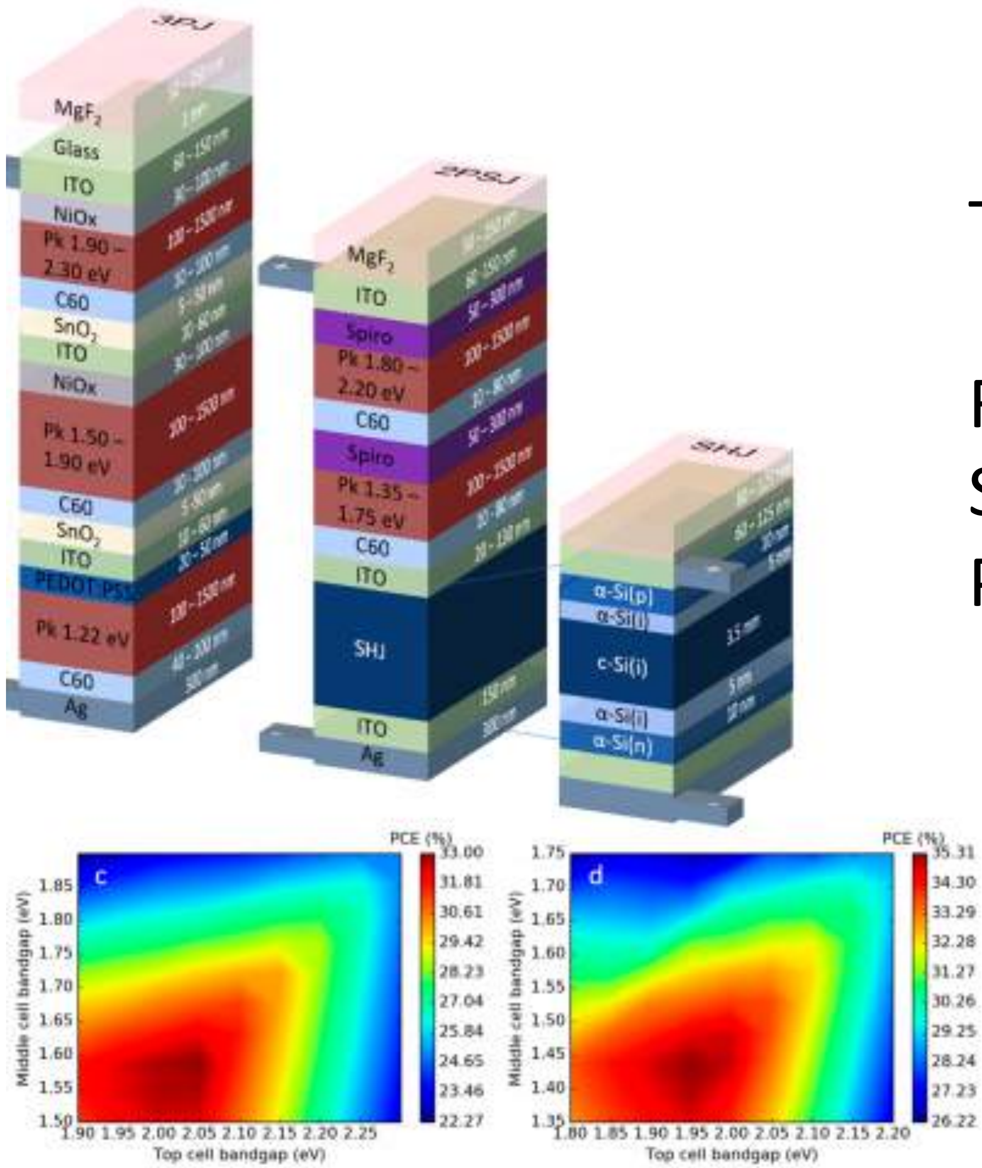




17% PCE

20.3% PCE

Perovskite based triple junctions?



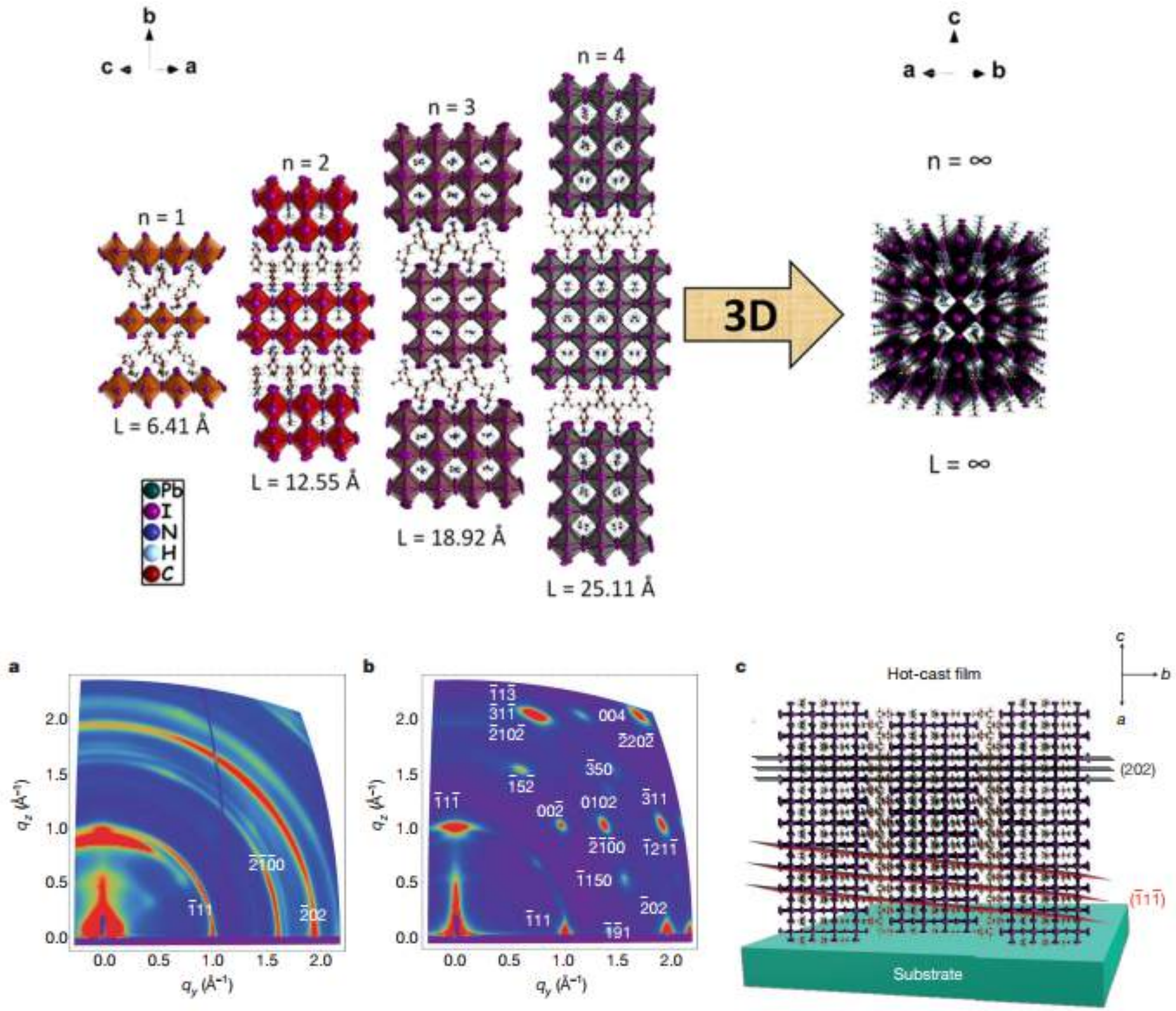
TMM + diode model

Feasible PCEs:

Si-perov-perov – 35%

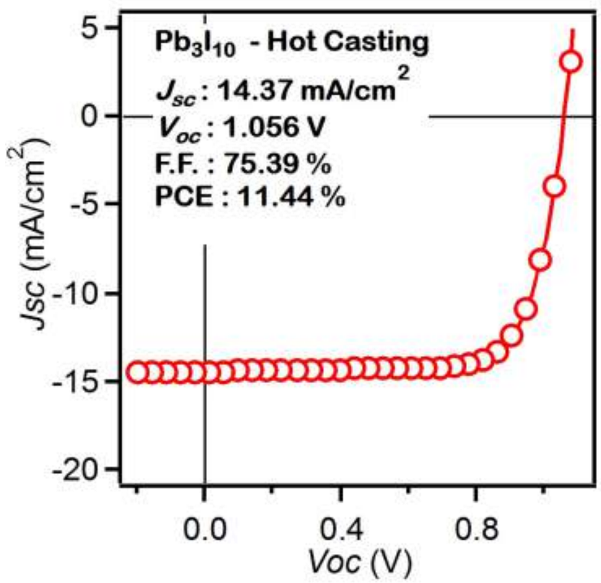
Perov-perov-perov – 33%

Layered (2D) perovskites



Tsai, Mohite et al, Nature 2016

2D perovskites – stability enhanced



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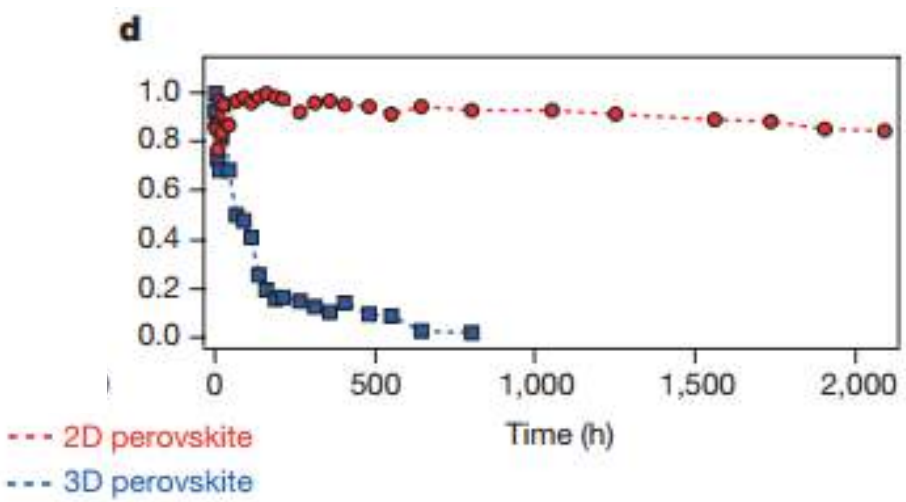
Perovskite energy funnels for efficient light-emitting diodes

Mingjian Yuan[1‡], Li Na Quan[1,2‡], Riccardo Comin[1], Grant Walters[1], Randy Sabatini[1], Oleksandr Voznyy[1], Sjoerd Hoogland[1], Yongbiao Zhao[1,3], Eric M. Beauregard[1], Pongsakorn Kanjanaboos[1†], Zhenghong Lu[3], Dong Ha Kim[2*] and Edward H. Sargent[1*]



Tsai, Mohite et al, Nature 2016

Outlook

- Perovskites are an efficient, rapidly scalable and low cost technology
- Stability issues valid, but being worked out
- Potential for multi-junction perovskite devices with very high efficiency