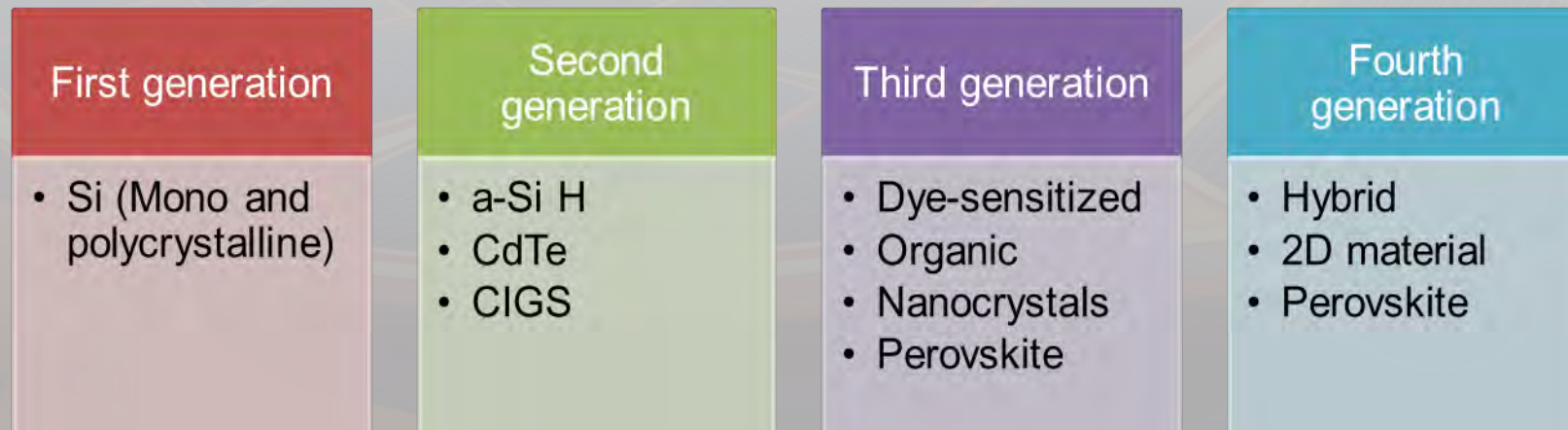


# Fourth generation solar cells based on halide perovskites: poking them with ultrafast light

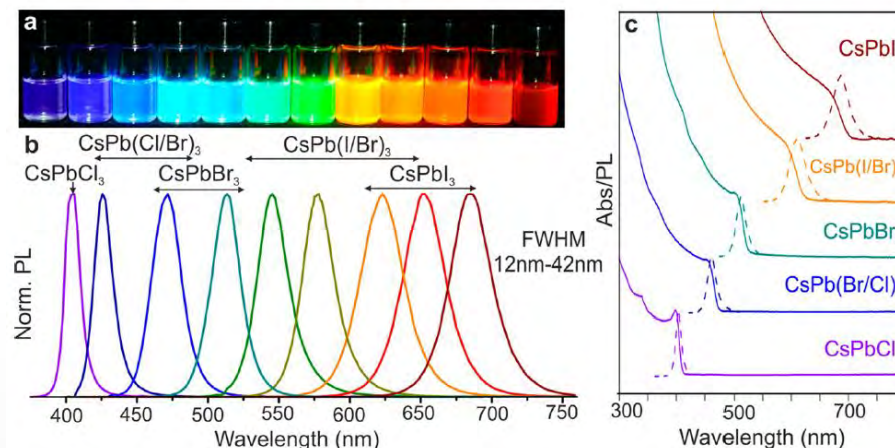
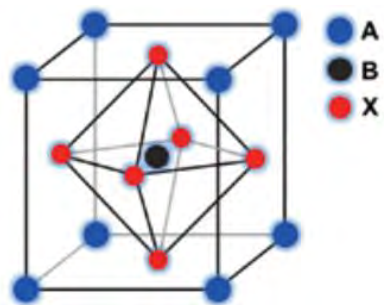
**Suchi Guha**

Department of Physics and Astronomy, University of Missouri, Columbia

E-mail: [guhas@missouri.edu](mailto:guhas@missouri.edu)

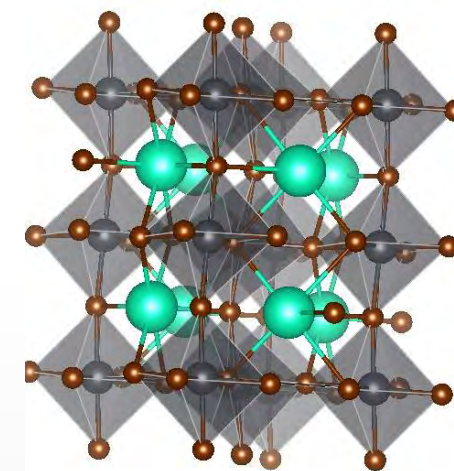


# Metal halide perovskites are (not) new

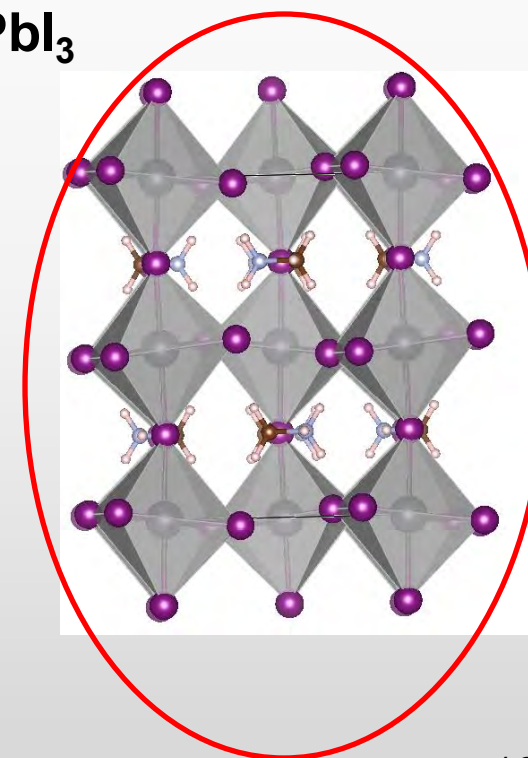


Protesescu *et al.* Nano Lett. **15**, 3692 (2015).

CsPbBr<sub>3</sub>



CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>



- all-inorganic metal halide perovskites (IHPs)
- organic-inorganic metal halide perovskites (OIHPs)

## CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, ein Pb(II)-System mit kubischer Perowskitstruktur

CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, a Pb(II)-System with Cubic Perovskite Structure

Dieter Weber

Institut für Anorganische Chemie der Universität Stuttgart

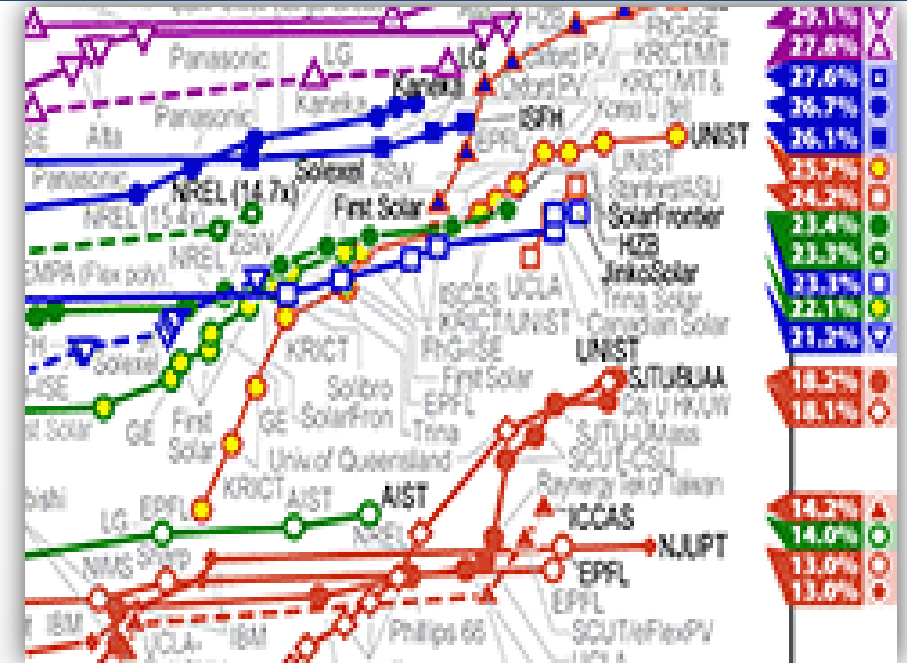
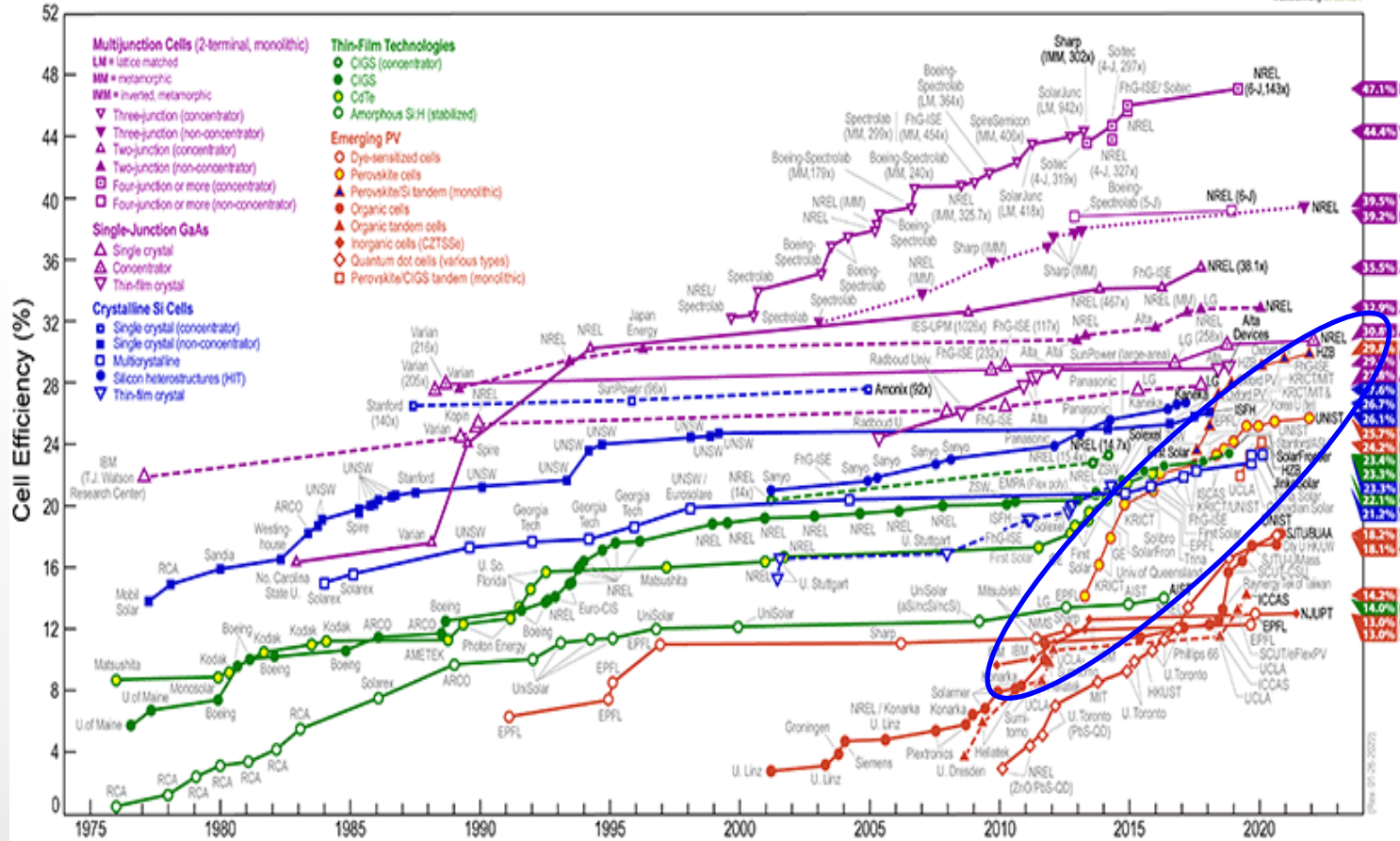
Z. Naturforsch. **33b**, 1443–1445 (1978); eingegangen am 21. August 1978

Synthesis, X-ray

CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> (X = Cl, Br, I) has the cubic perovskite structure with the unit cell parameters  $a = 5,68 \text{ \AA}$  (X = Cl),  $a = 5,92 \text{ \AA}$  (X = Br) and  $a = 6,27 \text{ \AA}$  (X = I). With exception of CH<sub>3</sub>NH<sub>3</sub>PbCl<sub>3</sub> 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.

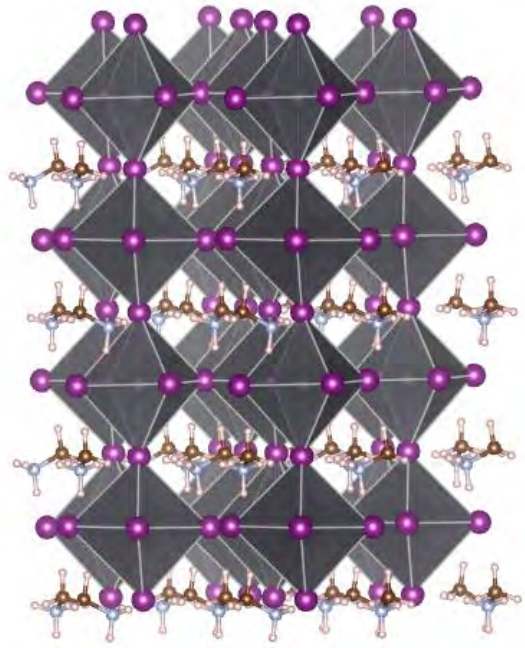
# Solar cell efficiencies

## Best Research-Cell Efficiencies

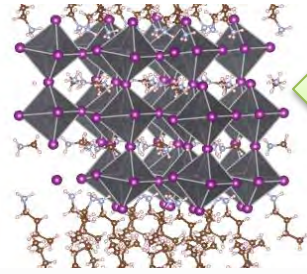


# From 3D to low dimensional

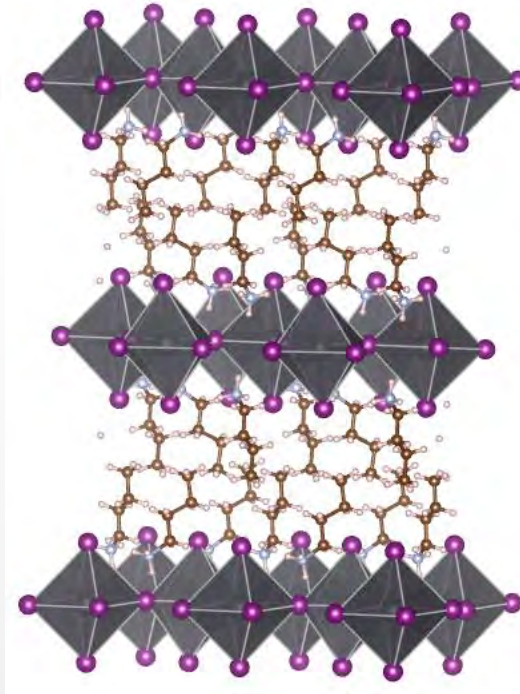
$ABX_3$



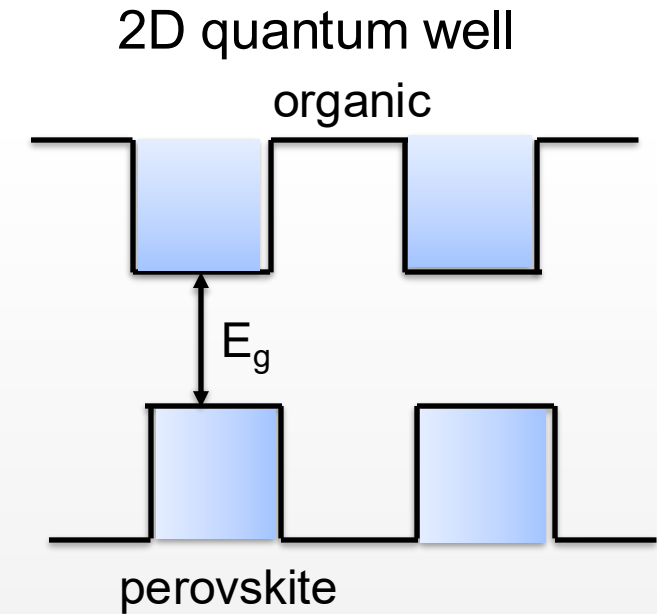
$=\infty$   
3D



Quasi 2D



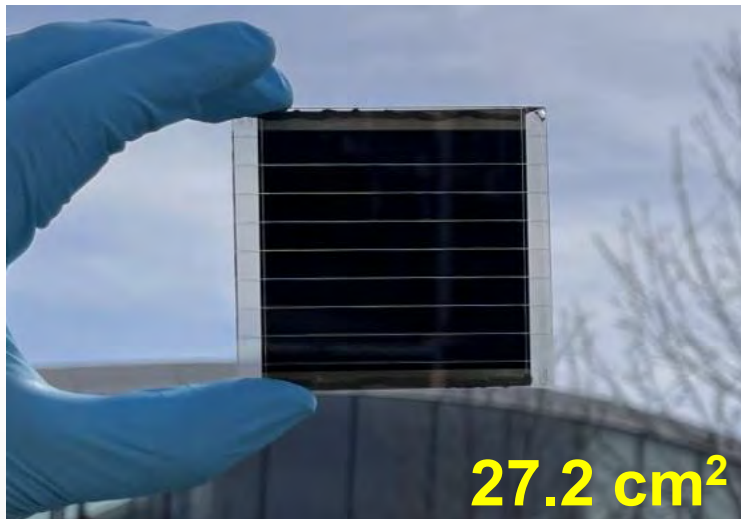
$n=1$   
2D



**Low D**

- Better solution processable and environmental stability
- Take advantage of quantum confinement

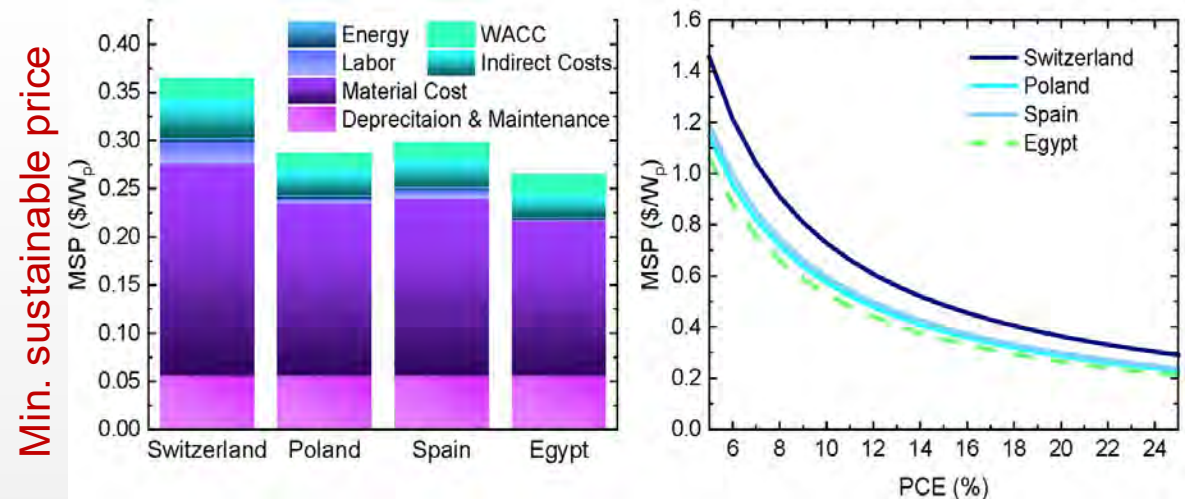
# Perovskite solar modules



27.2 cm<sup>2</sup>

EPFL, May 2024  
(3D/2D) 25.3%

Layer	Option 1	Option 2	Option 3	Option 4	Option 5
ETL 1	c-TiO <sub>2</sub>	c-TiO <sub>2</sub>	SnO <sub>2</sub>	SnO <sub>2</sub>	c-TiO <sub>2</sub>
ETL 2	m-TiO <sub>2</sub>	m-TiO <sub>2</sub>			m-TiO <sub>2</sub>
Perovskite	Perovskite	Perovskite	Perovskite	Perovskite	Perovskite
HTM	Spiro	Spiro	Spiro	Spiro	-
Electrode	Cr/Cu	Silver Ink	Cr/Cu	Silver Ink	C-Paste
Price/m <sup>2</sup> (100 MW)	\$5.9	\$6.6	\$2.7	\$3.4	\$8.1
Price/m <sup>2</sup> (1 GW)	\$5.0	\$5.1	\$1.9	\$2.0	\$6.2



Nazeeruddin *et al.* ACS Energy Lett. 2022, 7, 9, 3039

Perovskite solar panels : 0.25 - 0.69 \$/W<sub>p</sub>  
Si solar panels: 0.34 - 0.54 \$/W<sub>p</sub>

# Halide perovskites – 21<sup>st</sup> century semiconductors

Article

## Joint Forum on Halide Perovskite Materials and Devices for Energy and Electronic Applications


Suchismita Guha and Gerrit Boschloo


*ACS Applied Energy Materials* 2023, 6, 20, 10190-10192 (Editorial) [Subscribed](#)

Publication Date (Web): October 23, 2023

DOI: 10.1021/acsaem.3c02354

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Article

## Joint Forum on Halide Perovskite Materials and Devices for Energy and Electronic Applications

Suchismita Guha and Gerrit Boschloo

*ACS Applied Electronic Materials* 2023, 5, 10, 5258-5260 (Editorial) [Subscribed](#)

Publication Date (Web): October 24, 2023

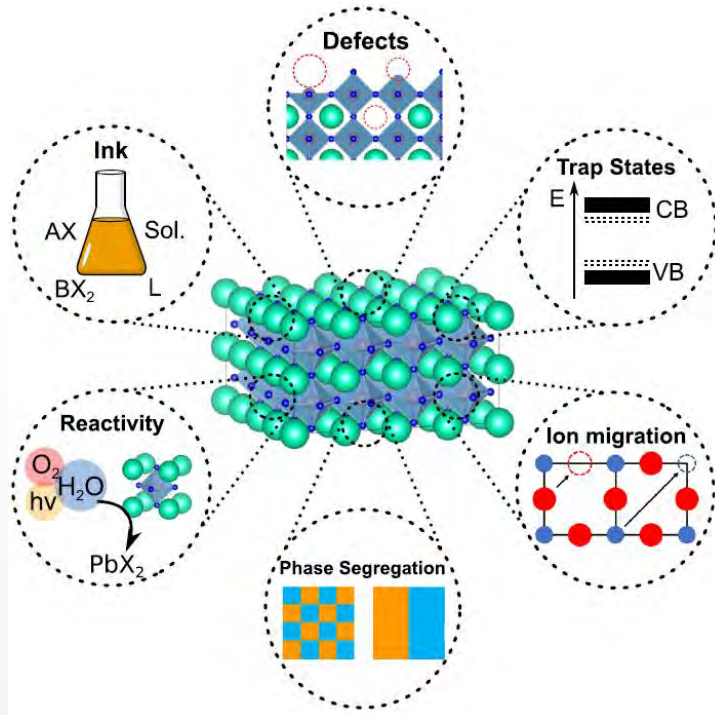
DOI: 10.1021/acsaelm.3c01305

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ELECTRONIC MATERIALS

"Interdisciplinary journal covering all aspects of electronic materials"

# What are the challenges?



Schmidt-Mende *et al.* APL Mater. **9**, 109202 (2021).

We are pursuing a solvent-free synthesis of halide perovskite thin films.

Shockley-Queisser limit

JOURNAL OF APPLIED PHYSICS

VOLUME 32, NUMBER 3

MARCH, 1961

## Detailed Balance Limit of Efficiency of $p$ - $n$ Junction Solar Cells\*

WILLIAM SHOCKLEY AND HANS J. QUEISSER

*Shockley Transistor, Unit of Clevite Transistor, Palo Alto, California*

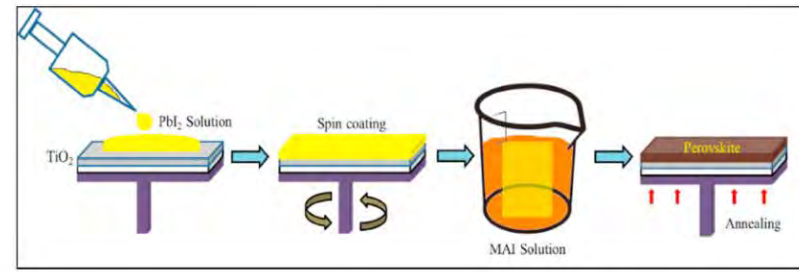
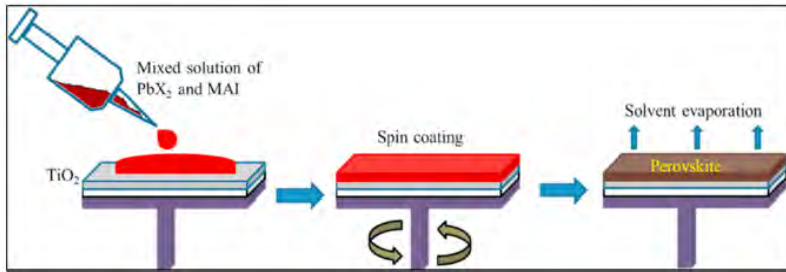
(Received May 3, 1960; in final form October 31, 1960)

In order to find an upper theoretical limit for the efficiency of  $p$ - $n$  junction solar energy converters, a limiting efficiency, called the *detailed balance limit* of efficiency, has been calculated for an ideal case in which the only recombination mechanism of hole-electron pairs is radiative as required by the principle of detailed balance. The efficiency is also calculated for the case in which radiative recombination is only a fixed fraction  $f_e$  of the total recombination, the rest being nonradiative. Efficiencies at the matched loads have been calculated with band gap and  $f_e$  as parameters, the sun and cell being assumed to be blackbodies with temperatures of 6000°K and 300°K, respectively. The maximum efficiency is found to be 30% for an energy gap of 1.1 eV and  $f_e=1$ . Actual junctions do not obey the predicted current-voltage relationship, and reasons for the difference and its relevance to efficiency are discussed.

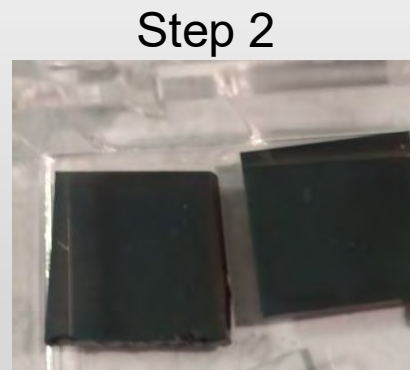
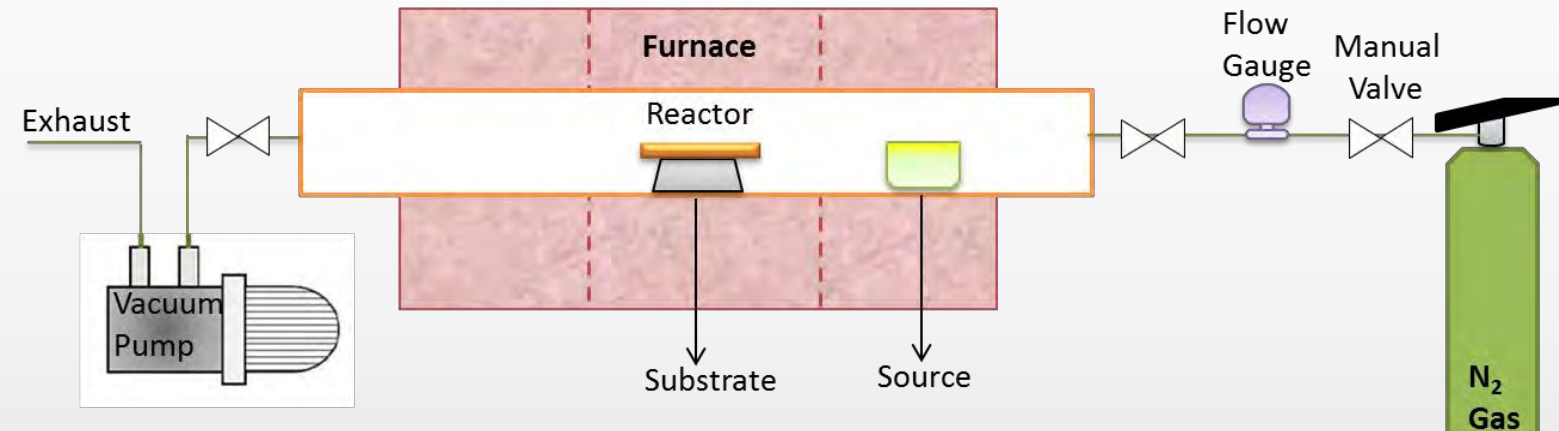
Carrier multiplication and hot carrier extraction are some pathways

Transient absorption techniques based on ultrafast laser techniques provide insights

# CVD growth of halide perovskites (MAPbI<sub>3</sub>)



Jamal *et al.* *Renew. Sustain. Energy Rev.* **98** 469 (2018).

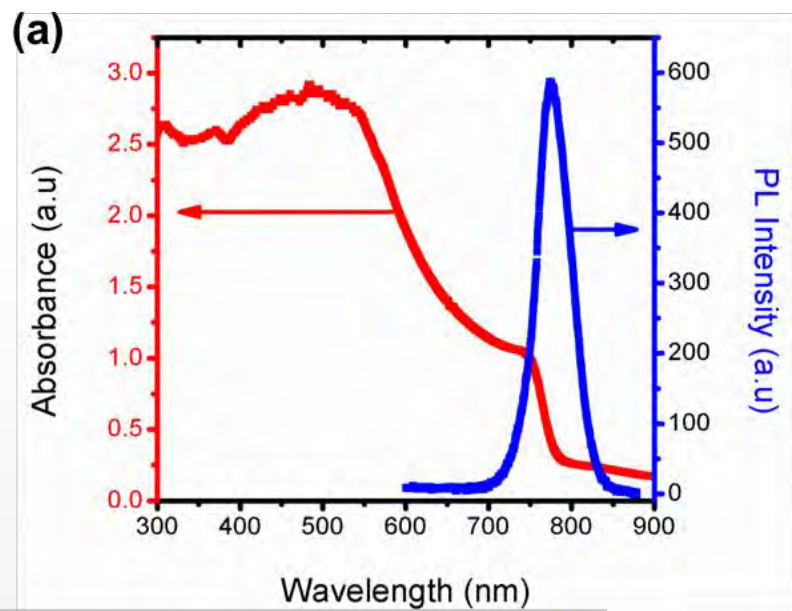


- Two or three zone furnace
- The PbI<sub>2</sub> source is vaporized at 380 °C
- MAI is vaporized at 180 °C

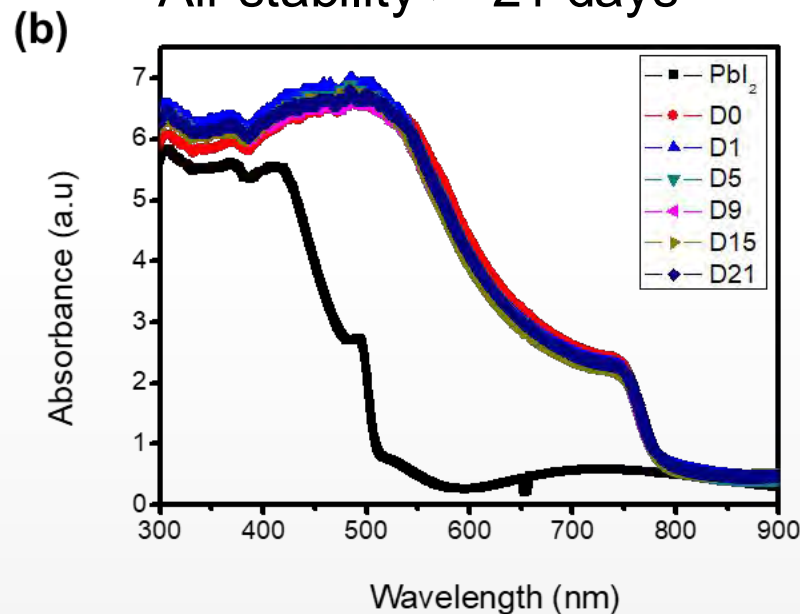


# Optical and solar cell properties

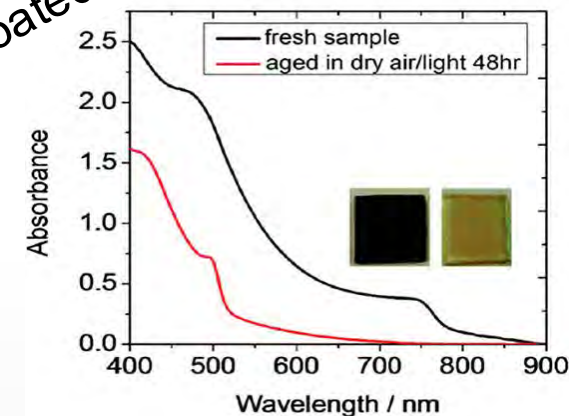
All measurements in air



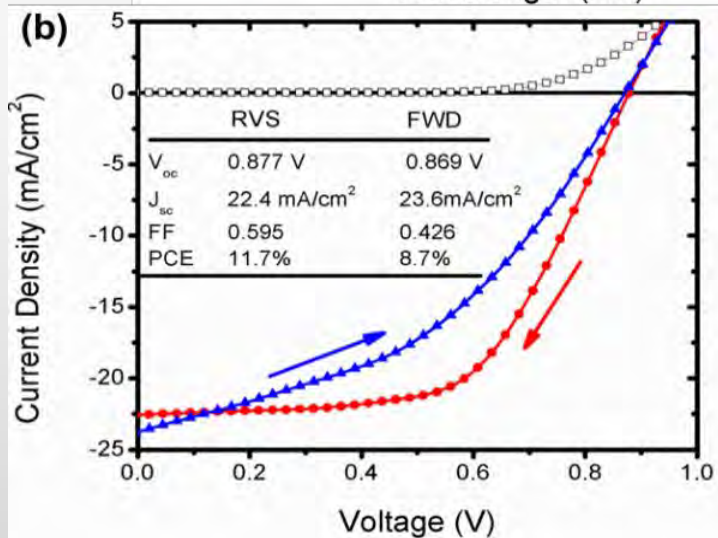
Air stability > 21 days



Spincoated films



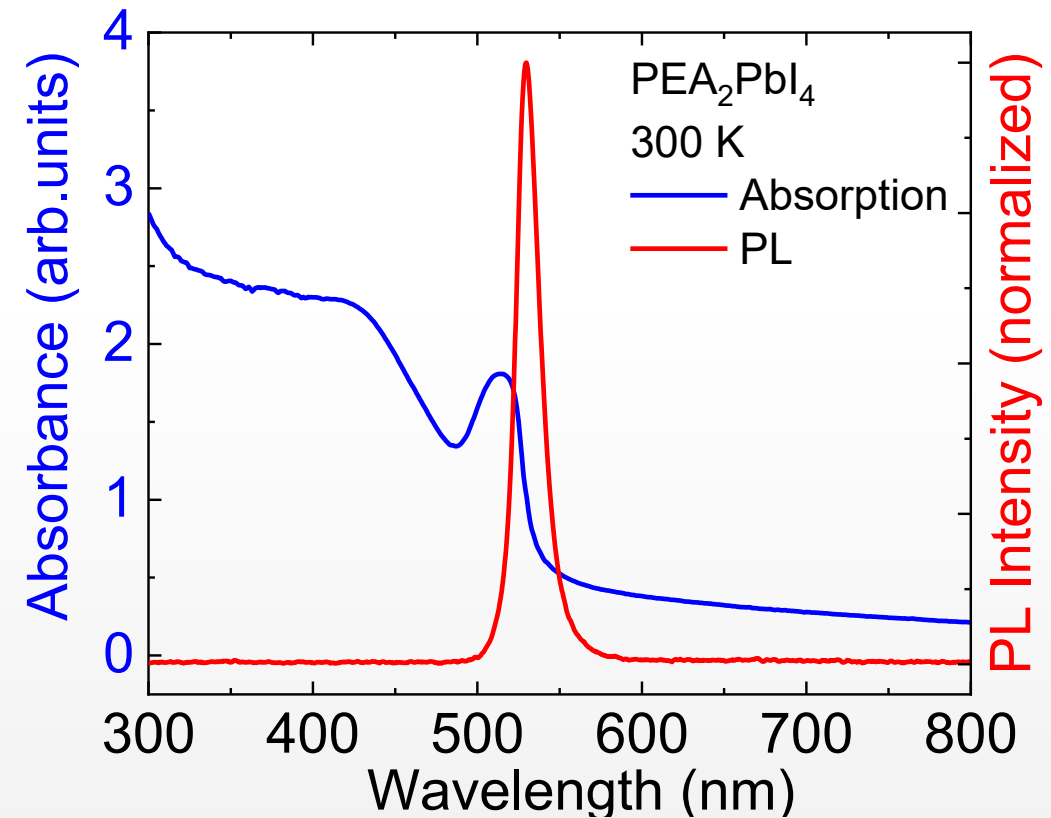
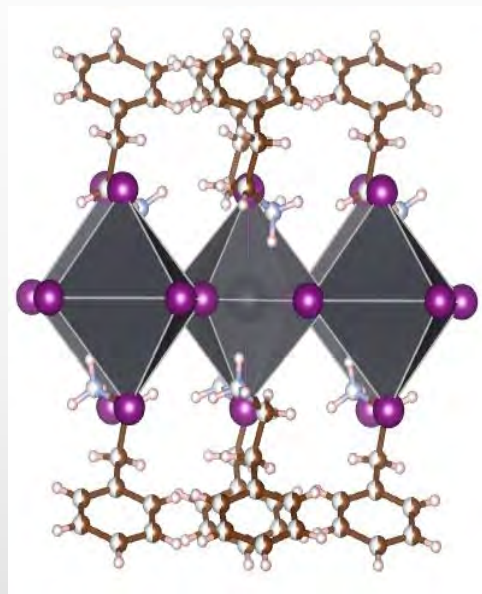
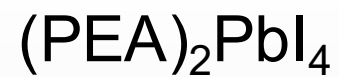
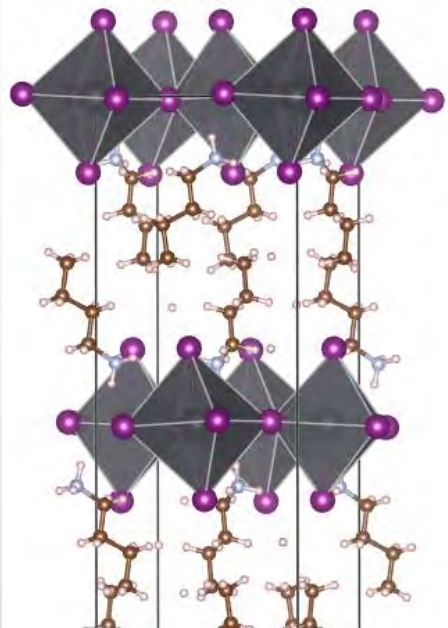
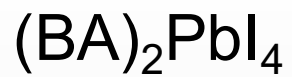
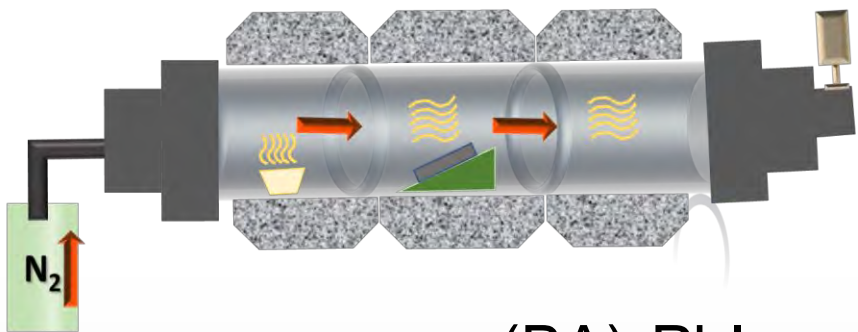
Bryant *et al.* Energy Environ. Sci. **9**, 1655 (2016).



$$\eta = \frac{FF \times V_{OC} \times J_{SC}}{P_{in}}$$

- Samples exposed to uncontrolled humidity (80%) and temperature up to 23 °C.
- Solar Cell PCE of 11.7%
- Maintains 85% of its PCE after 21 days in open air

# CVD growth of 2D perovskites



Strong excitonic features

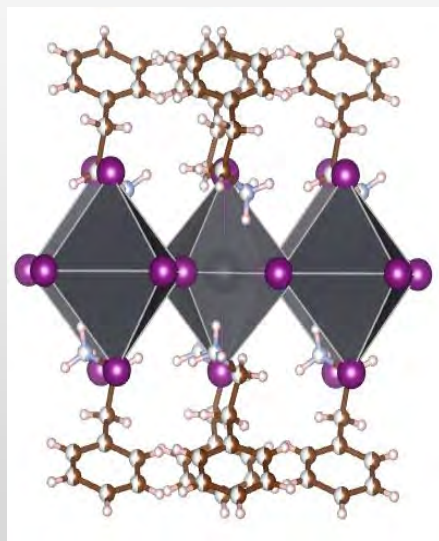
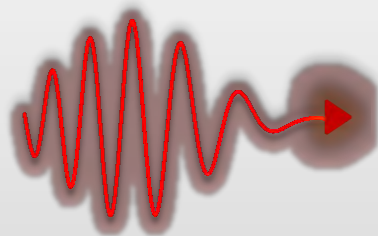
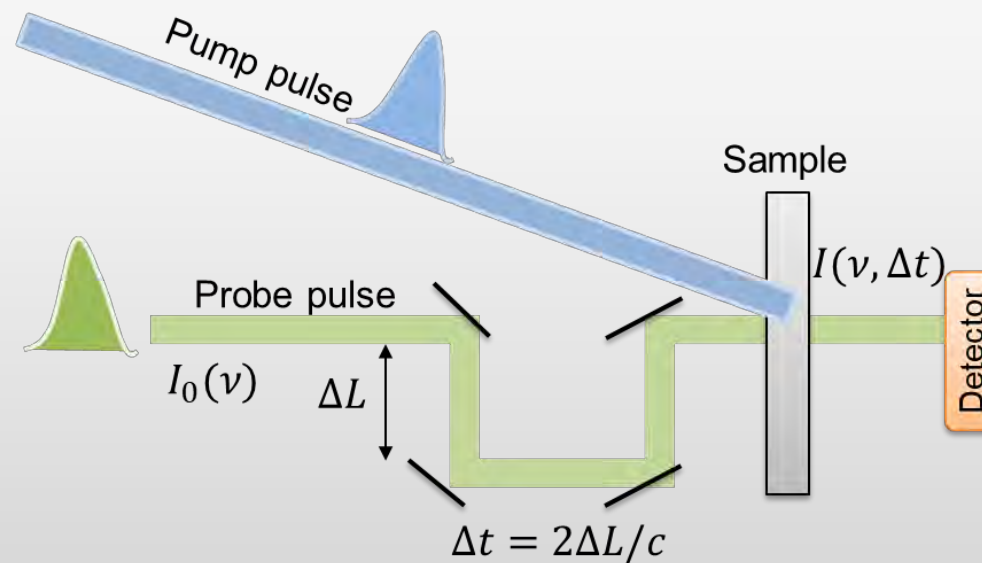
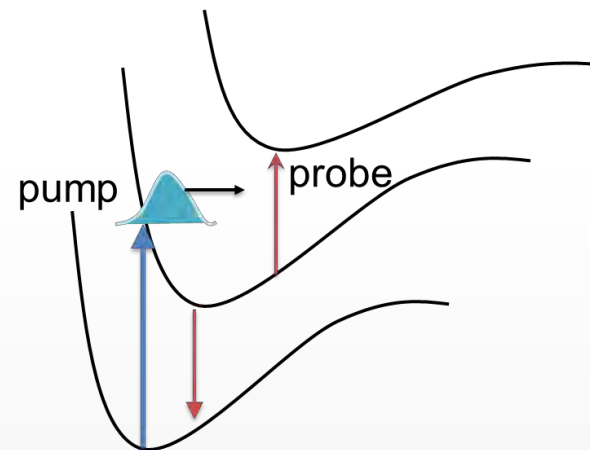
# Spectroscopy with short pulses



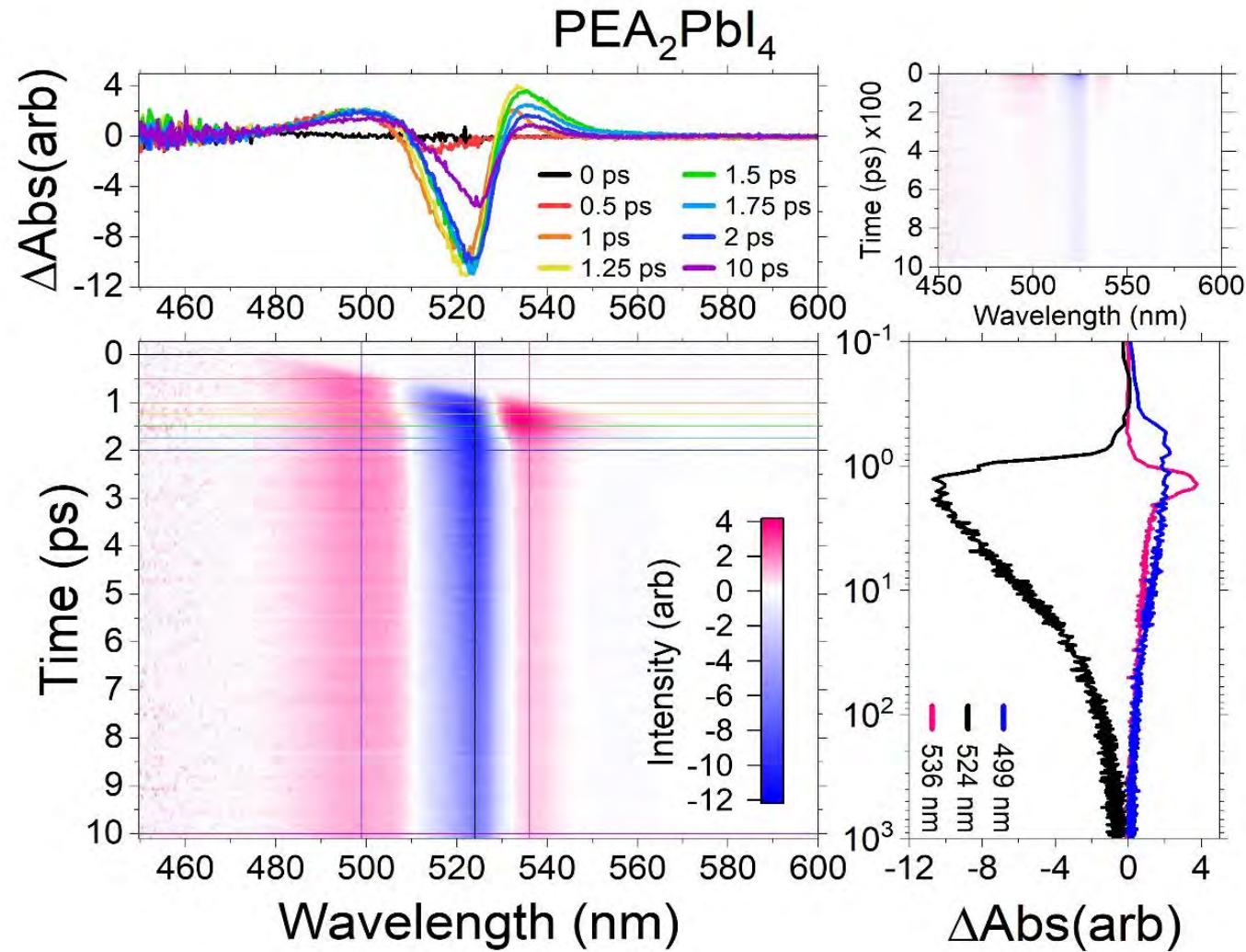
ECCS (MRI) 1827846



## Pump-probe spectroscopy

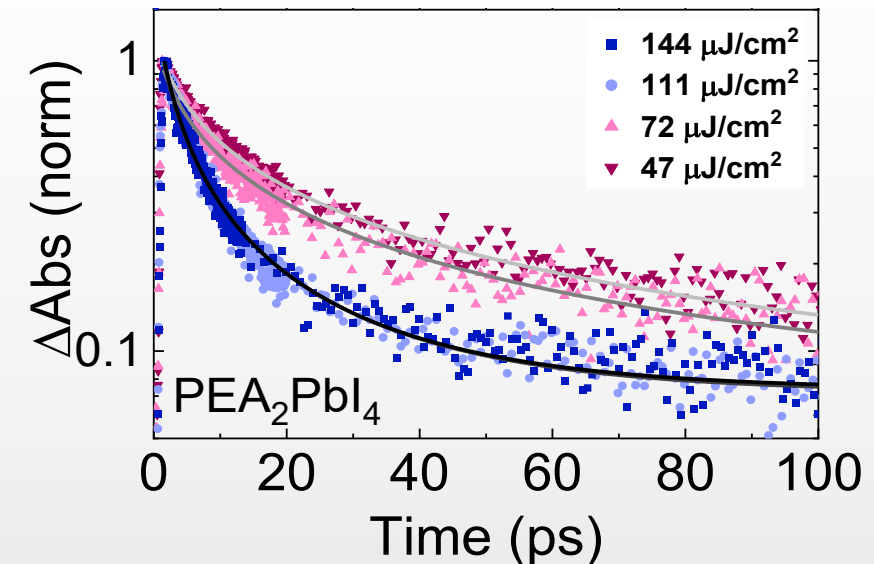


# Typical transient absorption features – 2D perovskites



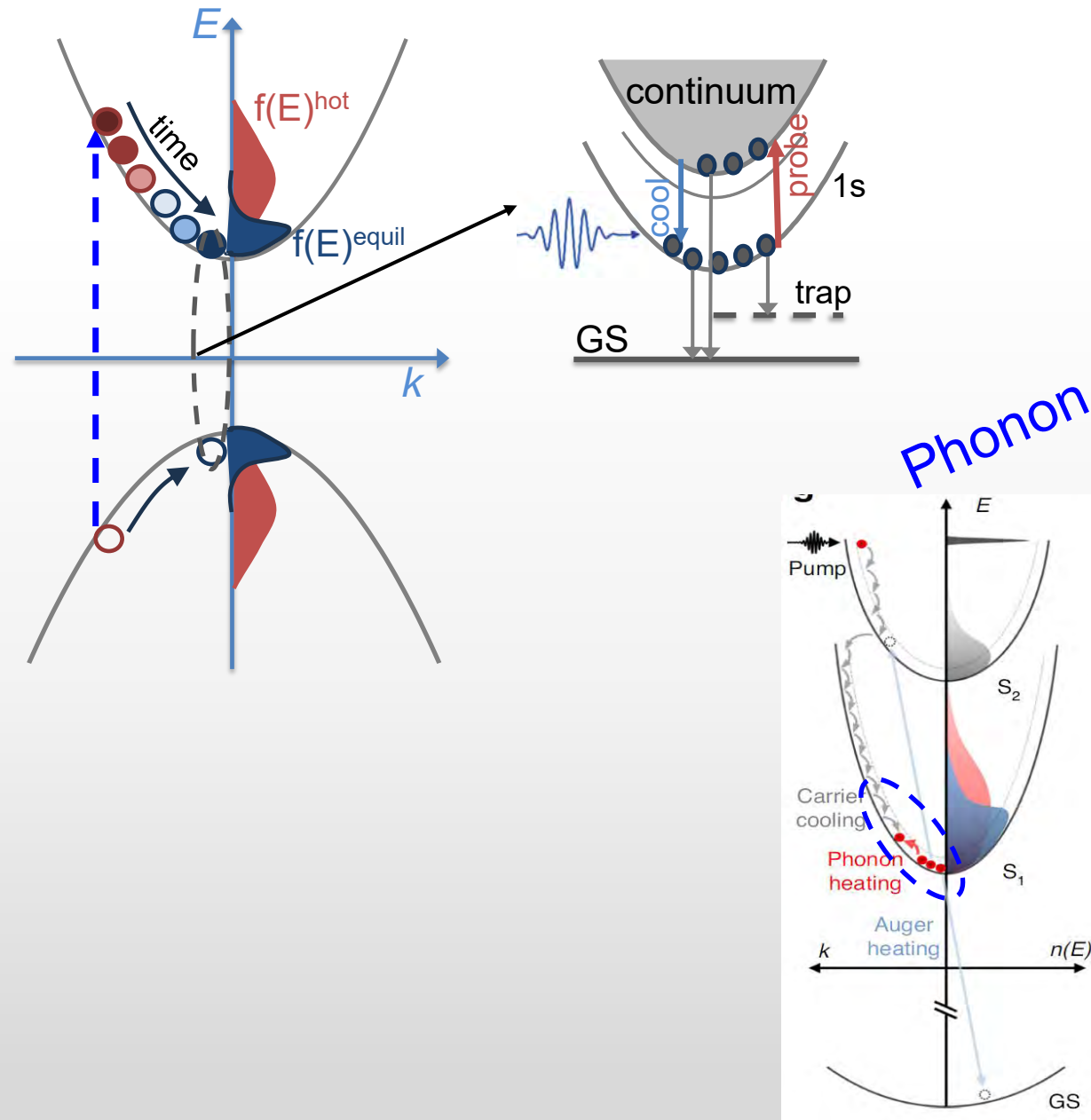
## Decay Kinetics

$$\frac{dn}{dt} = G - k_1 n - k_2 n^2 - \underbrace{k_3 n^3}_{\text{Auger recombination}}$$



$k_3$  dominates at early times  
 $k_1$  dominates at later times

# Relaxation and cooling dynamics



## Strategy for increasing $V_{oc}$

Hot carrier extraction – harness the resonant

“ ”



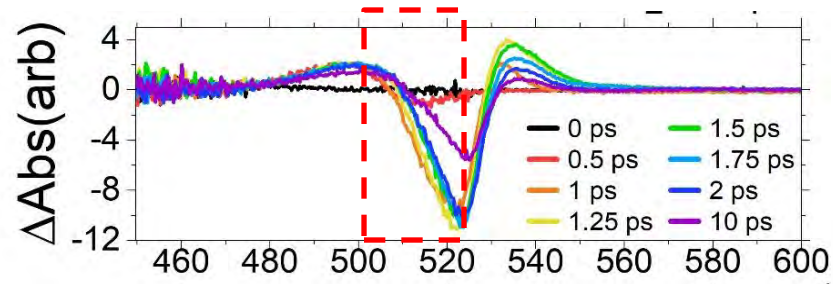
Phonon bottleneck

- Extended relaxation times ( $\sim$  ps)
- Low carrier-phonon coupling

Dai *et al.* Light: Science & Applications (2023) 12:208

# “Not so good news for 2D perovskites” and what next?

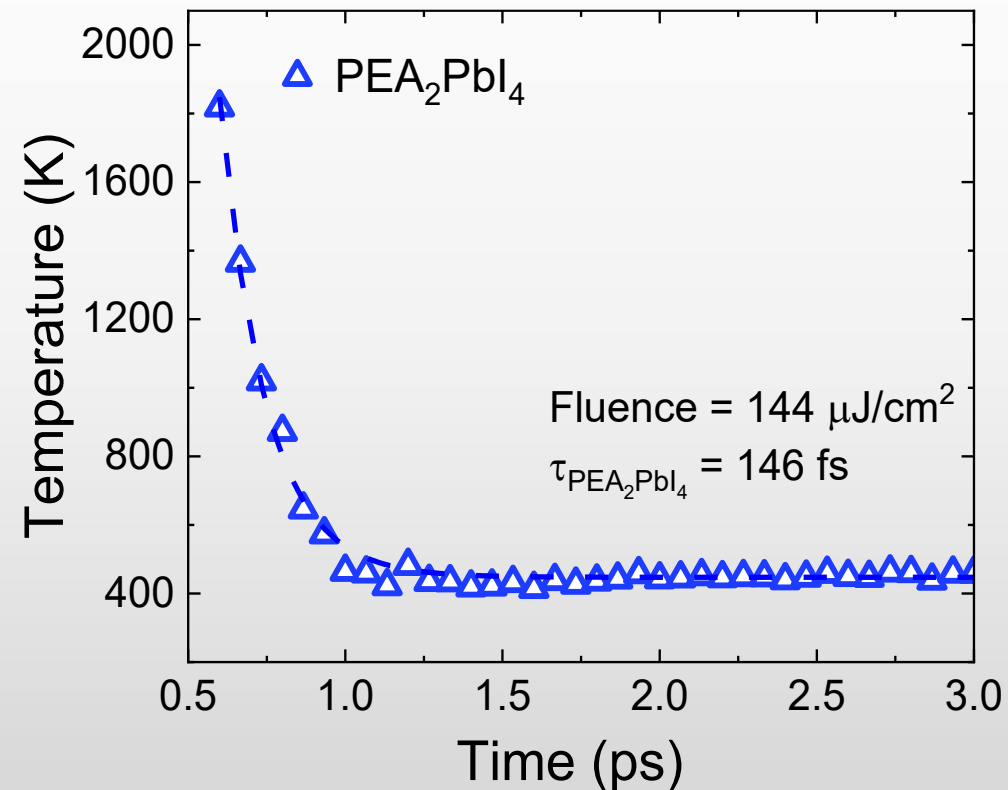
$$\Delta A(\hbar\omega) \propto \exp(-\hbar\omega/(k_B T_e))$$



- Very fast cooling times (compared to 3D perovskites).
- Relaxation of carriers via Fröhlich interaction.
- Absence of a phonon bottleneck process.

## What next?

- Mixed Pb-Sn perovskite nanocrystals show slow cooling times.
- Hetero-stacked perovskites with graphene and other 2D chalcogenides.
- “ ” supports a wide range of tunneling energy states.



# Thank You!



Funding  
NSF DMR 1807263  
NSF ECCS (MRI) 1827846

**Fourth generation solar cells based on halide perovskites: poking them with ultrafast light**

## U. Missouri - Columbia

Dallar  
Babaian



Randy  
Burns



Prof. Ping Yu



## U. Western Cape

Prof. Chris  
Arendse



- Prof. Paul Miceli (MU)
- Dr. Daniel Hill (MU)
- Stephen Klue (MU)
- David Beckwitt (MU)
- Dr. Evguenia Karapetrova (Argonne National Lab)