Solar Photovoltaics & Energy Systems

Lecture 5. Emerging Technologies

ChE-600

Wolfgang Tress, March 2018

Is there room for further technologies?

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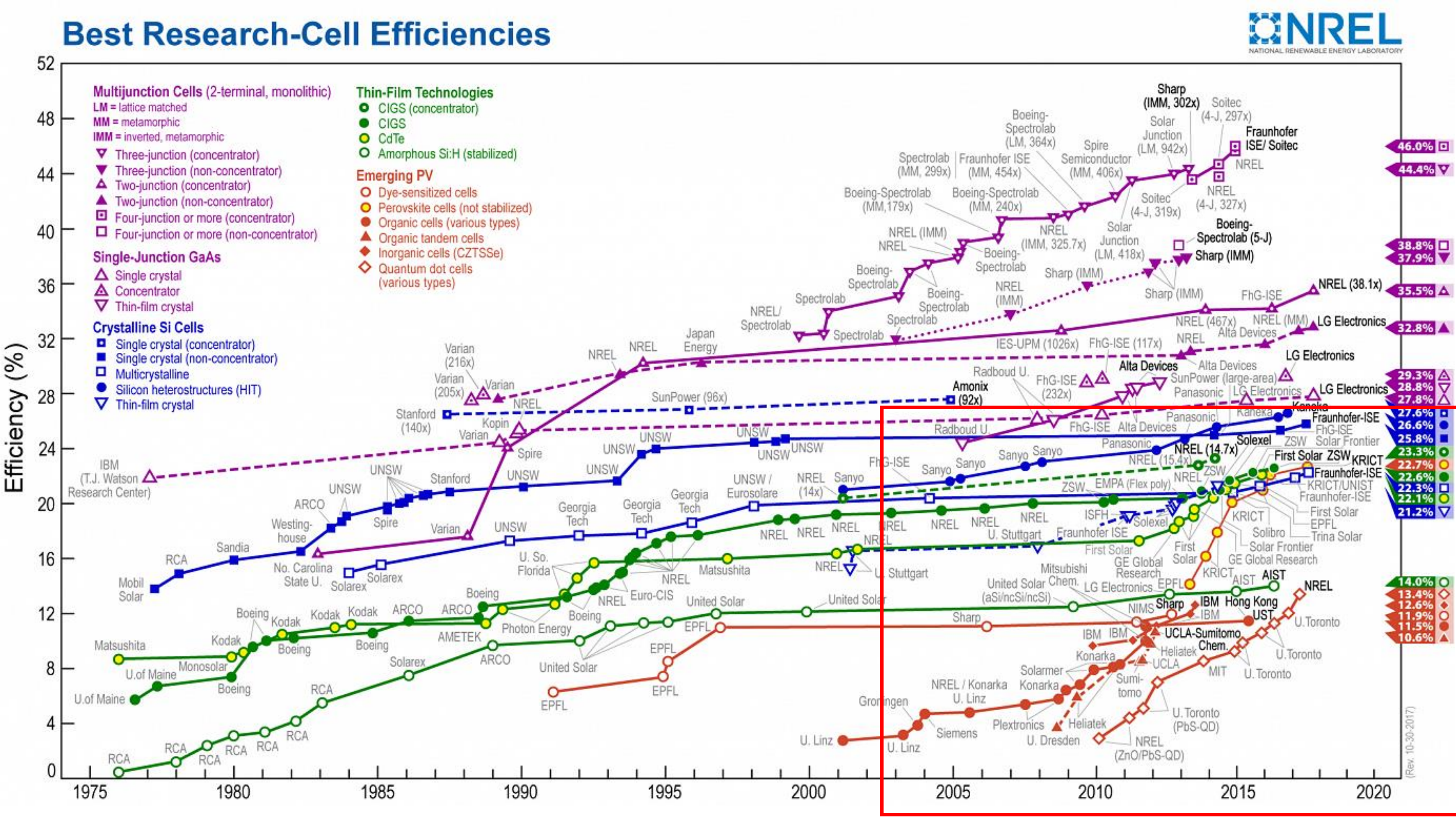
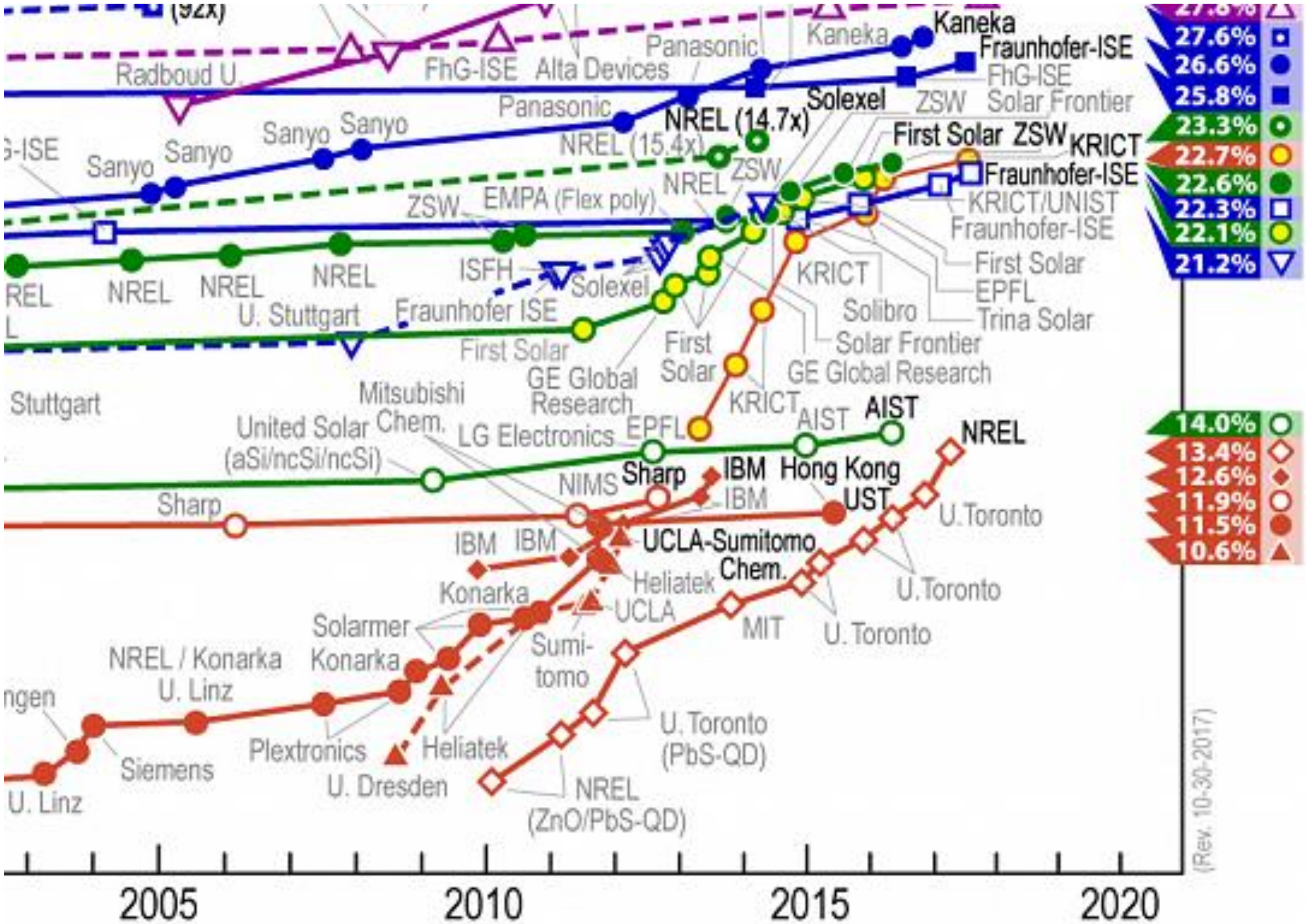
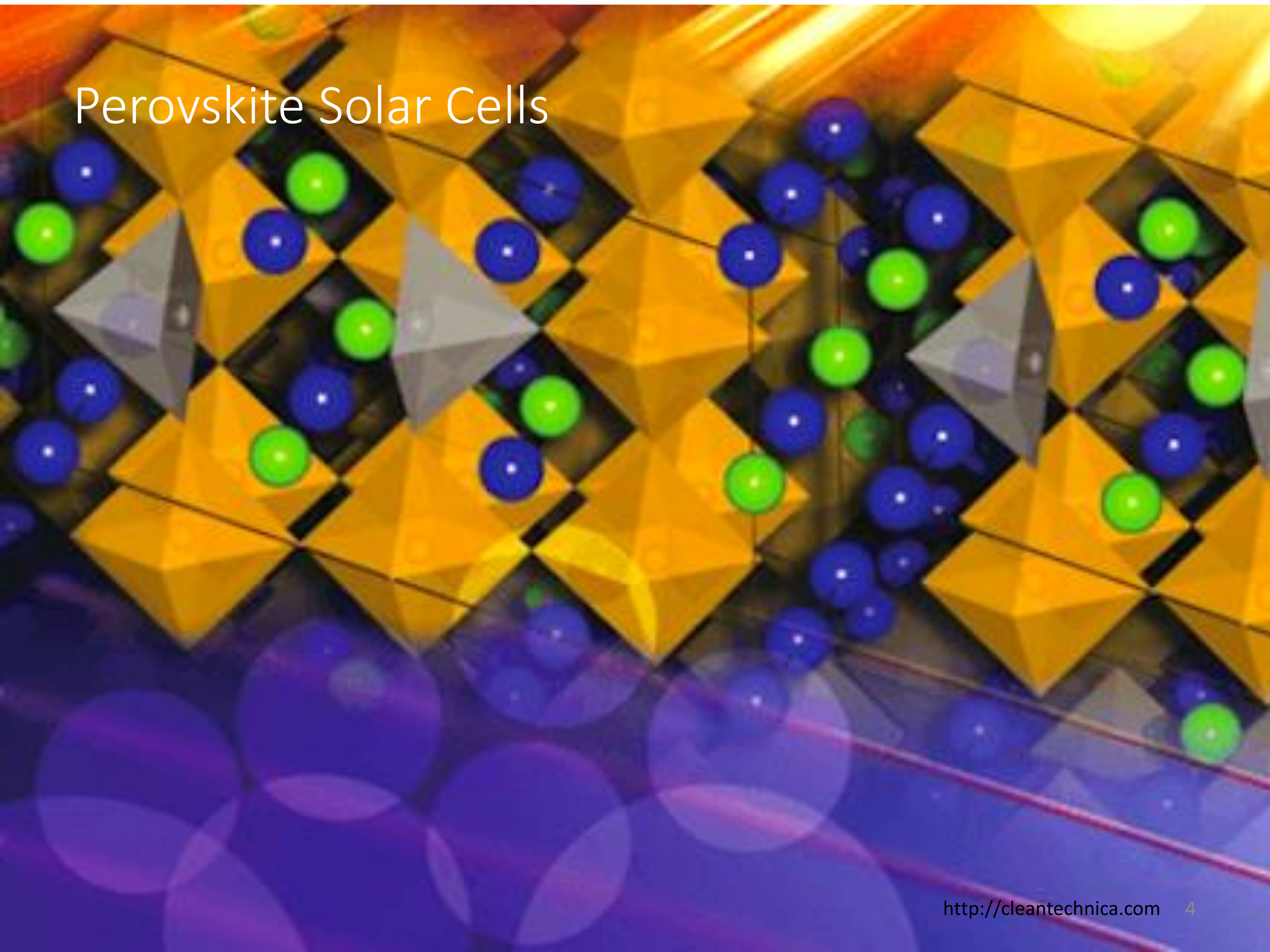


Is there room for further technologies?



Perovskite Solar Cells



http://cleantechnica.com

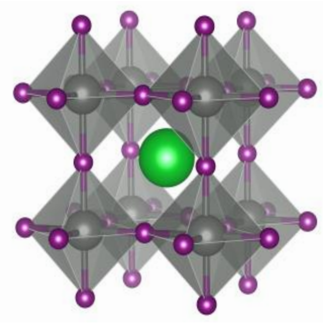
What is Perovskite?

- 1839: perovskite = $CaTiO_3$ discovered

- 1958: $CsPbX_3$ (X = Cl, Br, or I) perovskite structure determined

Møller, C. K. *Nature* **182,** 1436 (1958).

- 1978 Cs cation replaced by methylammonium cations $CH_3NH_3^+$ → organic–inorganic hybrid perovskites



Weber, D. *Z. Naturforsch.* **33b,** 1443–1445 (1978).
Weber, D. *Z. Naturforsch.* **33b,** 862–865 (1978).

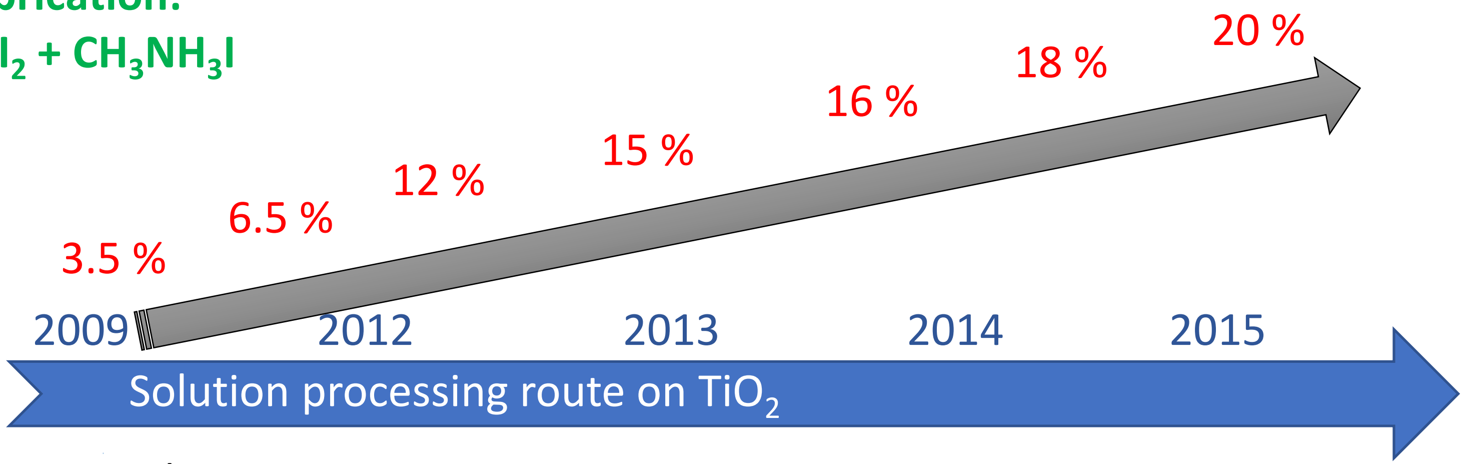
- Last two decades: perovskite researched in electronics

Mitzi, D. B. *Synthesis, Structure and Properties of Organic–Inorganic Perovskites and Related Materials: Progress in Inorganic Chemistry* Vol. 48 (ed. Karlin, K. D.) 1–121 (J. Wiley & Sons, 1999).

Ishihara, T. Optical properties of PbI-based perovskite structures. *Journal of Luminescence* **60–61,** 269–274 (1994).

History

Fabrication:
PbI_2 + CH_3NH_3I



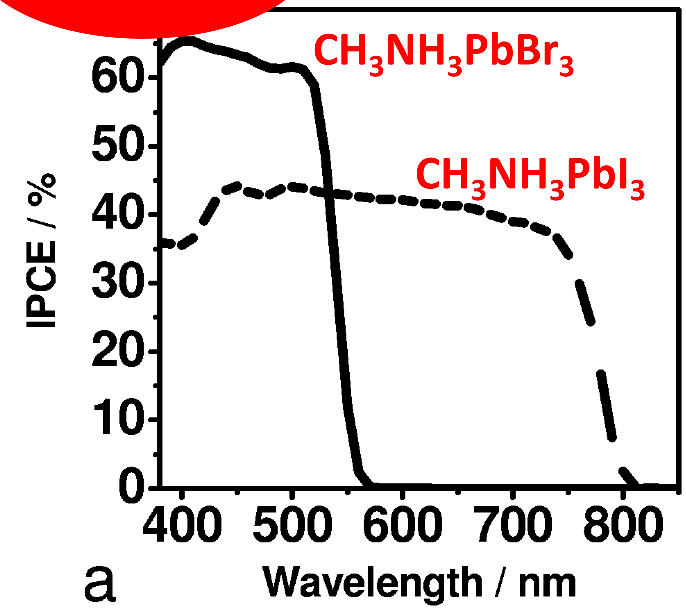
1. Perovskite replaces dye

Miyasaka, Park, Graetzel, Snaith, Seok, Bolink …

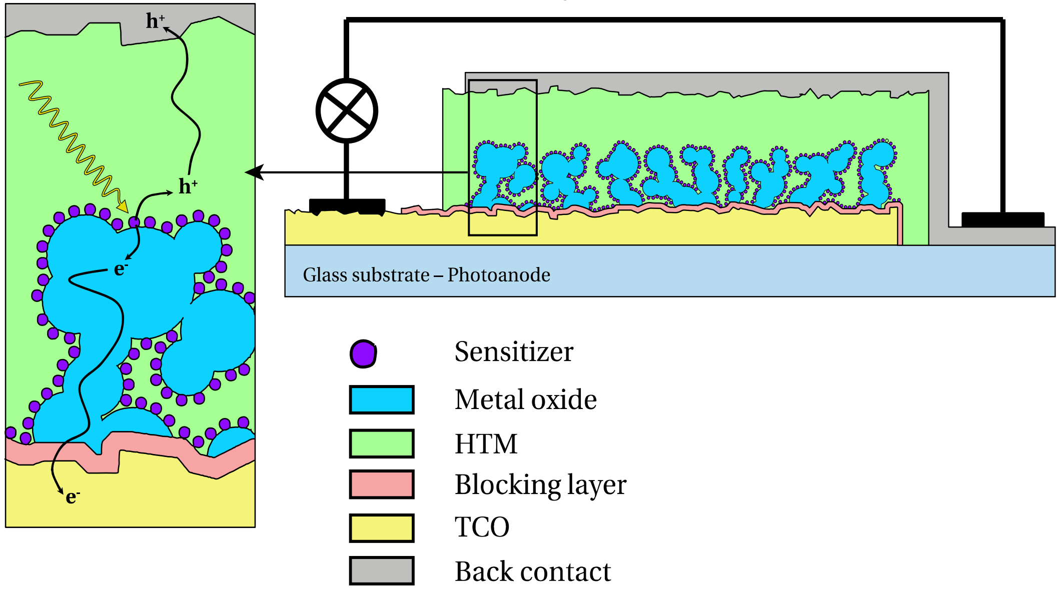
The First Solar Cells

2009

3.8 %



Structure of dye-sensitized solar cell



- perovskite replaces the molecular sensitizer in dye sensitized solar cell (DSSC)
- unstable (10 minutes operation), dissolves in liquid electrolyte

Kojima, A., Teshima, K., Shirai, Y. & Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **131,** 6050–6051 (2009).

CH_3NH_3Pb-Halide as Pigment in DSSC

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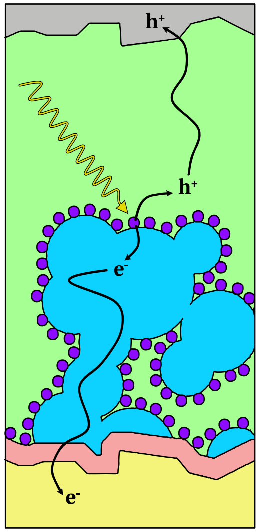
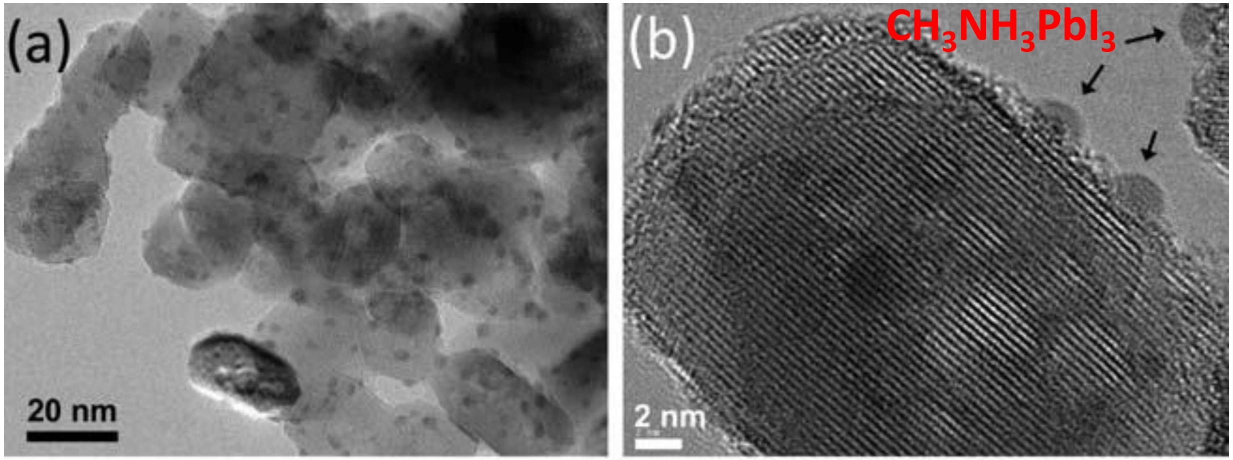
2011

6.5 %



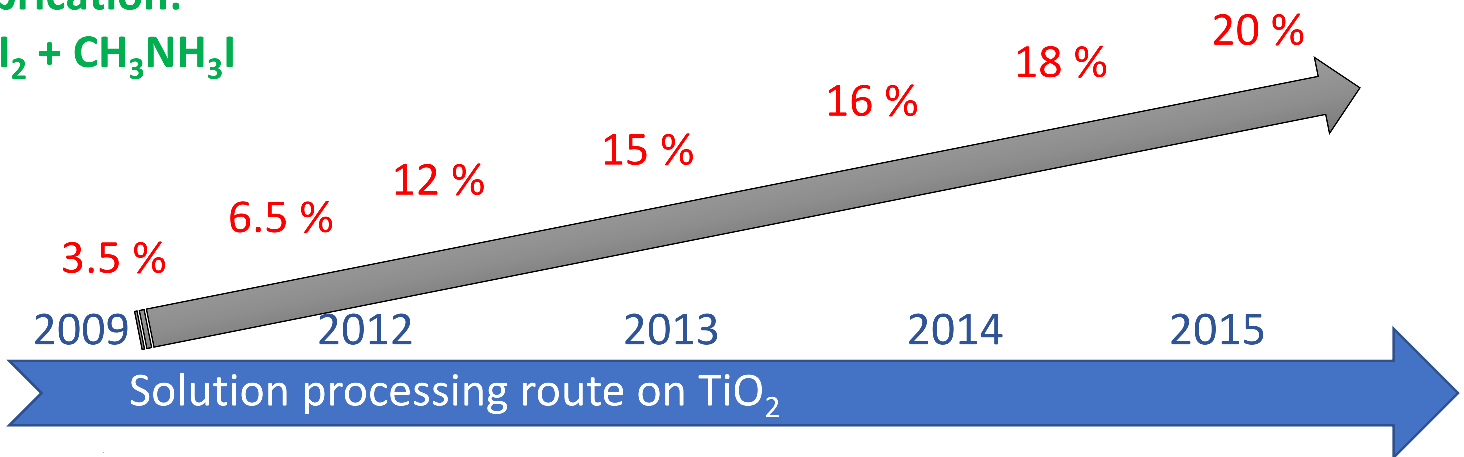


- perovskite replaces the molecular sensitizer in dye sensitized solar cell (DSSC)
- unstable (10 minutes operation), dissolves in liquid electrolyte

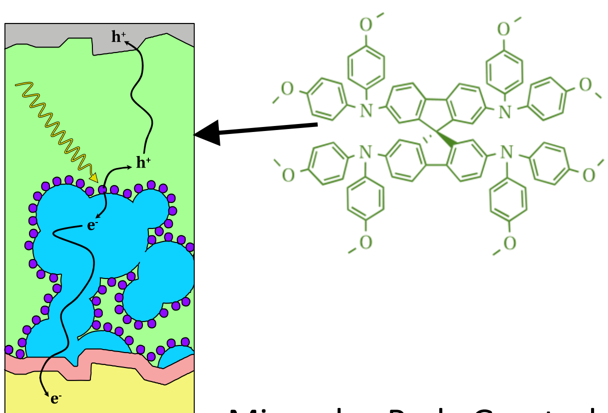
Im, J.-H., Lee, C.-R., Lee, J.-W., Park, S.-W. & Park, N.-G. 6.5% efficient perovskite quantum-dot-sensitized solar cell. *Nanoscale* **3,** 4088–4093 (2011).

History

Fabrication:
$PbI_2 + CH_3NH_3I$



1. Perovskite replaces dye
2. Solid state device
3. Sequential deposition



Miyasaka, Park, Graetzel, Snaith, Seok, Bolink …

Sequential Deposition

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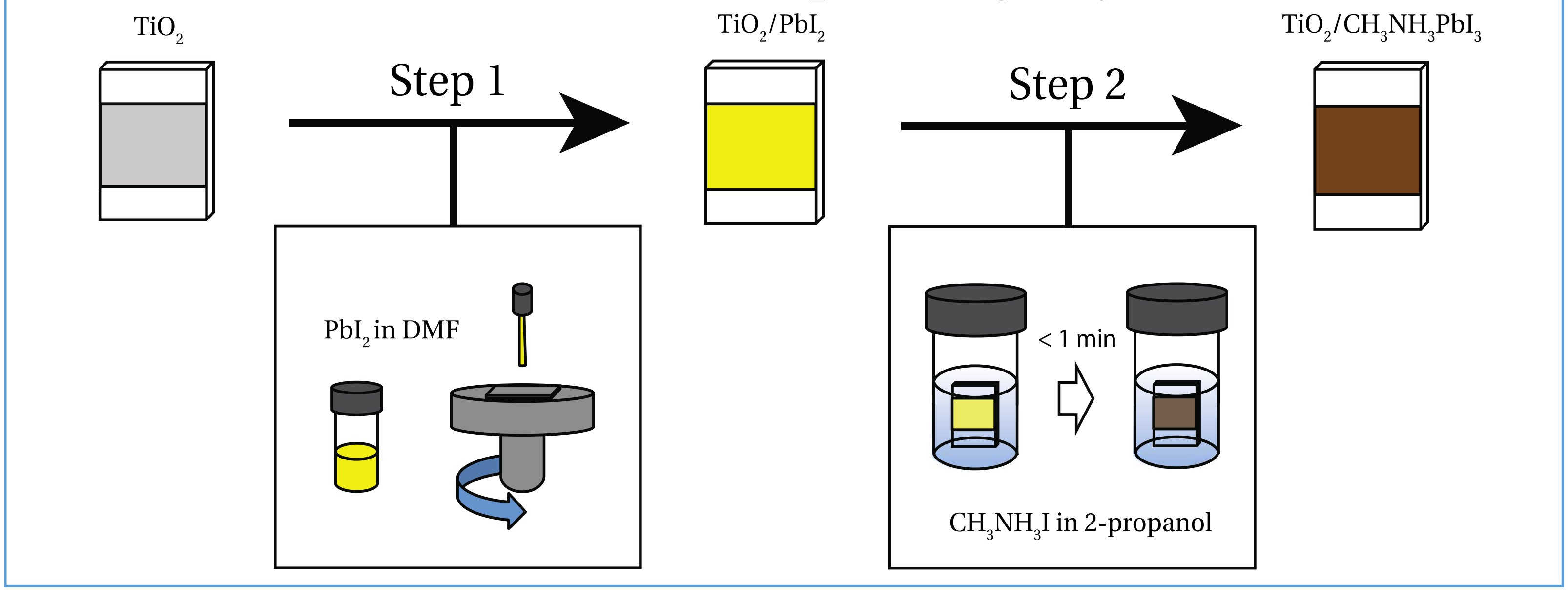
Use of a two-step technique to form the hybrid perovskite:

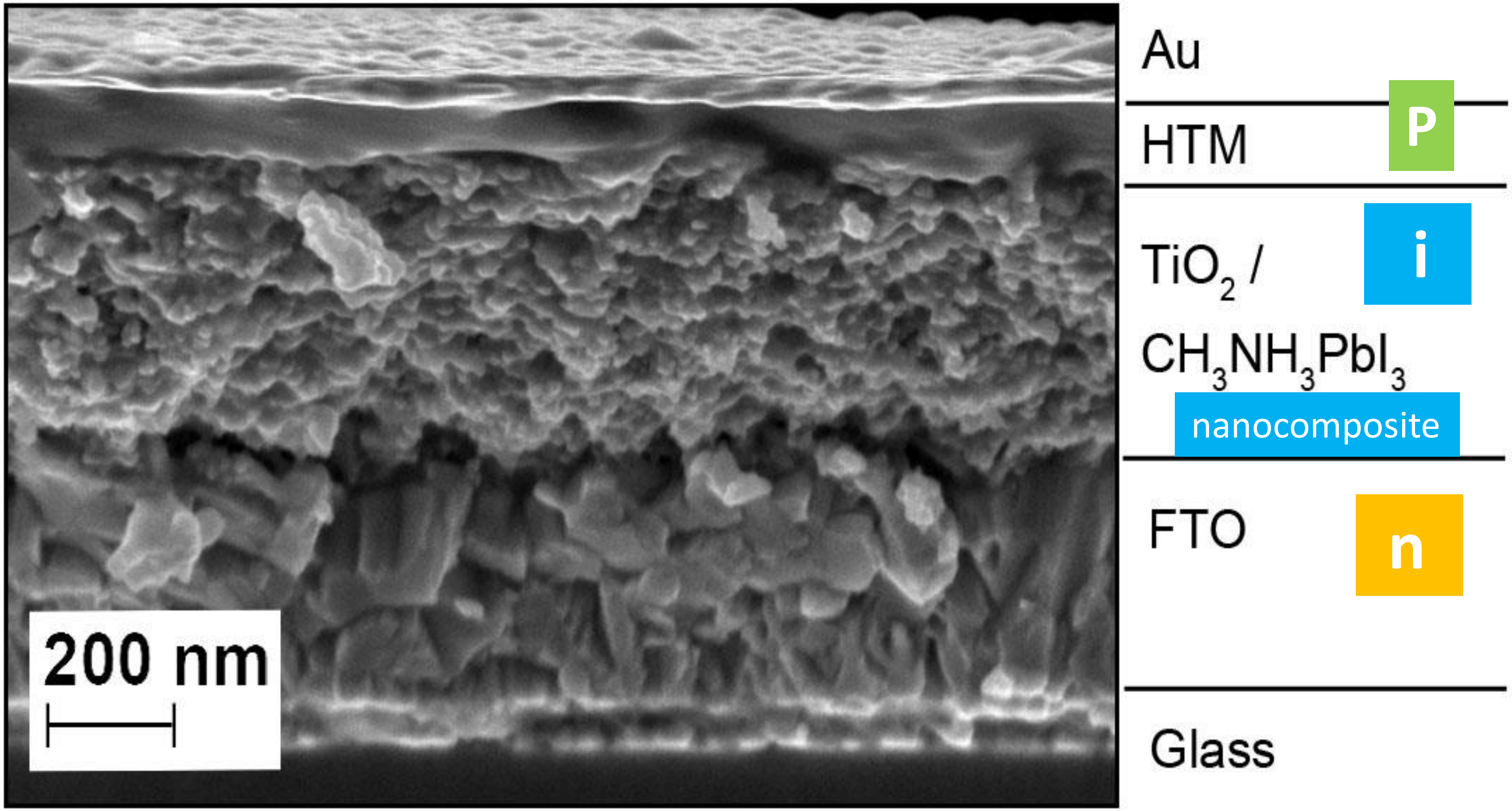
$$PbI_2 + CH_3NH_3I \Rightarrow CH_3NH_3PbI_3$$



- Better control of crystal morphology and conformal coating
- Tuning of dipping time, concentration, solvent, temperature etc.
- Correlation of perovskite loading, conversion and thickness

Burschka, J. *et al.* Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* **499,** 316–319 (2013)

Cross Sectional SEM

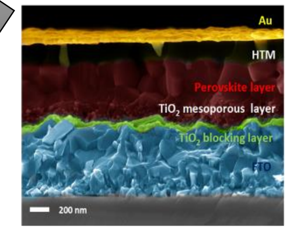


Burschka, J. *et al.* Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* **499,** 316–319 (2013).

History

Fabrication:
PbI_2 + CH_3NH_3I

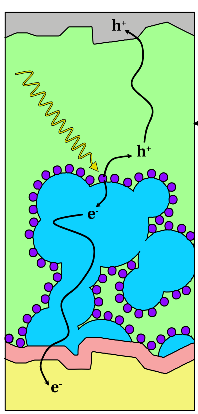
3.5 % 6.5 % 12 % 15 % 16 % 18 % 20 %

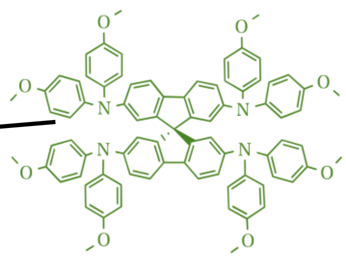


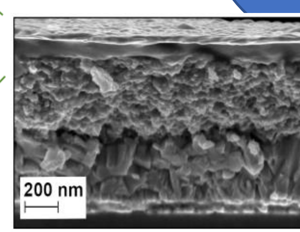
2009 2012 2013 2014 2015

Solution processing route on TiO_2

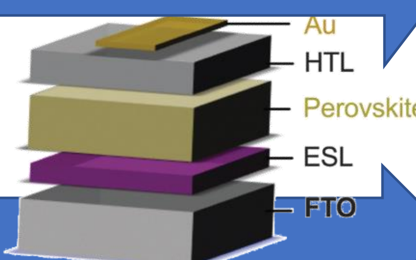
1. Perovskite replaces dye
2. Solid state device
3. Sequential deposition
4. Solvent engineering
5. Composition engineering







planar architectures



sublimation in vacuum

Compact films with large crystals

Miyasaka, Park, Graetzel, Snaith, Seok, Bolink …

Jiyoun Seo

$CH_3NH_3PbI_3$: A Good Solar Cell Material

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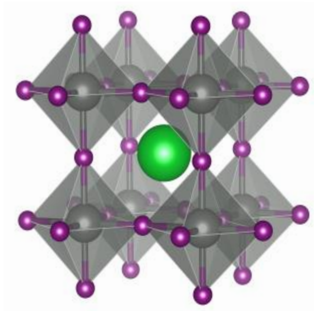

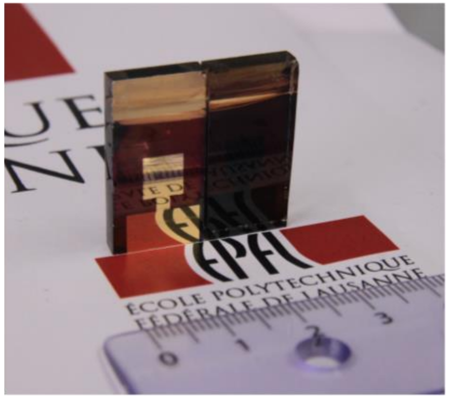

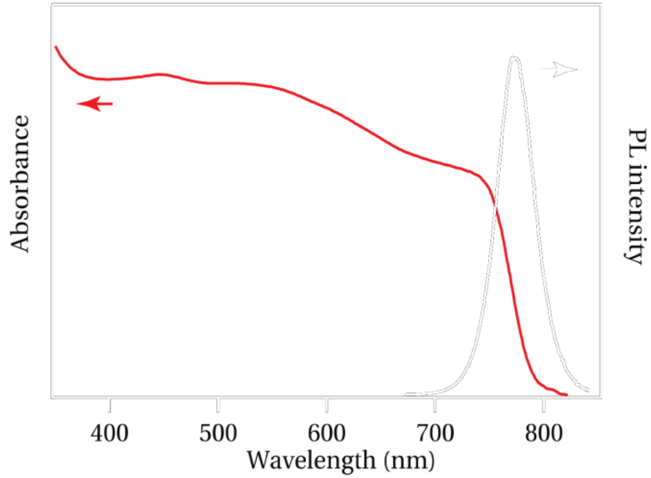

- High crystallinity
- Absorption coefficient of $10^4 \ldots 10^5$ cm^{-1}
- Band gap of 1.6 eV, valence band edge at -5.4 eV
- Ambipolar semiconductor with high charge carrier mobilities*
- Wannier excitons with fast dissociation at room temperature, high dielectric constant
- Low defect density, even if solution processed
- Characterized in stacks similar to solar cells → many intrinsic parameters and influence of morphology and grain boundaries not extensively quantified

*Stranks, S. D. *et al.* Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* **342,** 341–344 (2013); Xing, G. *et al.* Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH3NH3PbI3. *Science* **342,** 344–347 (2013).

Goldschmidt Tolerance Factor

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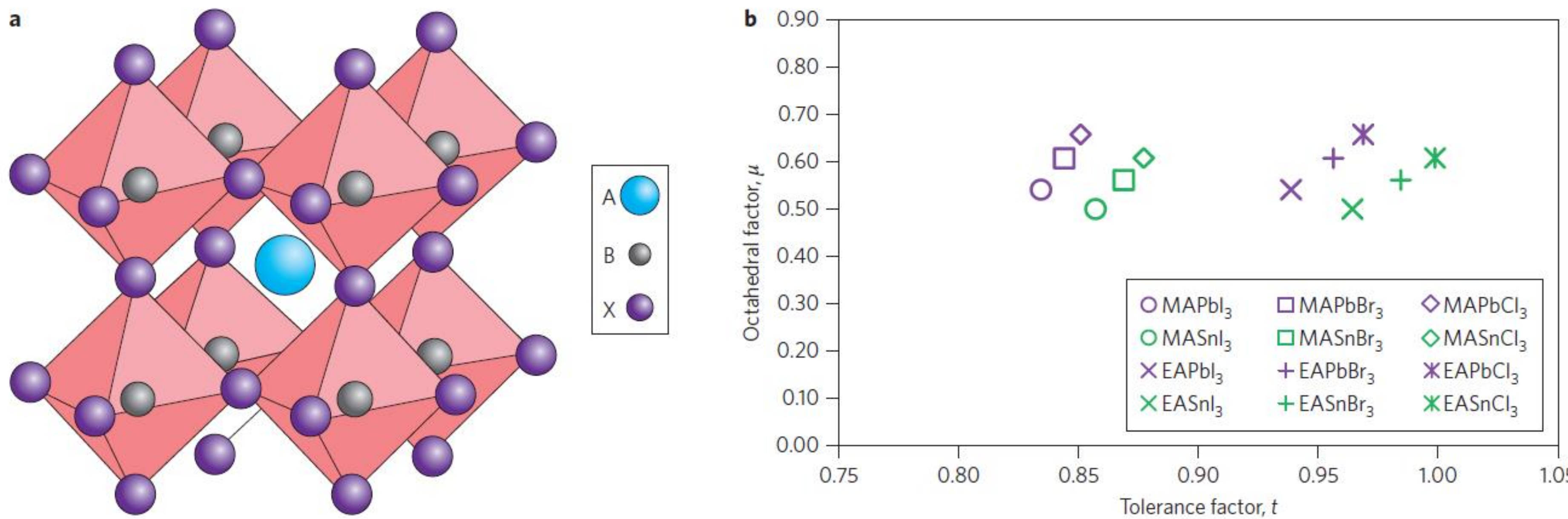
$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}$$

ABX$_3$

MA: methylammonium ($CH_3NH_3^+$)
EA: ethylammonium ($CH_3CH_2NH_3^+$)
FA: formamidinium ($NH_2CH{=}NH_2^+$)



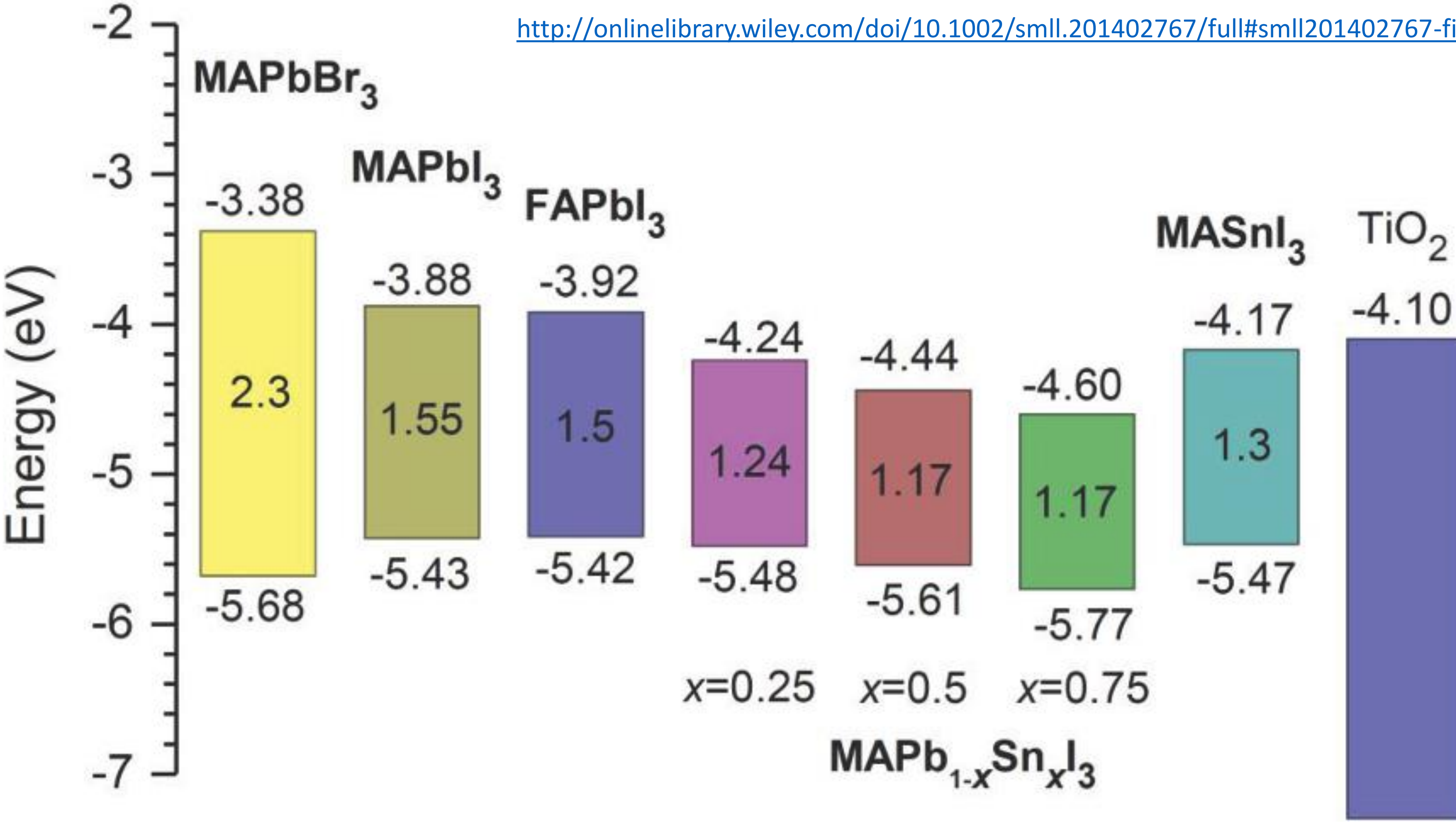
t = 0.89–1.0 → cubic structure

t = 0.8-1.0 → 3 D perovskite

NATURE PHOTONICS DOI: 10.1038/NPHOTON.2014.134

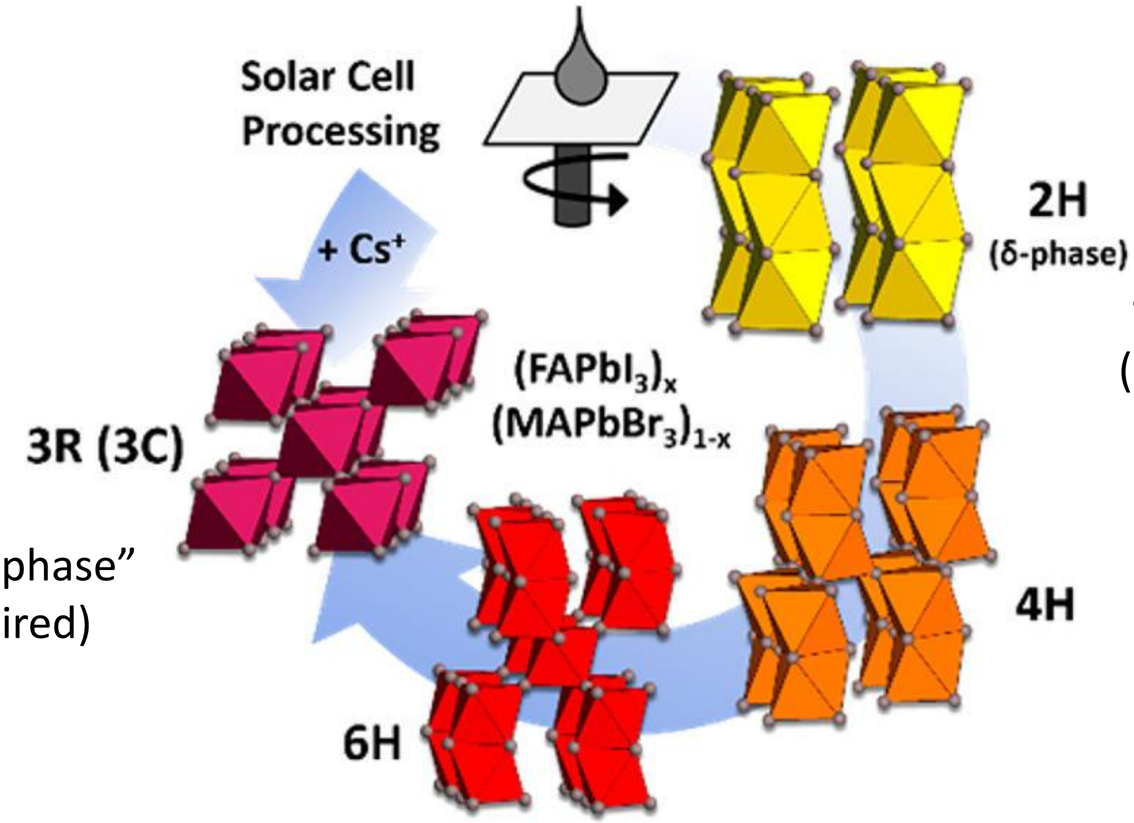
Band Gap Engineering

http://onlinelibrary.wiley.com/doi/10.1002/smll.201402767/full#smll201402767-fig-0002



Valence band formed by orbitals from B and X

Additives as “Crystallization Agents”



“yellow phase”
(weak absorber)

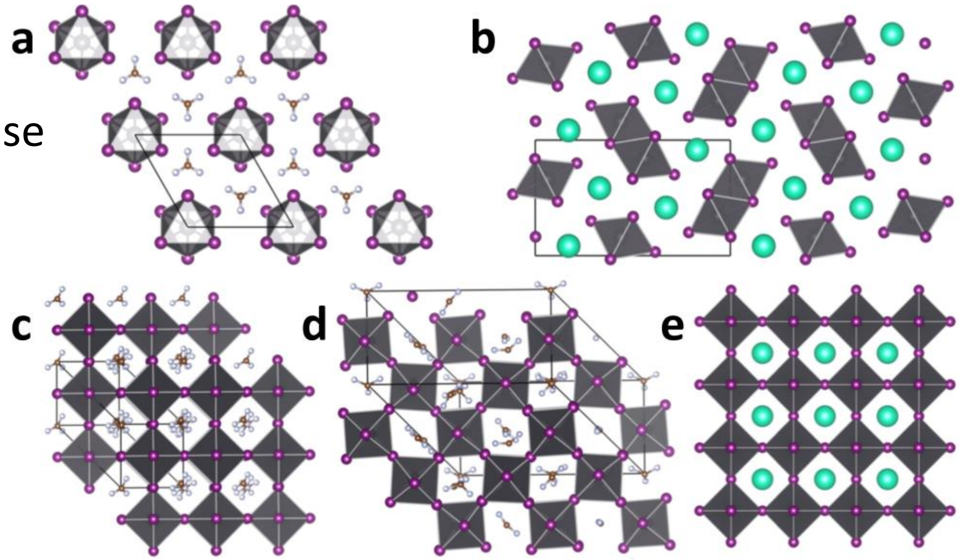
“black phase”
(Desired)

Gratia, P., Zimmermann, I., Schouwink, P., Yum, J.-H., Audinot, J.-N., Sivula, K., Wirtz, T. & Nazeeruddin, M. K. The Many Faces of Mixed Ion Perovskites: Unraveling and Understanding the Crystallization Process. *ACS Energy Lett.* **2,** 2686–2693 (2017).

Entropic Stabilization

“yellow phase”
(weak absorber)

FAPbI$_3$ δ-phase



CsPbI$_3$ δ-phase

“black phases”
perovskite
(Desired)

FAPbI$_3$ and CsPbI$_3$: δ-phase energetically favorable

Mixing FA and Cs → entropy favors a mixed phase
FA$_x$Cs$_{1-x}$PbI$_3$ perovskite phase energetically favorable

Yi, C., Luo, J., Meloni, S., Boziki, A., Ashari-Astani, N., Grätzel, C., Zakeeruddin, S. M., Röthlisberger, U. & Grätzel, M. Entropic stabilization of mixed A-cation ABX3 metal halide perovskites for high performance perovskite solar cells. *Energy Environ. Sci.* **9,** 656–662 (2016).

Certification

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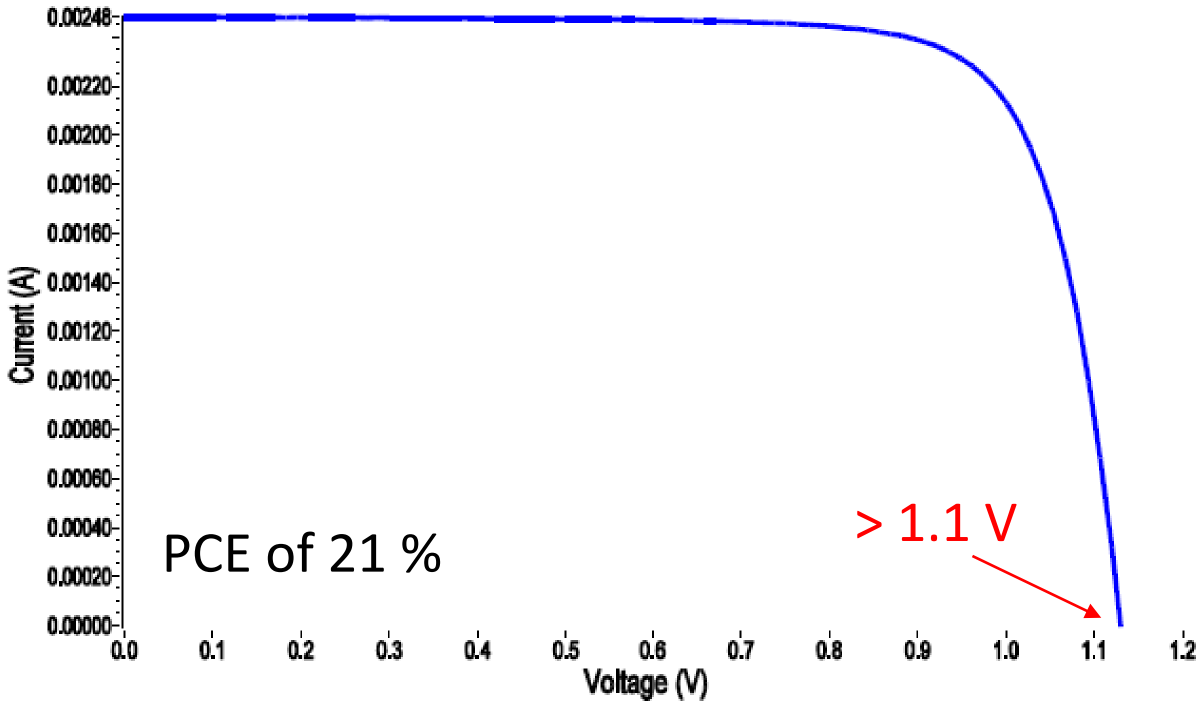
Newport		Technology and Application Center PV Lab Calibration Number 1356

IV Curve Cell # 1356 CBN19_62F 75 ms Small Ap 2



19.5 %
on 1 cm^2

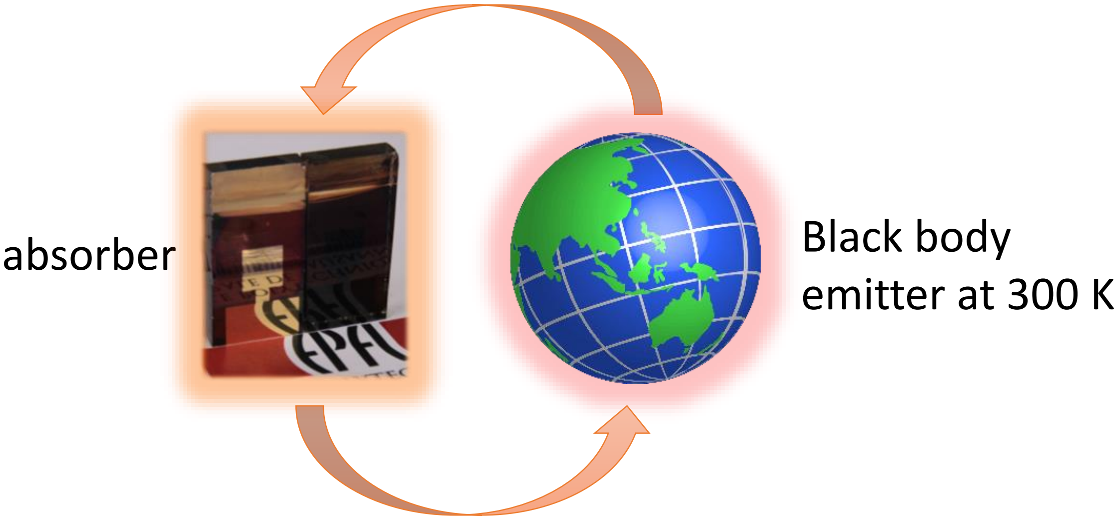
Cal Cert Data V1_2	Issue Date: Dec 01, 2015	Page 1of 4
	Reviewed and Approved by: Geoffrey Wicks	

Luminescence and Open-Circuit Voltage

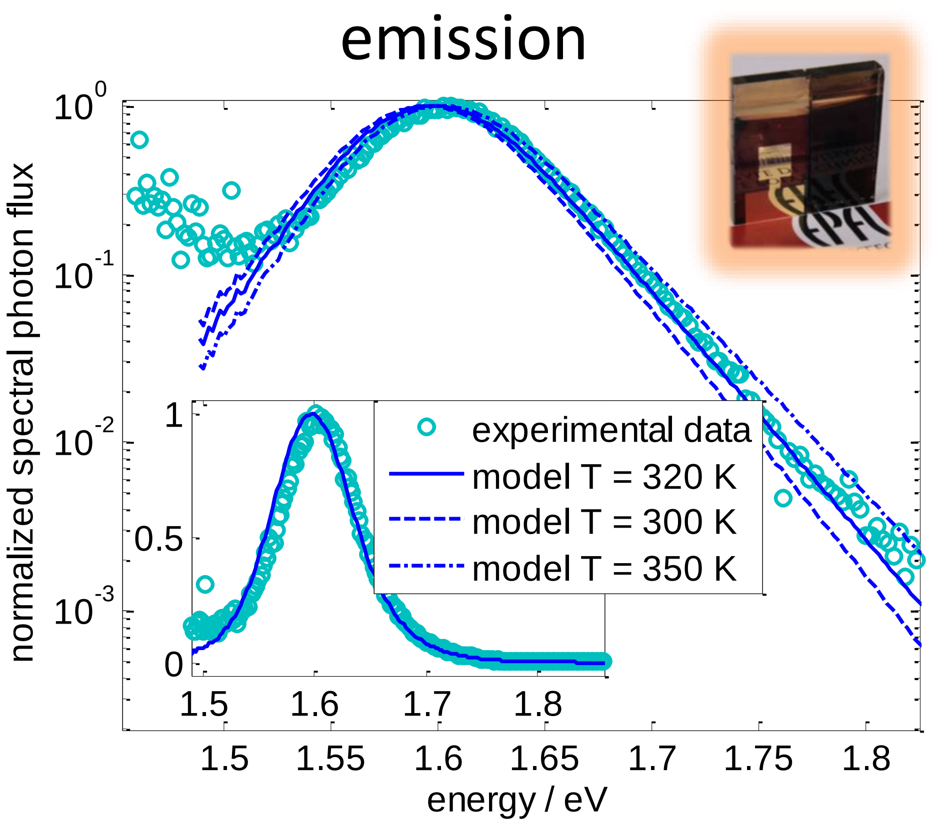
- If there is absorption, there will be emission.
- The solar cell in the dark is in thermal equilibrium with its surroundings, meaning that it absorbs and thus emits:

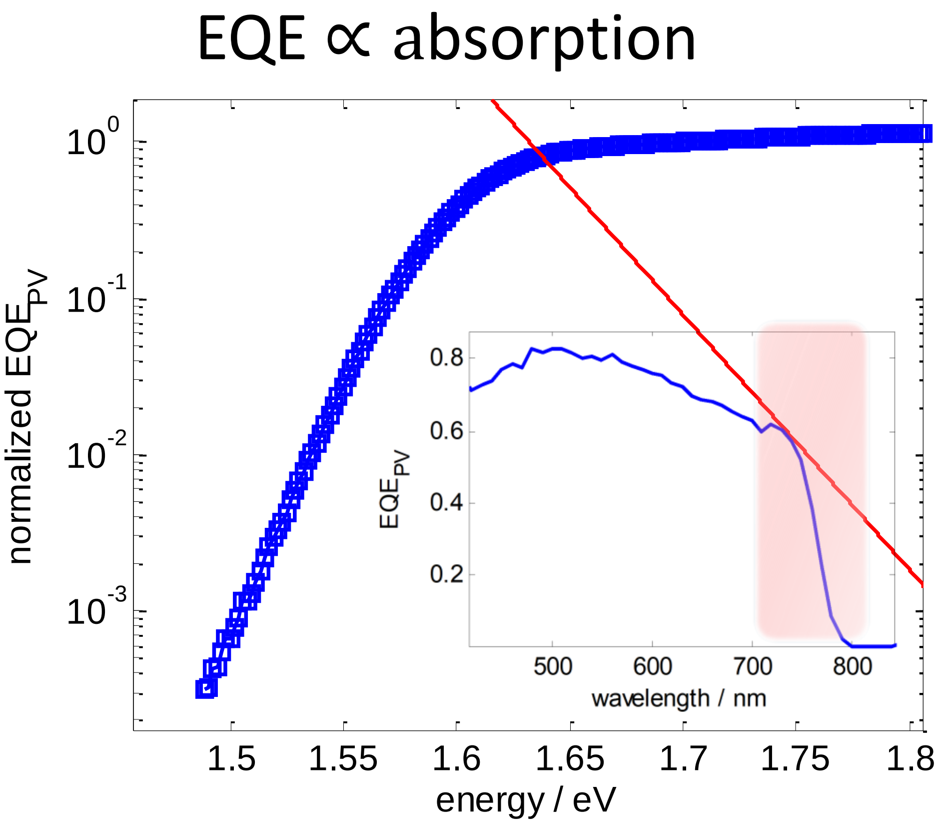
$$a(E)\,\Phi_{\mathrm{BB}}(T = 300\mathrm{K}, E)$$

→Emission spectrum can be predicted from absorption



Spectra of Perovskite Device





→ Steep absorption onset, Urbach energy of approx. 15 meV

Tress, W. *et al.* Predicting the Open-Circuit Voltage of CH3NH3PbI3 Perovskite Solar Cells Using Electroluminescence and Photovoltaic Quantum Efficiency Spectra: the Role of Radiative and Non-Radiative Recombination. *Adv. Energy Mater.* (2015). doi:10.1002/aenm.201400812

Luminescence and Open-Circuit Voltage

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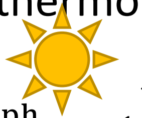
- The solar cell in the dark is in thermal equilibrium with its surroundings, meaning that it absorbs and thus emits:

$$a(E)\ \Phi_{\mathrm{BB}}(T = 300\mathrm{K}, E)$$

→Emission spectrum can be predicted from absorption

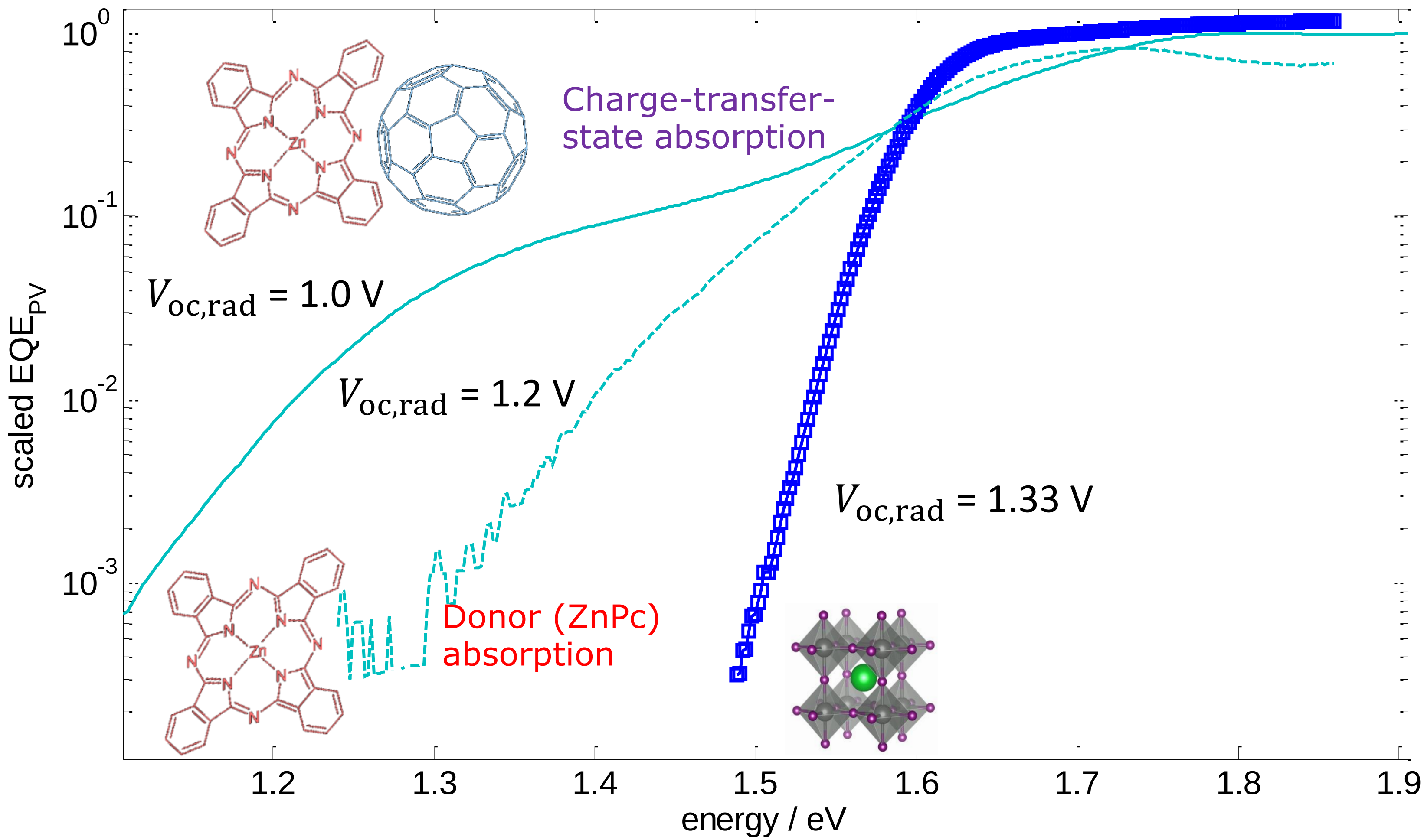
- Under illumination (thermodynamic limit):



$$V_{\mathrm{oc,rad}} = \frac{k_{\mathrm{B}}T}{e}\ln\left(\frac{J_{\mathrm{ph}}}{J_{\mathrm{em,0}}} + 1\right) \qquad J_{\mathrm{em,0}} = e\int a(E)\ \Phi_{\mathrm{BB}}(T = 300\mathrm{K}, E)dE$$

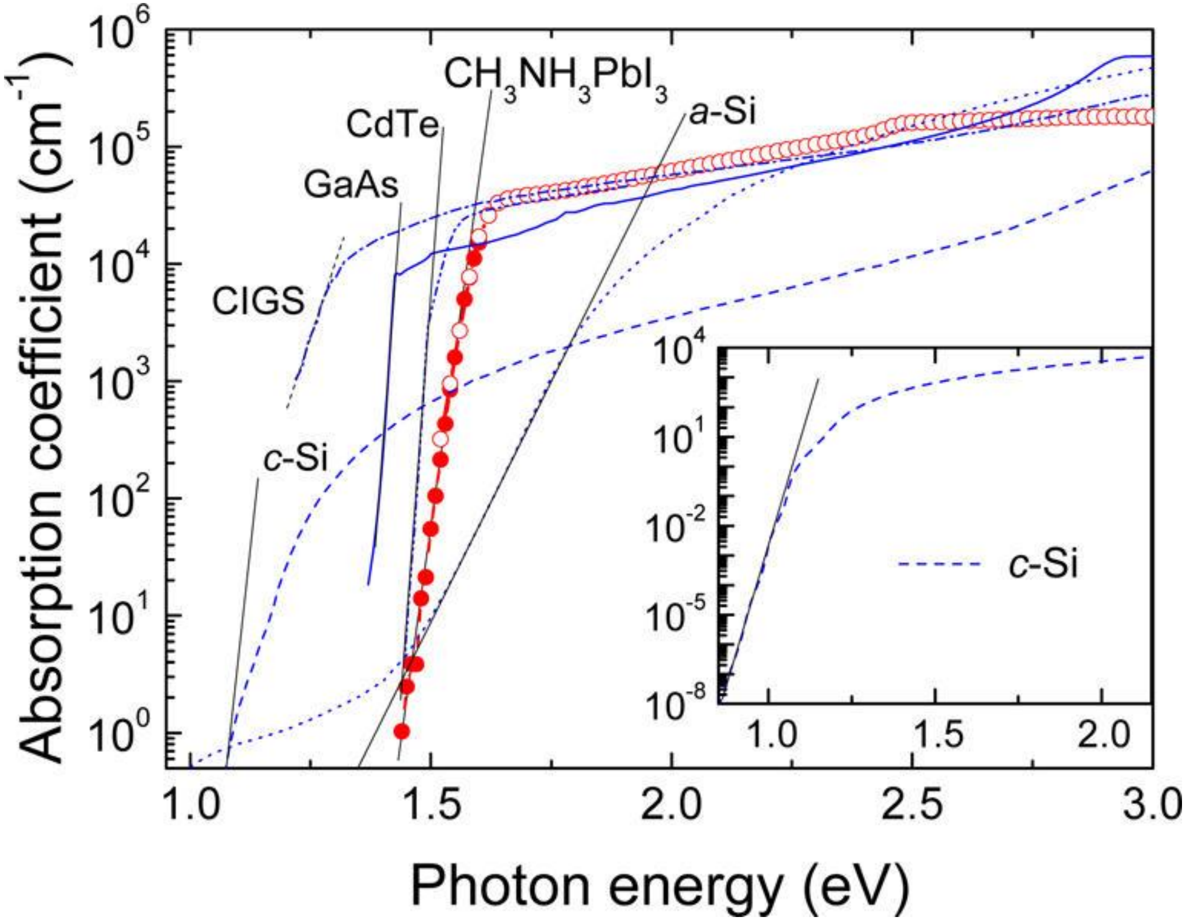
Rau, U. Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells. Phys. Rev. B **76,** 085303 (2007).

Compared to Organics



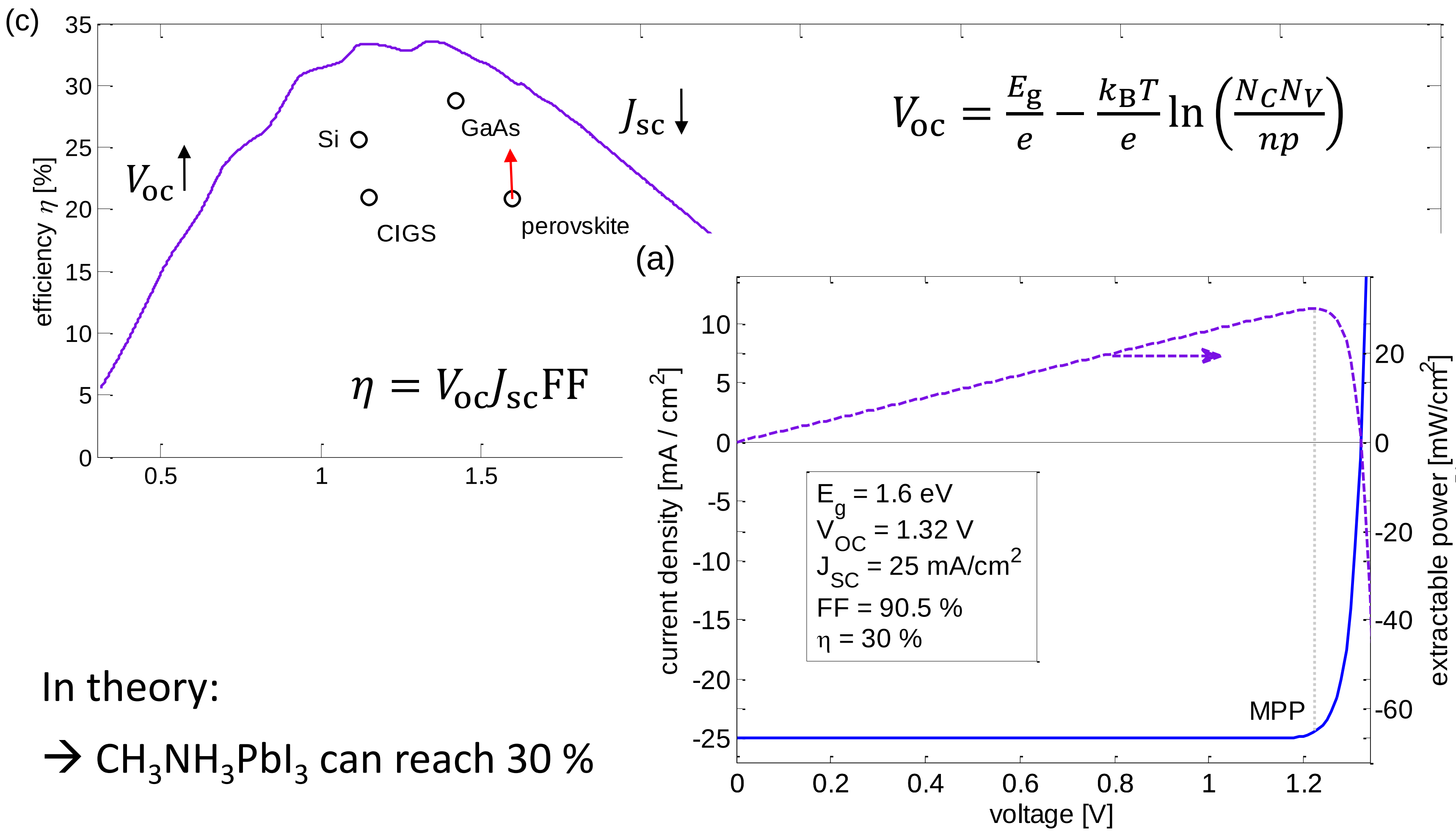
Steeper absorption onset → higher V_{oc}

Tail States



De Wolf, S. *et al.* Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. *J. Phys. Chem. Lett.* **5,** 1035–1039 (2014).

Shockley Queisser Limit



$$V_{oc} = \frac{E_g}{e} - \frac{k_B T}{e} \ln\left(\frac{N_C N_V}{np}\right)$$

$$\eta = V_{oc} J_{sc} \mathrm{FF}$$

In theory:

→ $CH_3NH_3PbI_3$ can reach 30 %

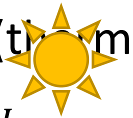
Luminescence and Open-Circuit Voltage

- If there is absorption, there will be emission.
- The solar cell in the dark is in thermal equilibrium with its surroundings, meaning that it absorbs and thus emits:

$$a(E)\,\Phi_{\mathrm{BB}}(T = 300\mathrm{K}, E)$$

→Emission spectrum can be predicted from absorption

- Under illumination (thermodynamic limit):



$$V_{\mathrm{oc,rad}} = \frac{k_{\mathrm{B}}T}{e}\ln\left(\frac{J_{\mathrm{ph}}}{J_{\mathrm{em,0}}} + 1\right) \qquad e\int a(E)\,\Phi_{\mathrm{BB}}(T = 300\mathrm{K}, E)dE$$

Rau, U. Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells. Phys. Rev. B **76,** 085303 (2007).

Recombination

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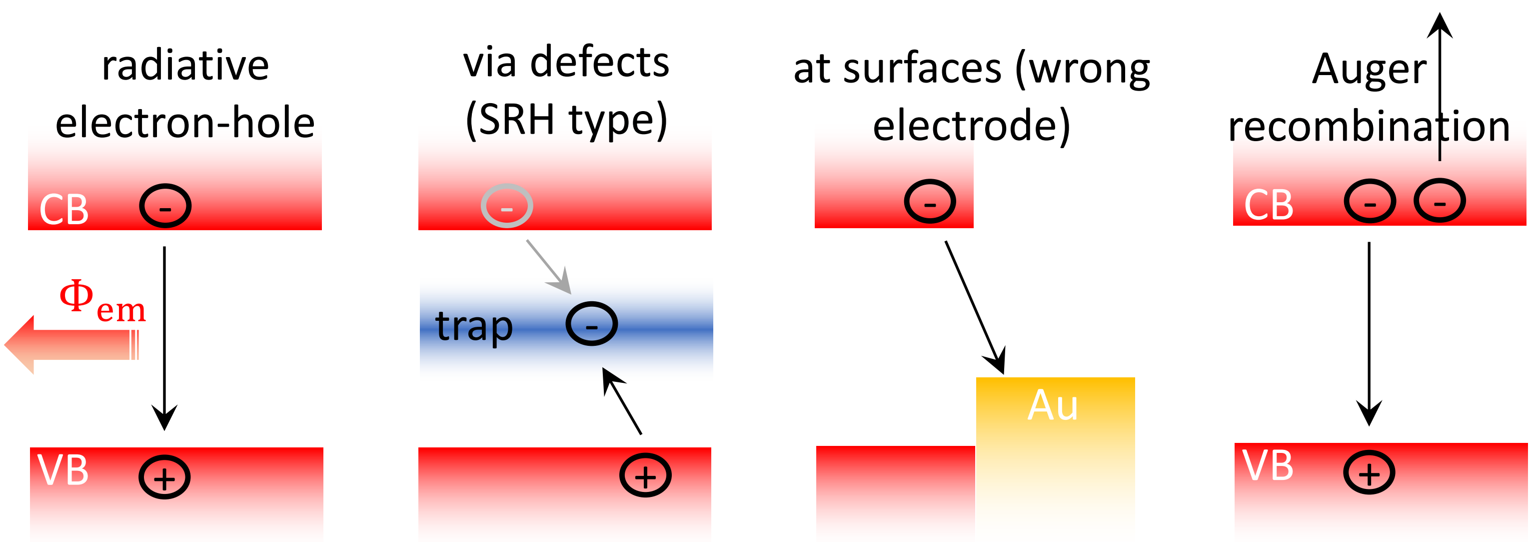


→ enters thermodynamic limit

→ pure, defect-free material

→ passivation, reduction of contact area

→ material property (indirect semiconductor)

unavoidable in absorber

to be avoided

→ non-radiative recombination

Luminescence and Open-Circuit Voltage

- If there is absorption, there will be emission.
- The solar cell in the dark is in thermal equilibrium with its surroundings, meaning that it absorbs and thus emits:

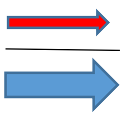
$$a(E)\,\Phi_{\mathrm{BB}}(T = 300\mathrm{K}, E)$$

→Emission spectrum can be predicted from absorption

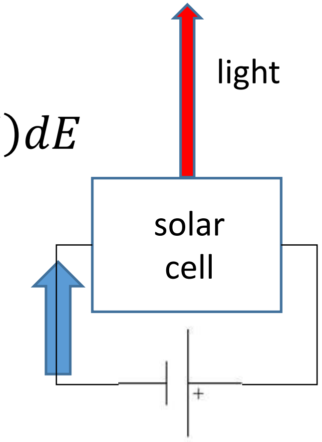
- Under illumination (thermodynamic limit):

$$V_{\mathrm{oc,rad}} = \frac{k_{\mathrm{B}}T}{e}\ln\left(\frac{J_{\mathrm{ph}}}{J_{\mathrm{em,0}}} + 1\right)$$

$$e\int a(E)\,\Phi_{\mathrm{BB}}(T = 300\mathrm{K}, E)dE$$

$\mathrm{EQE}_{\mathrm{EL}} =$ 

$$V_{\mathrm{oc,real}} = \frac{k_{\mathrm{B}}T}{e}\ln\left(\mathrm{EQE}_{\mathrm{EL}}\frac{J_{\mathrm{ph}}}{J_0} + 1\right)$$



Rau, U. Reciprocity relation between photovoltaic quantum efficiency and electroluminescent emission of solar cells. Phys. Rev. B **76,** 085303 (2007).

Driving the solar cell as LED

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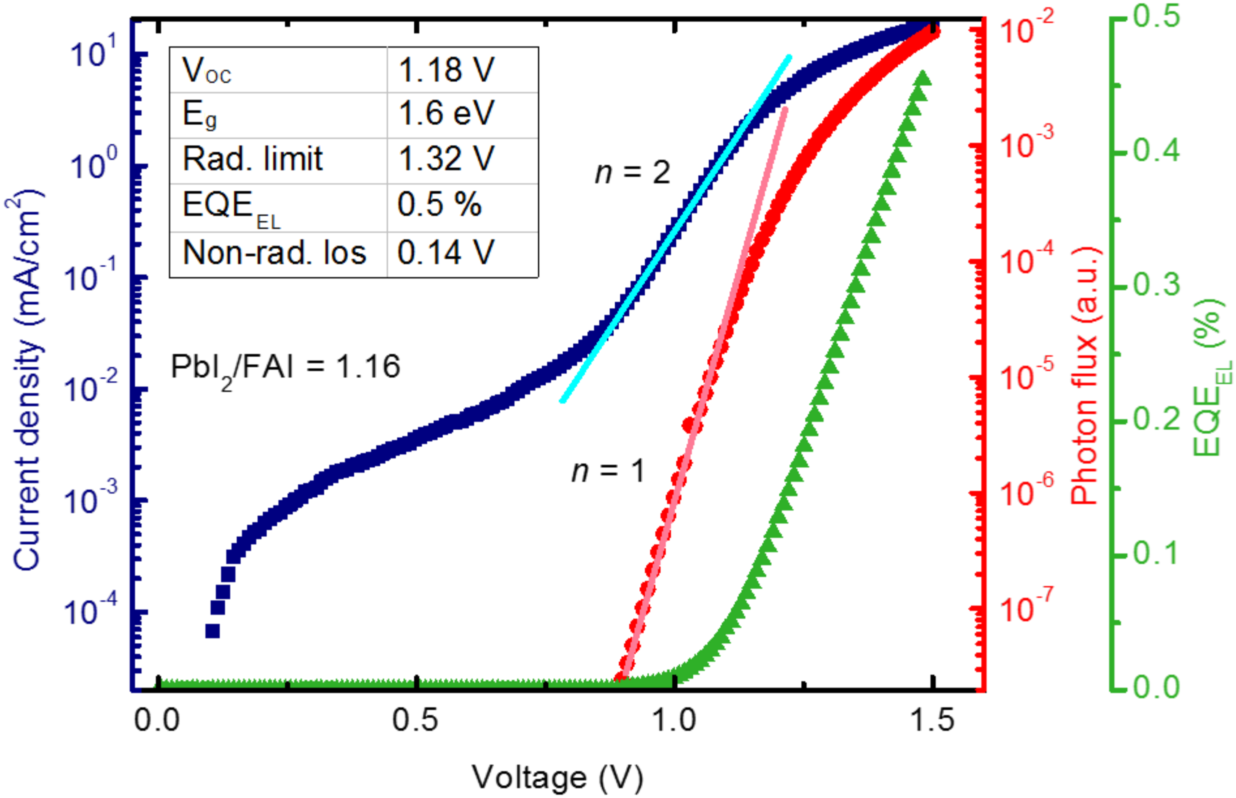
JV curve in the dark, emitted photon flux and the resulting quantum efficiency of EL

$$J_{\text{inj}} = J_0\left(\exp\frac{eV}{\boldsymbol{n}\,k_{\text{B}}T} - 1\right)$$

ideality factor

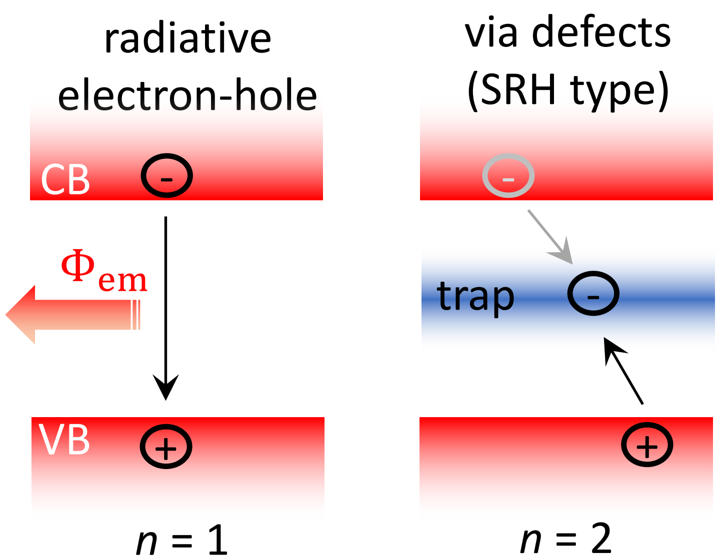
Arun Paraecattil

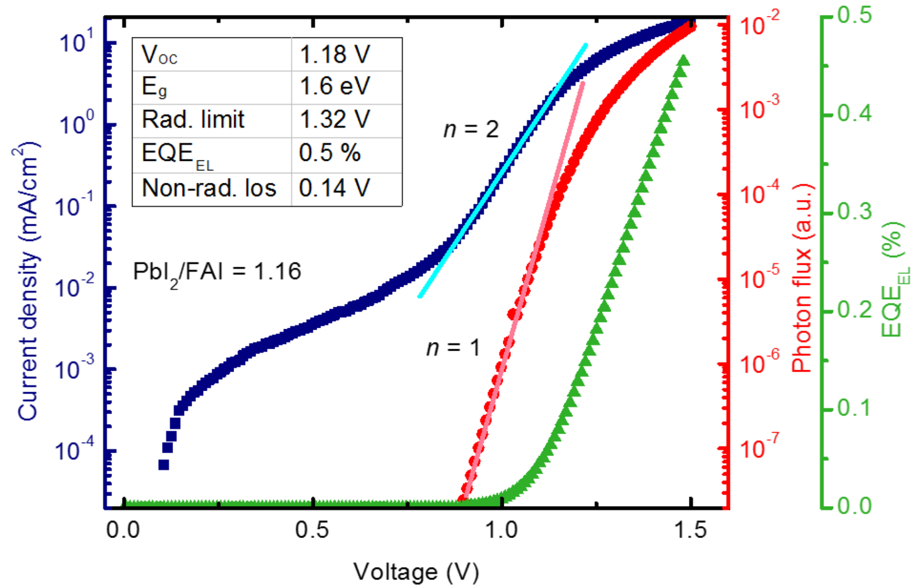


→ EL reaches 0.5 %, non-rad. recombination dominant

Bi, D. *et al.* Efficient luminescent solar cells based on tailored mixed-cation perovskites. *Science Advances* **2,** e1501170 (2016).

Recombination Mechanisms





βnp $\qquad kn = \frac{1}{\tau} n$

$$\frac{dn}{dt} = -\beta n^2(t) - \frac{1}{\tau} n(t)$$

$$V_{\mathrm{oc}} = \frac{E_{\mathrm{g}}}{e} - \frac{k_{\mathrm{B}} T}{e} \ln\left(\frac{N_C N_V}{np}\right)$$

Ideally: $G_0 = \int \alpha(E)\, \Phi_{\mathrm{BB}}(E) dE = \beta n_0 p_0 = \beta n_{\mathrm{i}}^2$ $\quad \rightarrow \beta \approx 10^{-11} \mathrm{cm}^3 \mathrm{s}^{-1}$

Measure Recombination Rates

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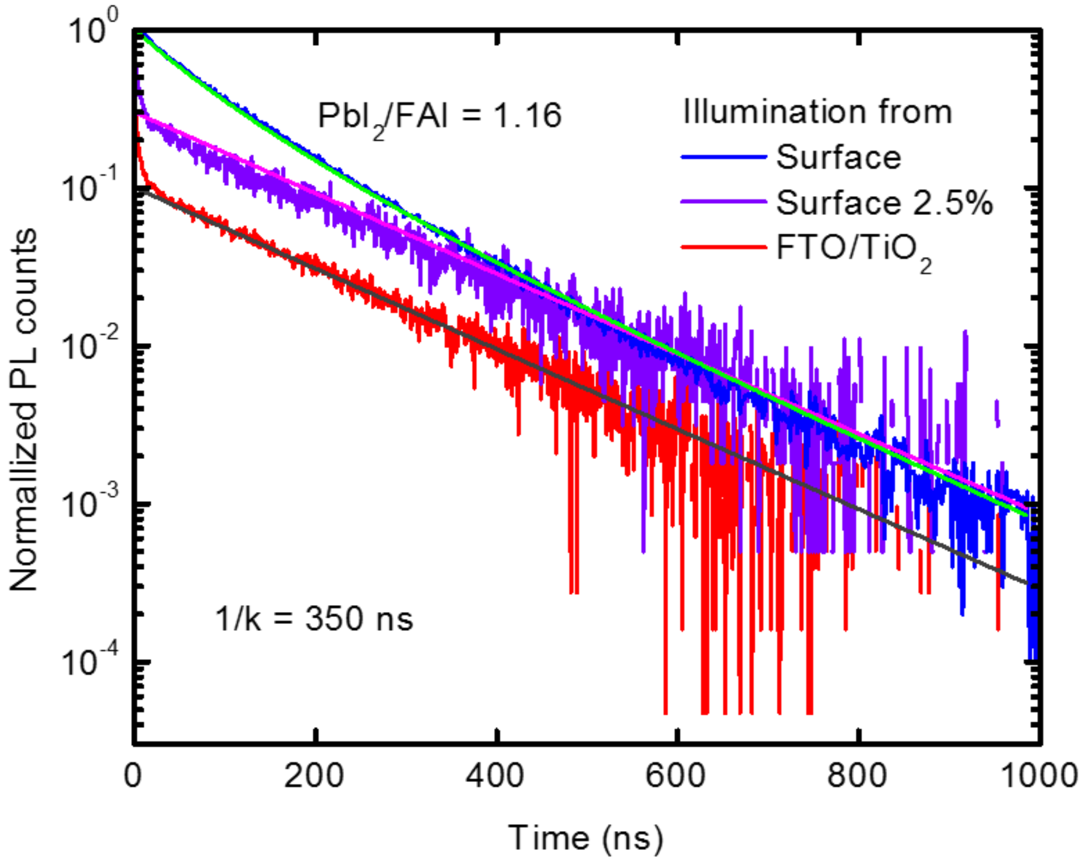
PL decay



$$\frac{dn}{dt} = -\beta n^2(t) - \frac{1}{\tau} n(t)$$

$$\beta \approx 10^{-11} \mathrm{cm}^3 \mathrm{s}^{-1}$$

$$\tau = 350 \text{ ns}$$

Long PL lifetime → reduced non-radiative recombination

Bi, D. *et al.* Efficient luminescent solar cells based on tailored mixed-cation perovskites. *Science Advances* **2,** e1501170 (2016).

V_{oc}: Light Intensity and Lifetime

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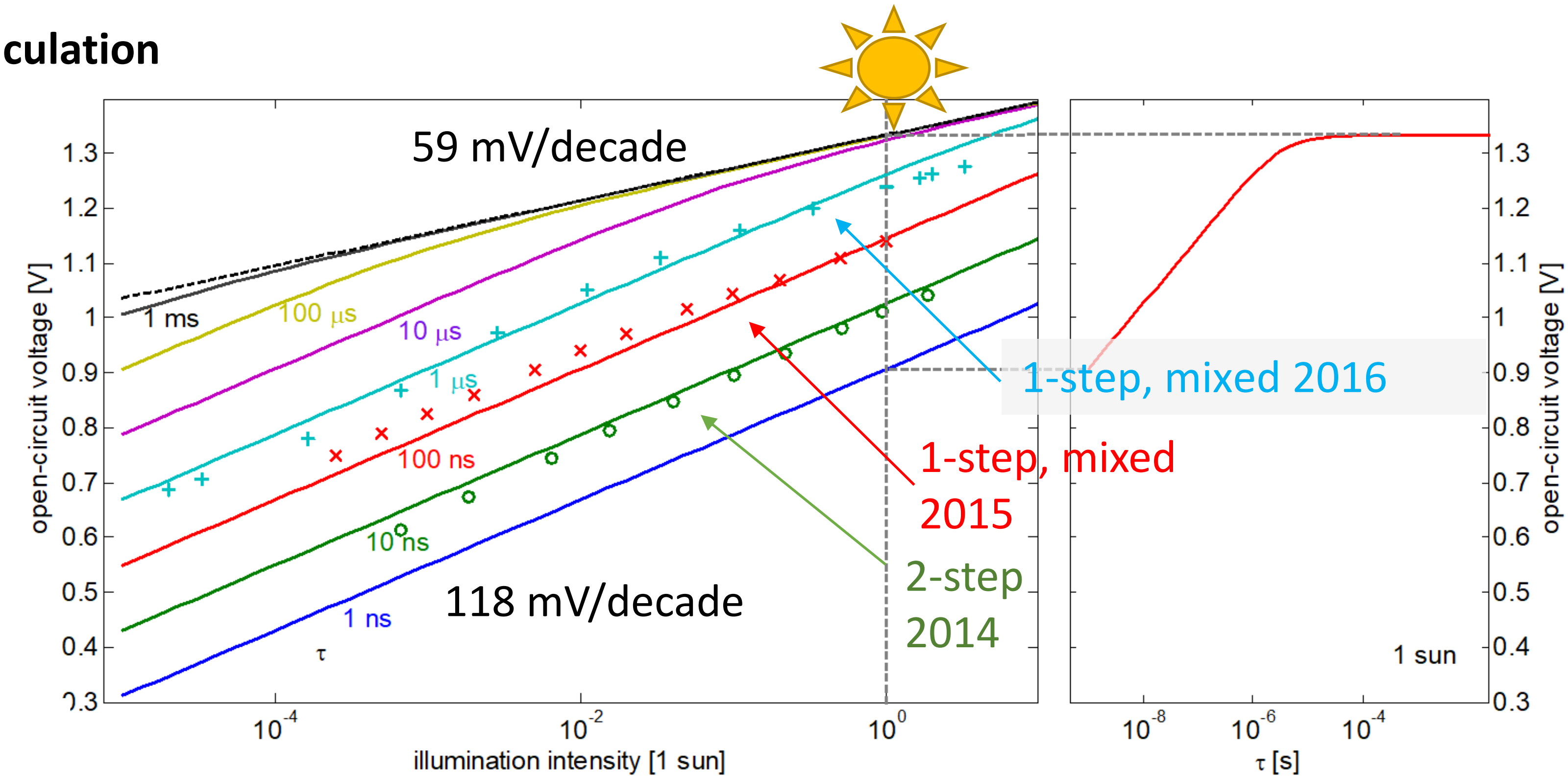
Calculation



→ Lifetime of 10 µs sufficient to reach ideal V_{oc} under 1 sun

Tress, W. Progress Report: Perovskite Solar Cells on the Way to Their Radiative Efficiency Limit – Insights Into a Success Story of High Open-Circuit Voltage and Low Recombination. *Adv. Energy Mater.* **7**, 1602358(2017).

Why is Defect Recombination so Low?

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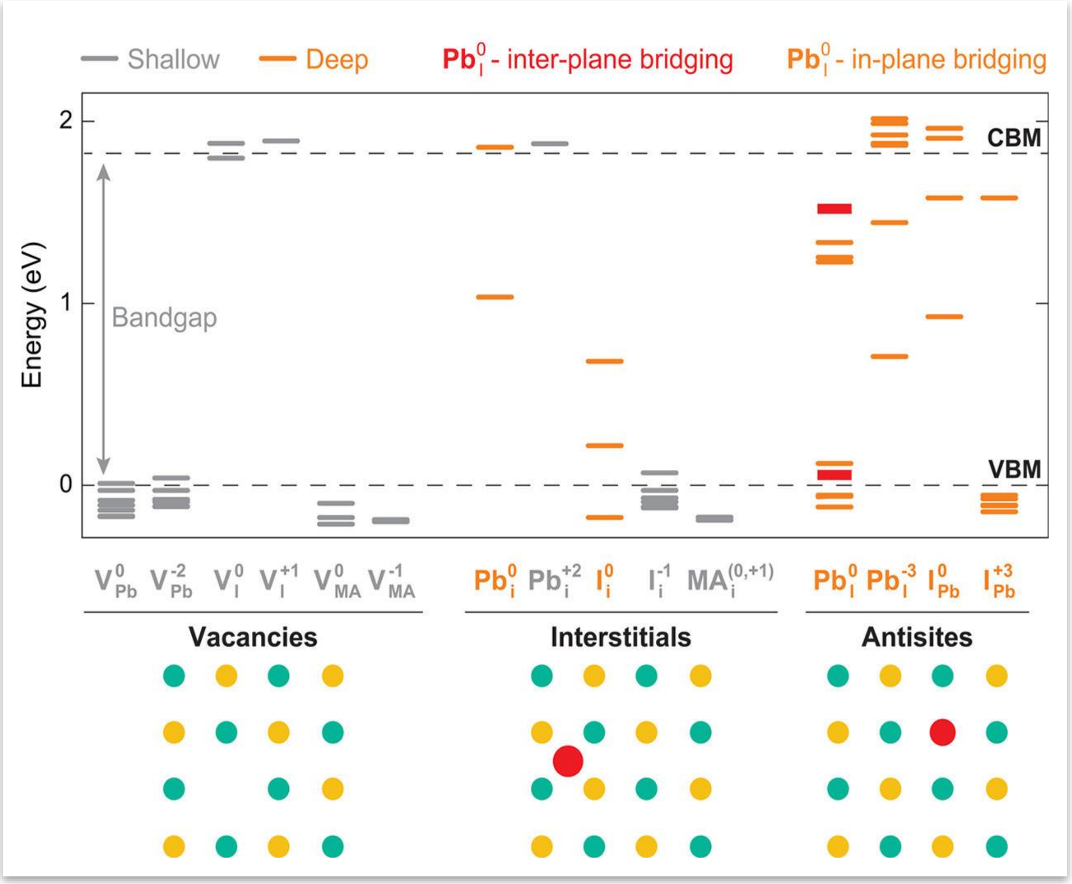
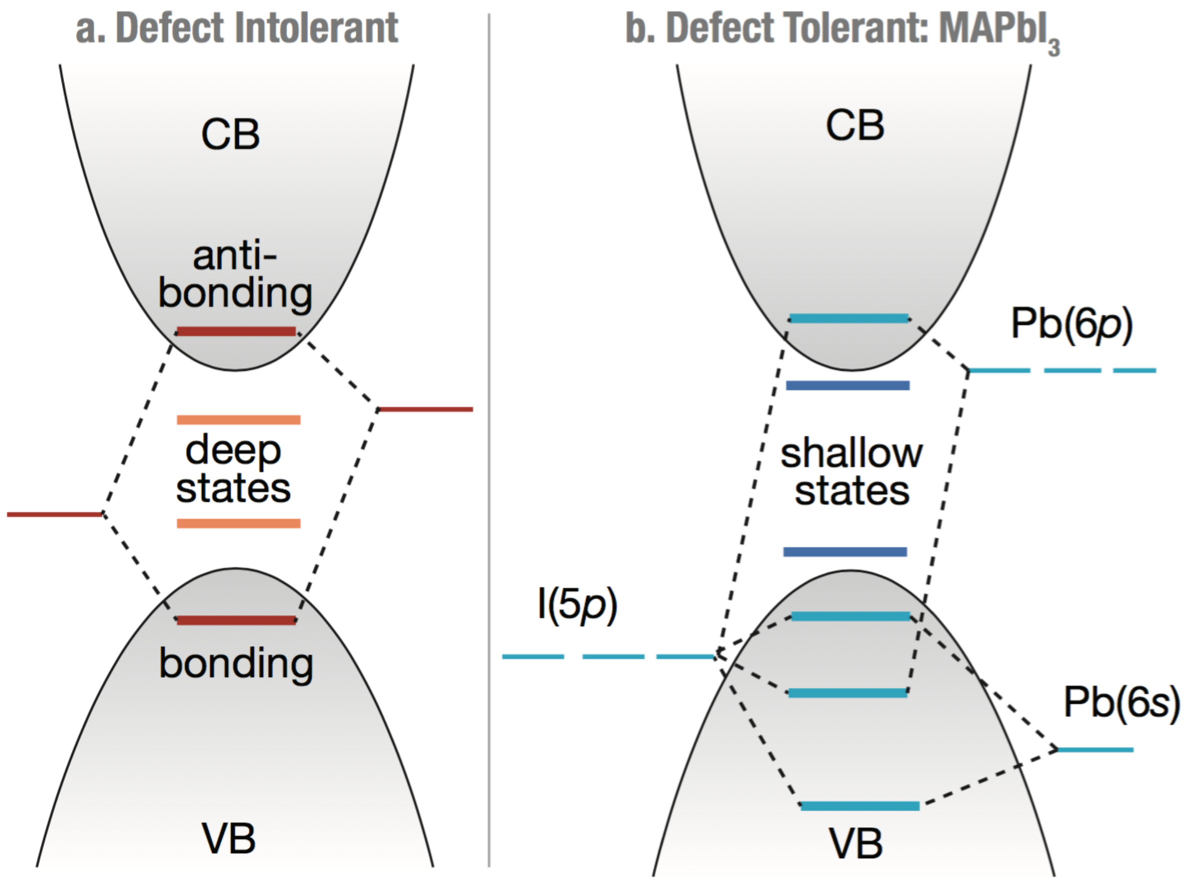
- anti bonding valence states → intrinsic traps are shallow
- high dielectric constant → low capture cross section
- role of grain boundaries and "self passivation"?



Buin, A. *et al.* Materials Processing Routes to Trap-Free Halide Perovskites. *Nano Lett.* **14,** 6281–6286 (2014).

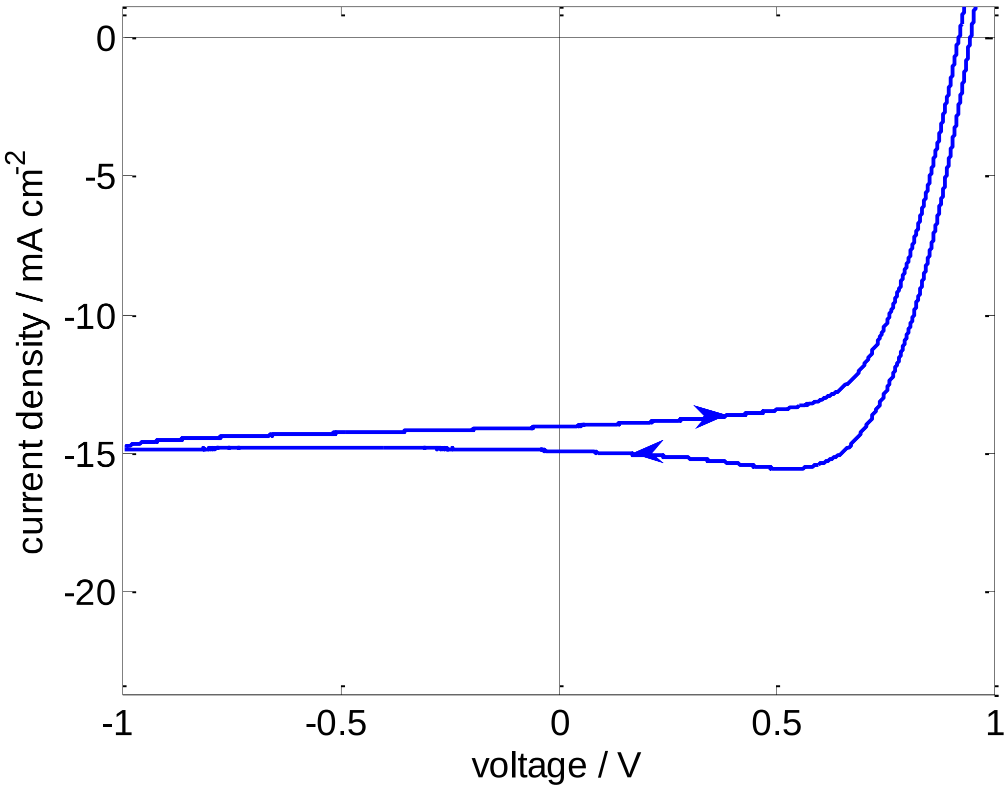
Defect Tolerance



R. E. Brandt, et al., *Chemistry of Materials*, 2017, DOI: 10.1021/acs.chemmater.6b05496.

Hysteresis: Backward and Forward Scan

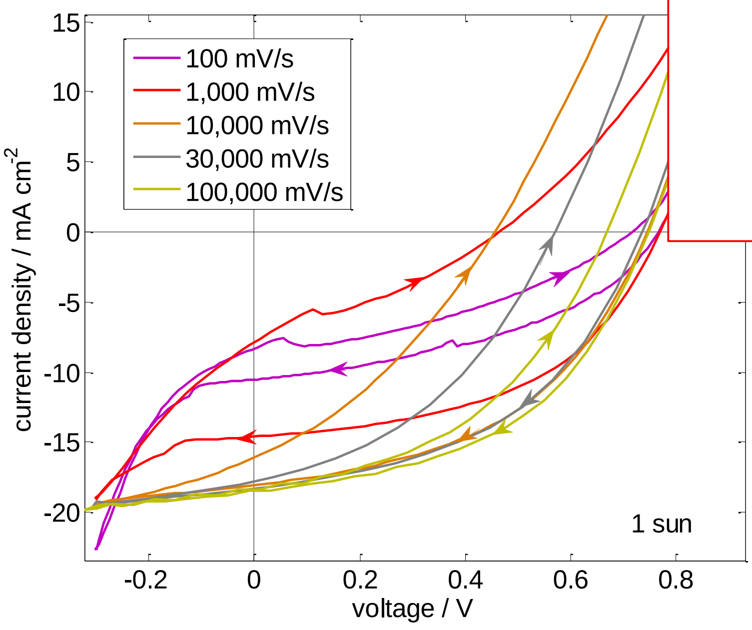
- Result depends on
  - preconditioning
  - scan direction

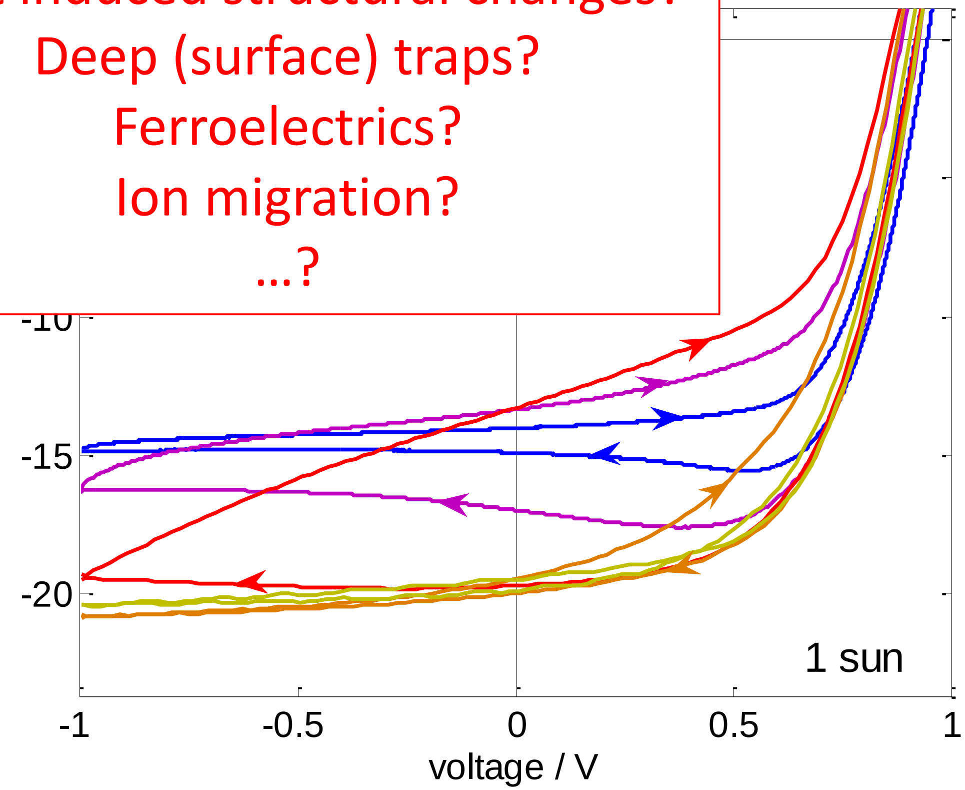


→ *JV* curve not sufficient to accurately determine efficiency
→ Hysteresis related to long-term instability and device degradation?

Hysteresis: Voltage Sweep Rates

without TiO_2 blocking layer





Light induced structural changes?
Deep (surface) traps?
Ferroelectrics?
Ion migration?
…?

Charge carrier collection efficiency → recombination

Tress, W. *et al.* Understanding the rate-dependent J–V hysteresis, slow time component, and aging in CH3NH3PbI3 perovskite solar cells: the role of a compensated electric field. *Energy Environ. Sci.* **8,** 995–1004 (2015).

Hysteresis: What Happens?

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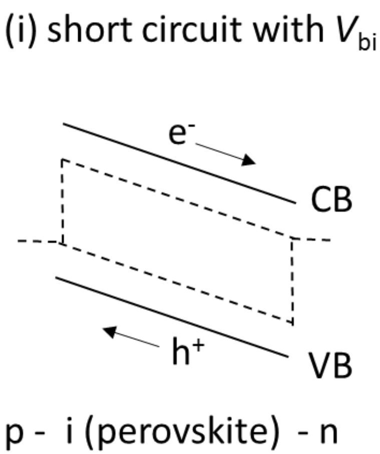
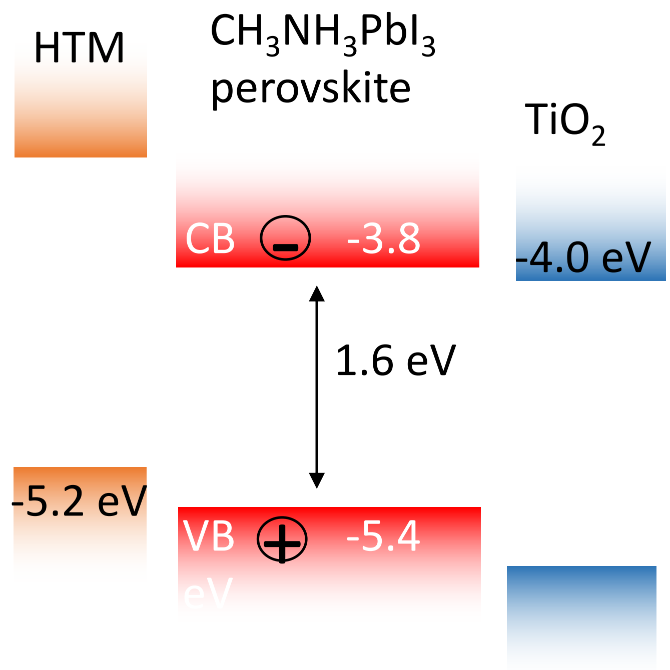
Solar cell works as a pin device with built-in potential V_{bi} dropping over the approx. intrinsic perovskite layer*

*Bergmann, V. W. *et al.* Real-space observation of unbalanced charge distribution inside a perovskite-sensitized solar cell. *Nat Commun* **5,** (2014).





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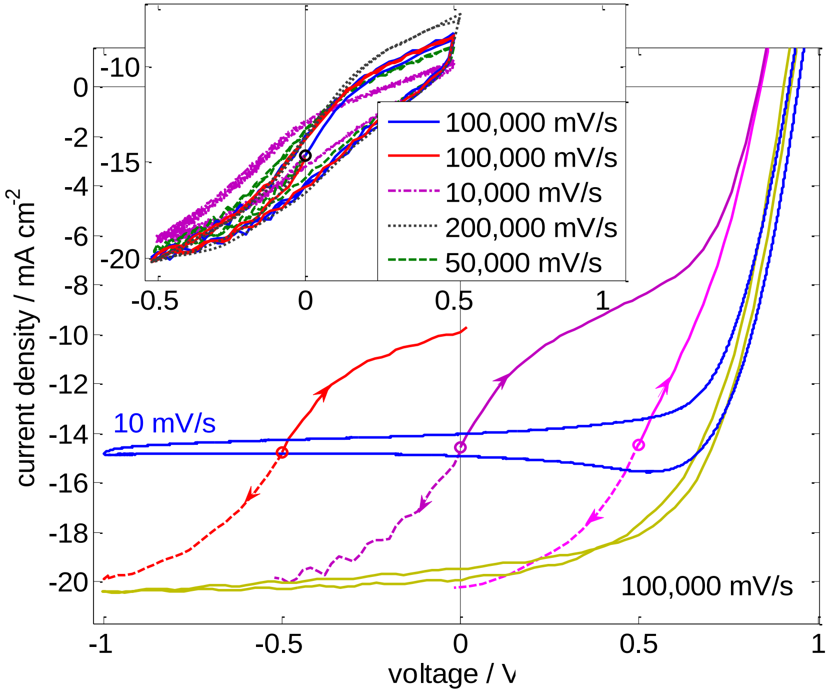

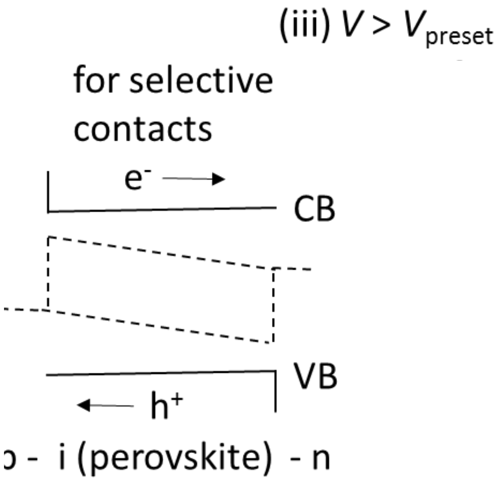

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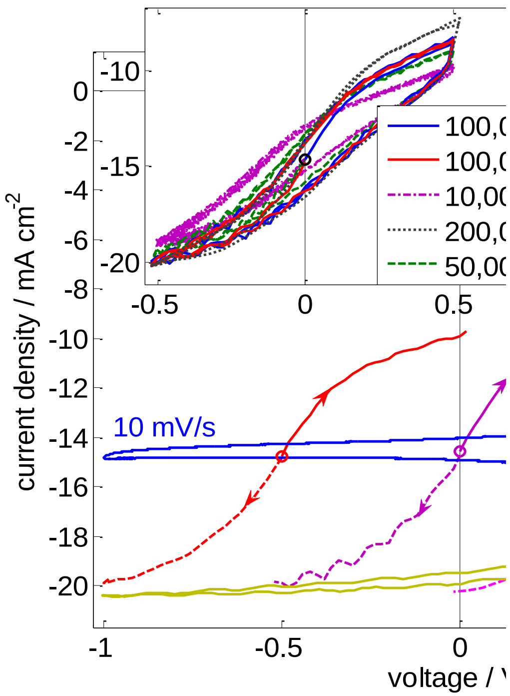
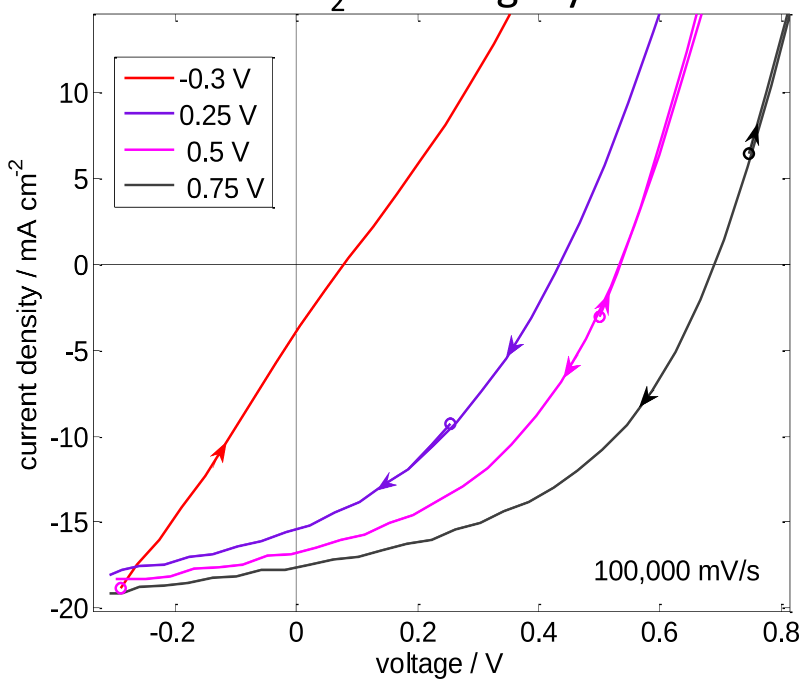
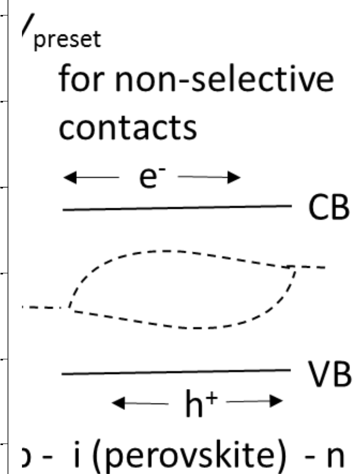
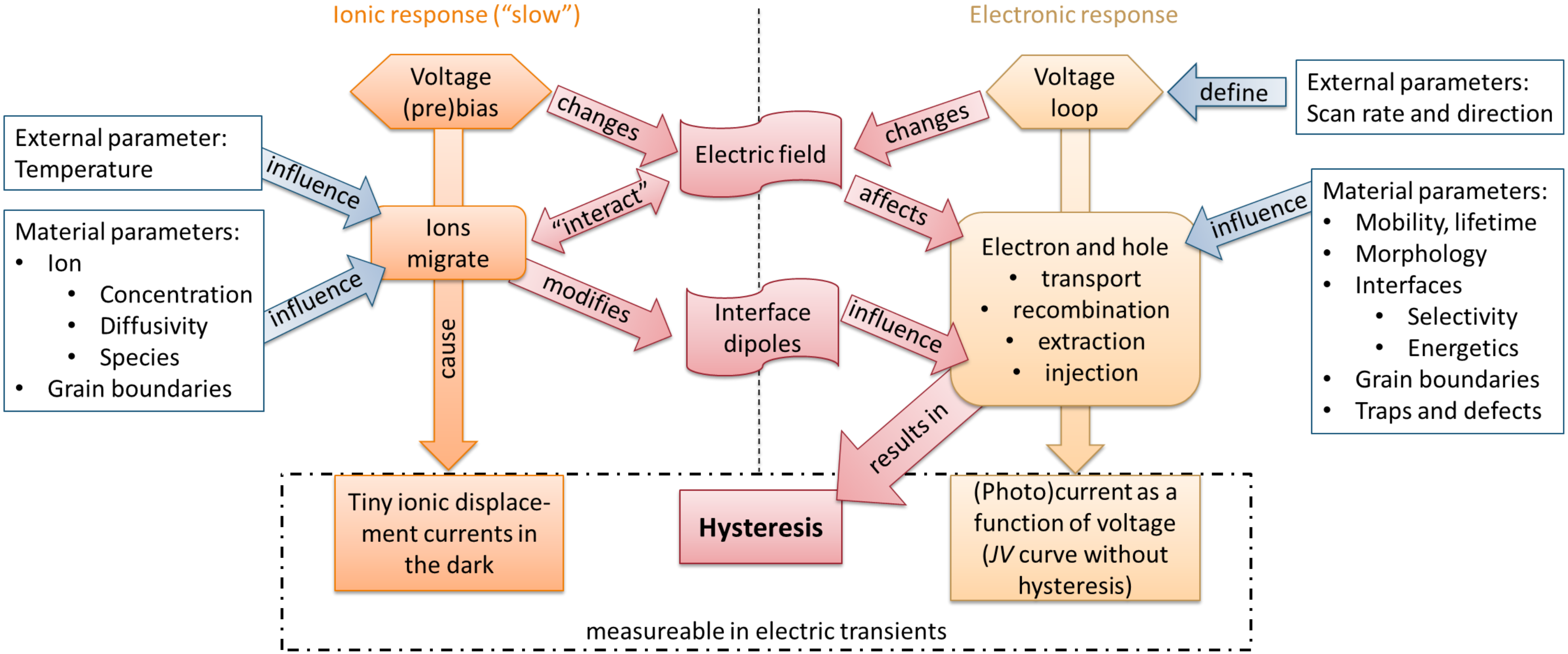


without TiO_2 blocking layer





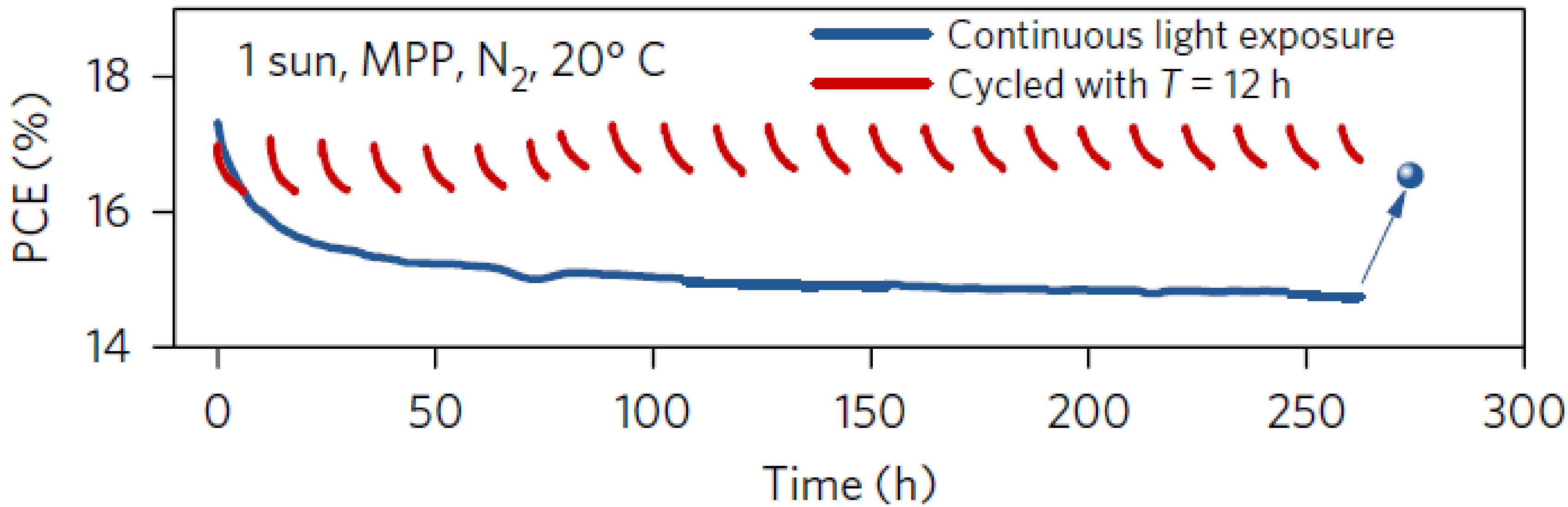
Hysteresis



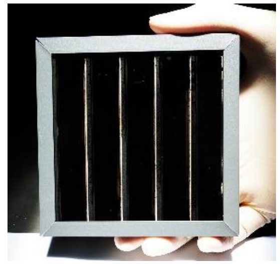
Tress, W., Metal Halide Perovskites as Mixed Electronic-Ionic Conductors: Challenges and Chances – from Hysteresis to Memristivity. *JPCL Perspective* (2017)

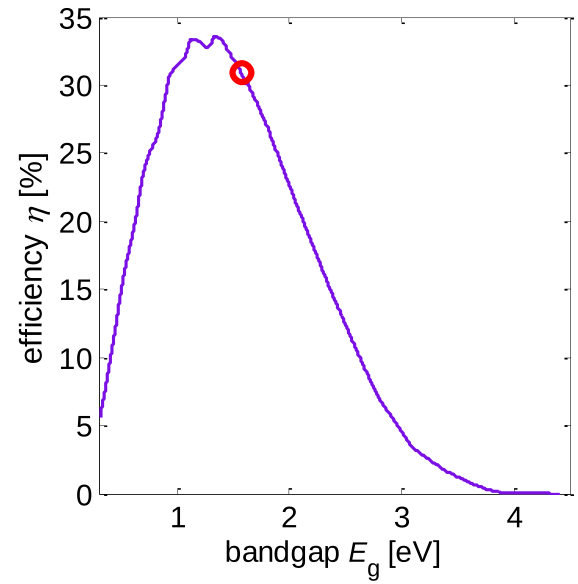
Reversible Transients

Domanski, K., *et al*. *Nature Energy* **3,** 61–67 (2018).



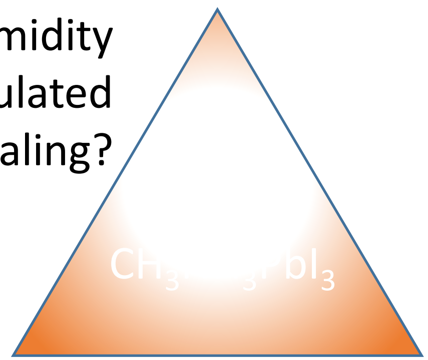
Perovskite Solar Cells: Outlook





Lifetime / Stability

- Sensitive to humidity
- Stable when encapsulated
- Upscaling?



Costs

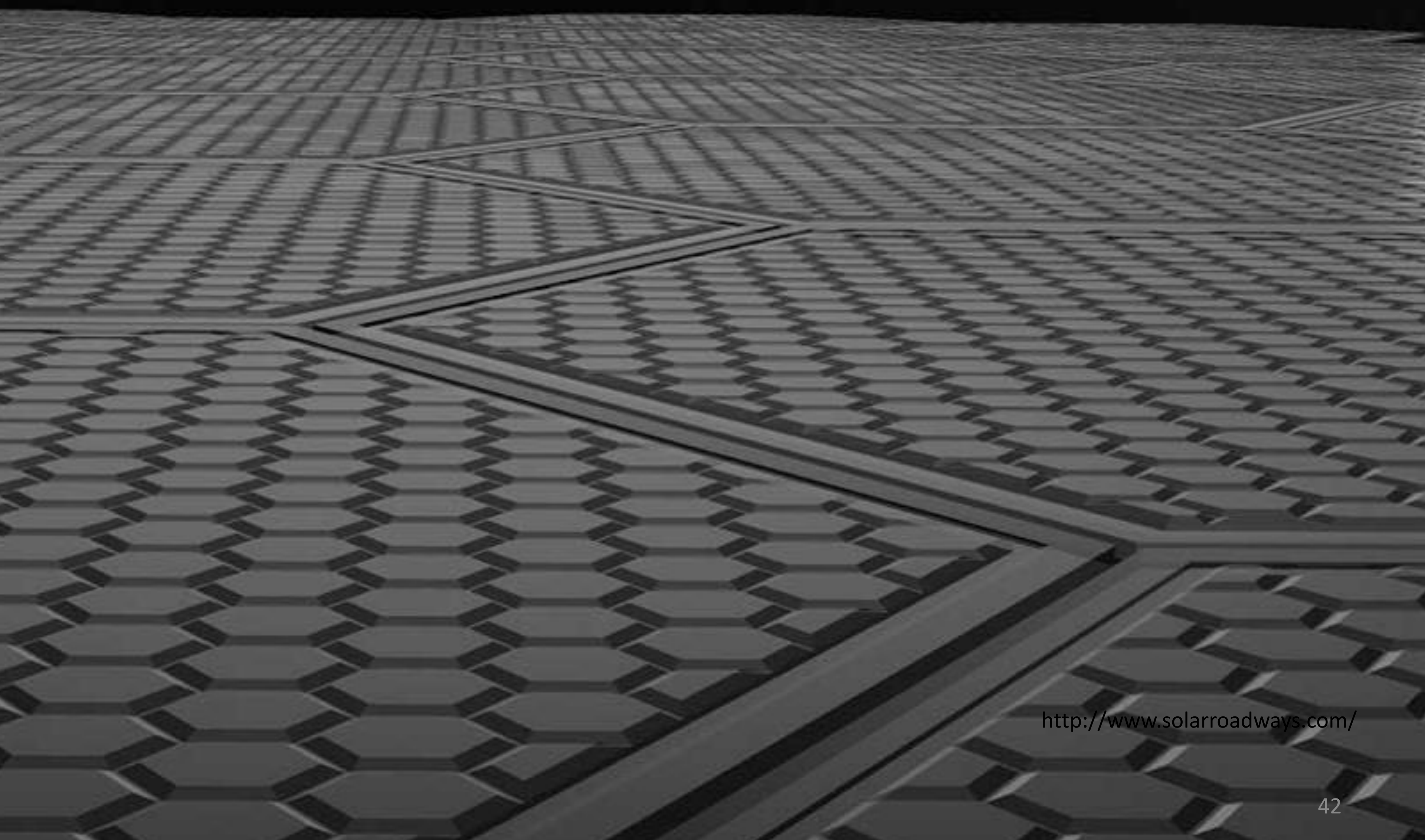
- Solution processing
- Low-*T* processes
- Absorber material low-cost
- Encapsulation?

Efficiency

- **Theoretical** SQ limit with 1.57 eV gap: $\boldsymbol{\eta}$ **= 31 %**
- Considering the predicted max. V_{oc} (incl. tail) of 1.32 V, 24 mA/cm² → η = **29 %**, (V_{MPP} = 1.2 V, FF ≈ 90 %)
- Considering **state-of-the-art recombination** (SRH): V_{oc} = 1.2 V, FF = 83 % → η = **24 %**

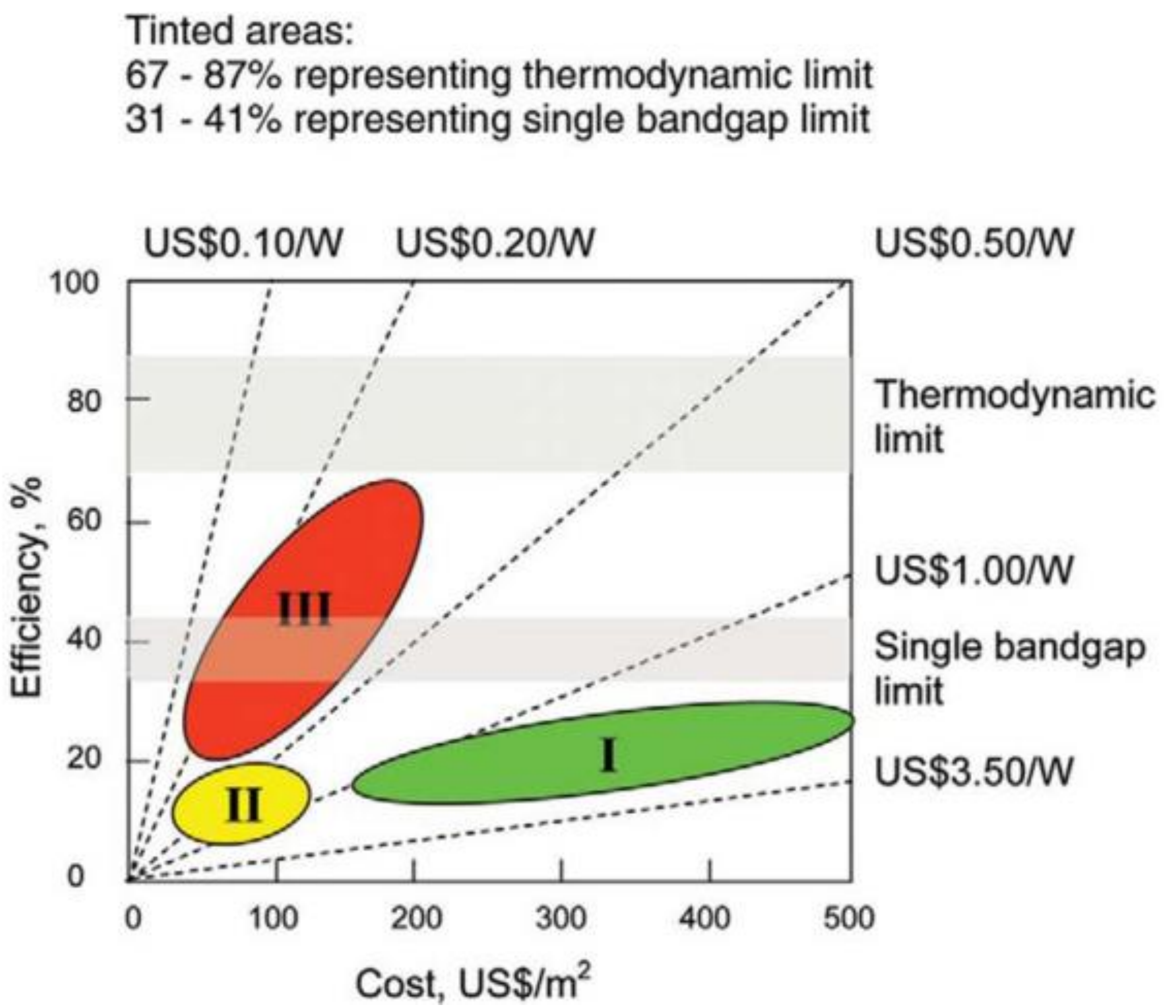
- Toxicity?
- Acceptance?

Third Generation Concepts



http://www.solarroadways.com/

Overcoming the SQ Limit



http://www.intechopen.com/books/solar-cells-research-and-application-perspectives/optimization-of-third-generation-nanostructured-silicon-based-solar-cells

Intermediate Band Solar Cells

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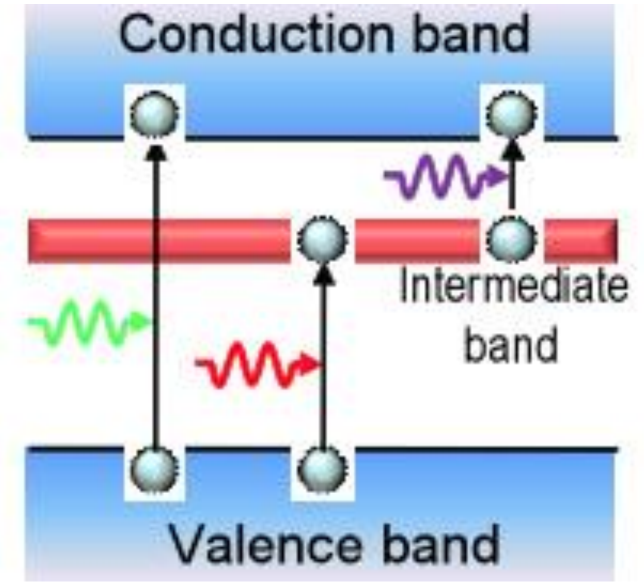
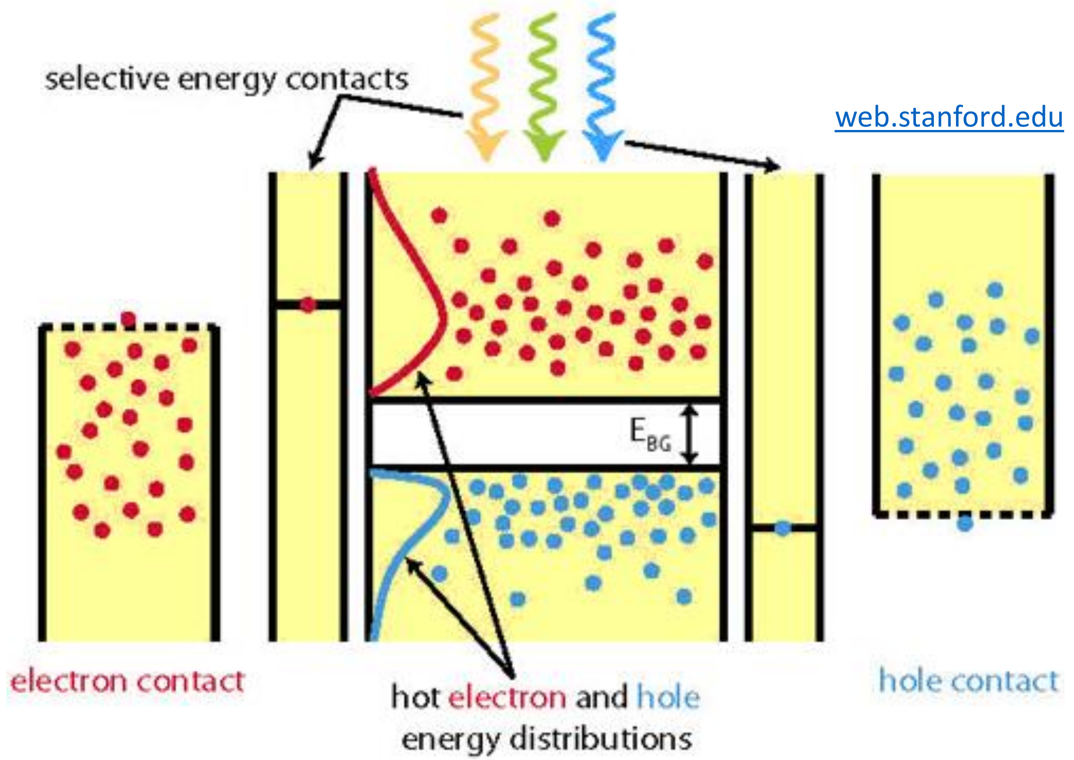
cstec.engin.umich.edu



- Maintain high voltage
- Increase current
- 3 quasi Fermi levels

- Experimental trials: InAs QDs in GaAs not yet very successful

Hot Carrier Solar Cells



- Avoiding thermalization by introducing "phonon bottleneck"
- Energy selective contacts

→ not yet successfully realized

Up- and Down Conversion

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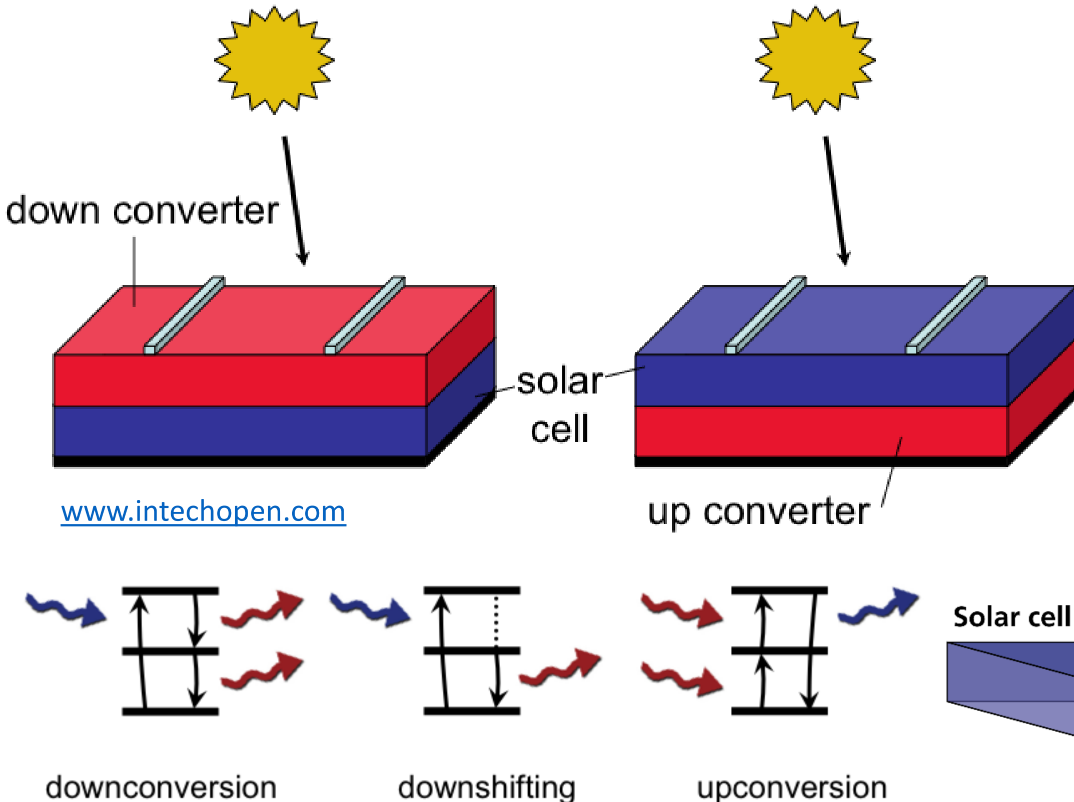
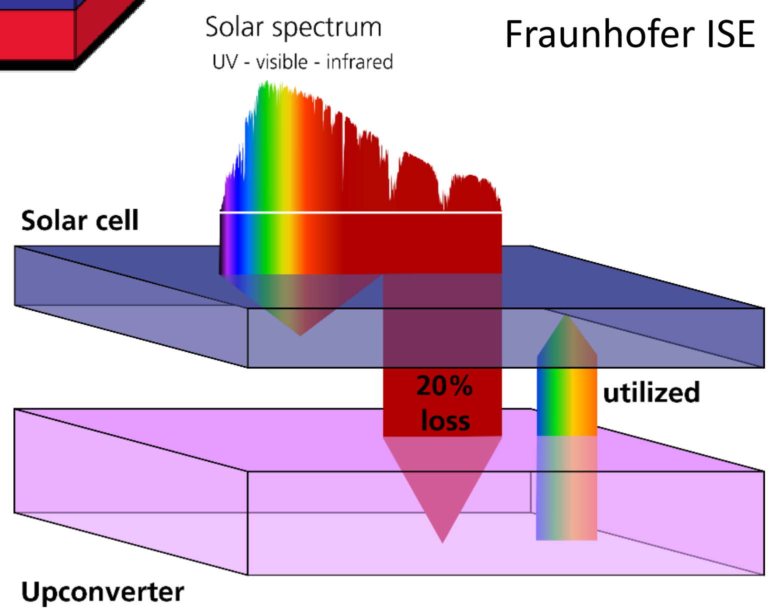


www.intechopen.com



Fraunhofer ISE

- Effects shown, however with low yield