Energy Conversion by Semiconductor Devices

Jun-Ho YUM
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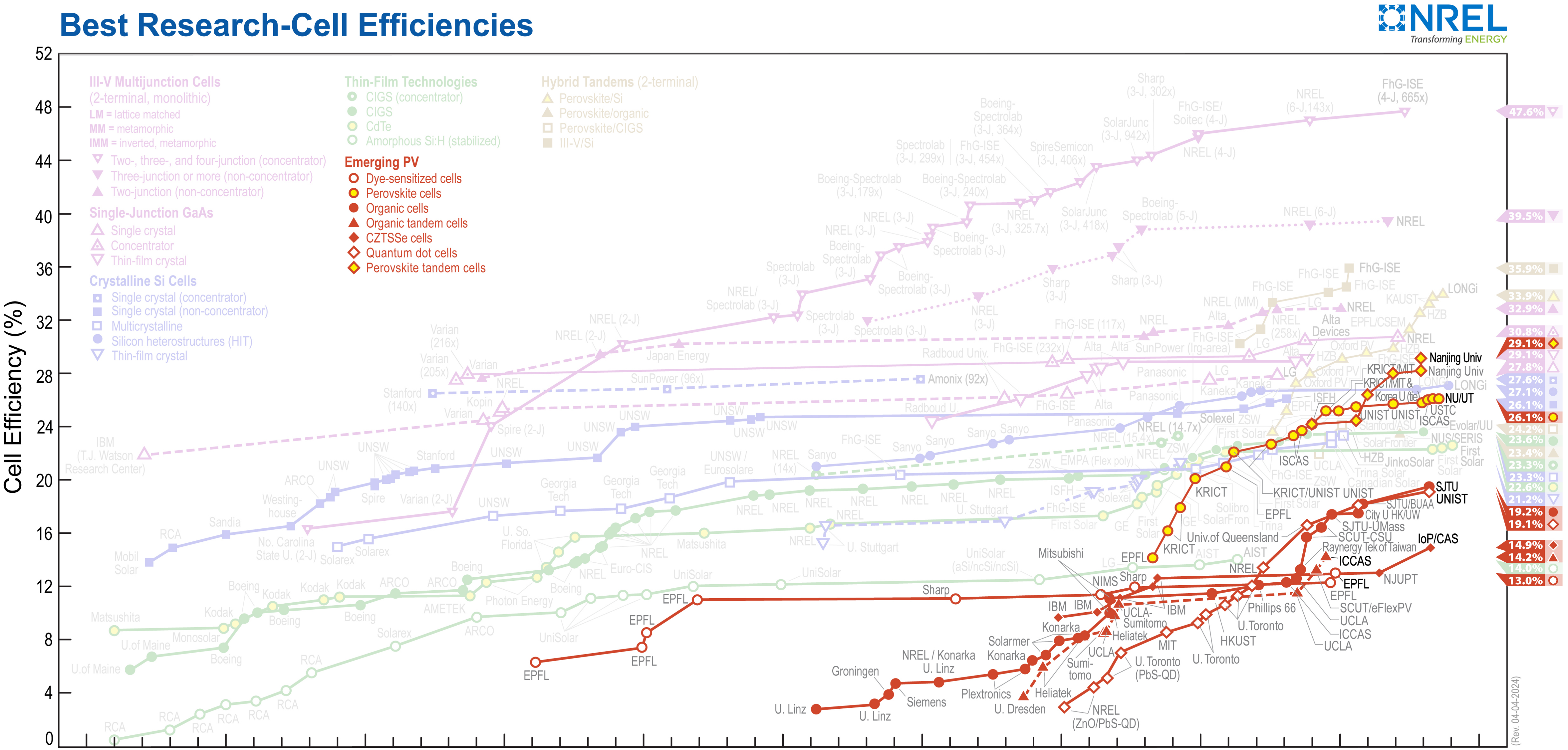
Halide Perovskite



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What is Perovskite?

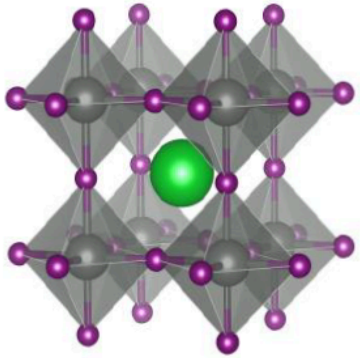
- 1839: perovskite = $CaTiO_3$ discovered

- 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

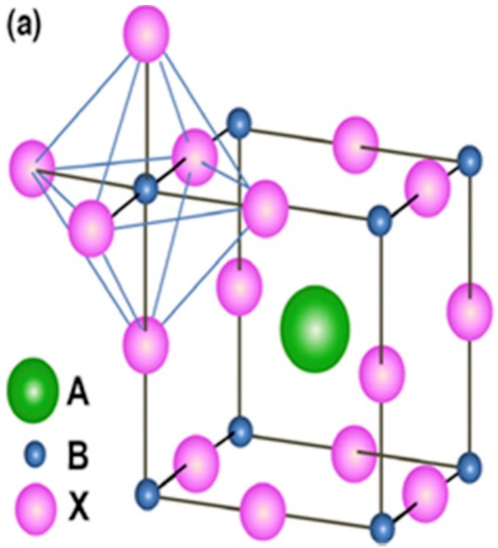
Weber, D. *Z. Naturforsch.* **33b,** 1443–1445 (1978).
Weber, D. *Z. Naturforsch.* **33b,** 862–865 (1978).

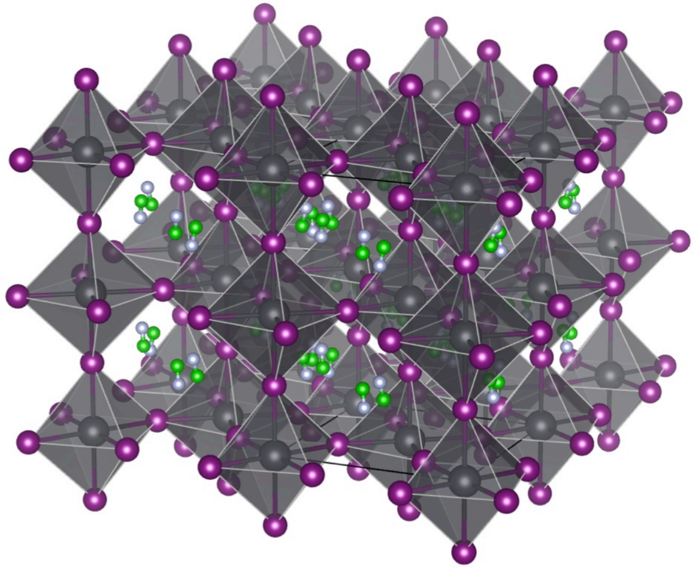


- Last two decades: perovskite researched in electronics

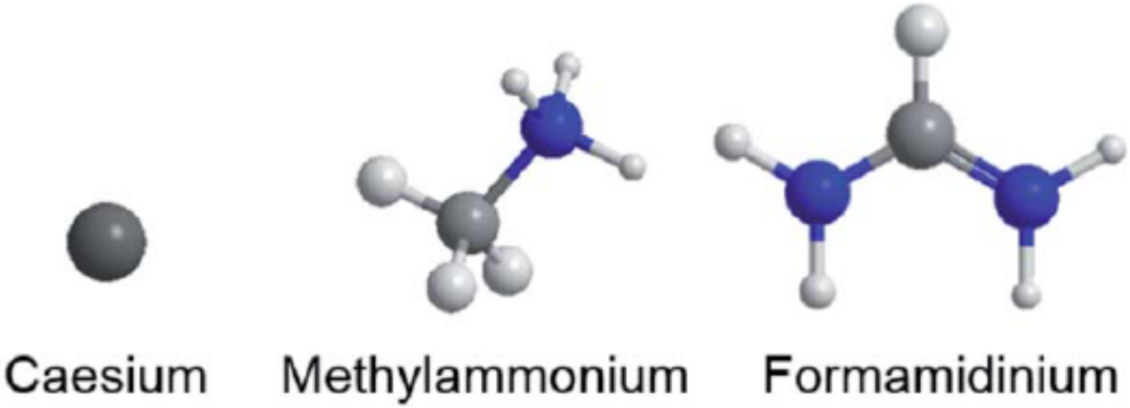
D. B. Mitzi, *Progress in Inorganic Chemistry* Vol. 48 (ed. Karlin, K. D.) 1–121 (J. Wiley & Sons, 1999).
T. Ishihara, *Journal of Luminescence* **60–61,** 269–274 (1994).

What is Perovskite for Solar Cells?





ABX_3:
A (green) is a large metal cation such as Cs^+, $CH_3NH_3^+$, $HC(NH_2)_2^+$
B (blue) is a small metal cation such as Pb^{2+}, Sn^{2+}
X (purple) is Cl^-, Br^-, I^-



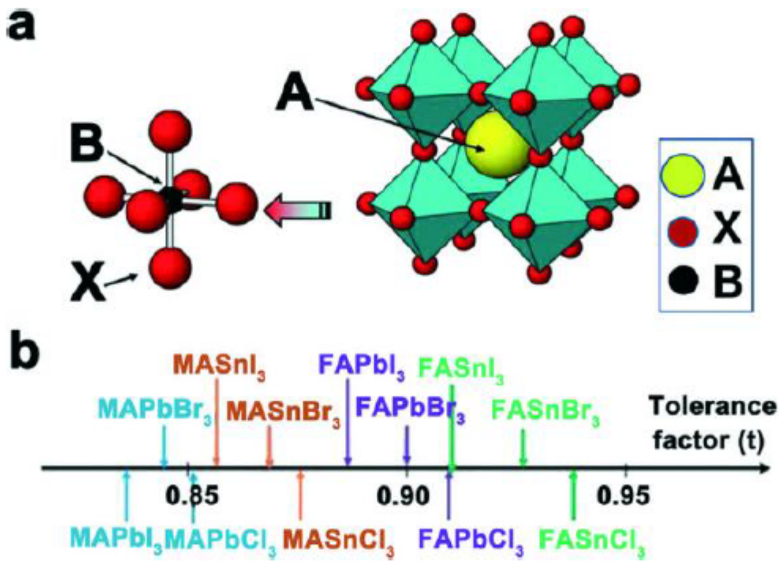
Mono-cation: $CH_3NH_3PbI_3$ ($MAPbI_3$ or MALI), $HC(NH_2)_2PbI_3$ ($FAPbI_3$), $CsPbI_3$
Multi-cations: $MA_xFA_{1-x}PbI_3$, $Cs_xFA_{1-x}PbI_3$, $Cs_xMA_yFA_{1-x-y}PbI_3$ ($CsMAFAPbI_3$)
Multi-anions: $MAPb(I_xBr_{1-x})_3$, $MAPb(I_xCl_{1-x})_3$

Goldschmidt Tolerance Factor & Octahedral Factor

In the typical ABX_3, the crystallographic stability and probable structure can be deduced by considering a Goldschmidt tolerance factor *t* and and octahedral factor μ.

The A cation can fit within the BX_3 framework of corner sharing octahedra.
The range from 0.8 to 1 indicates perovskite formation (*t* = 1 indicates a perfect fit).

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$



Z. Fan et al., *J. Mater. Chem. A,* **3**, 18809–18828 (2015).

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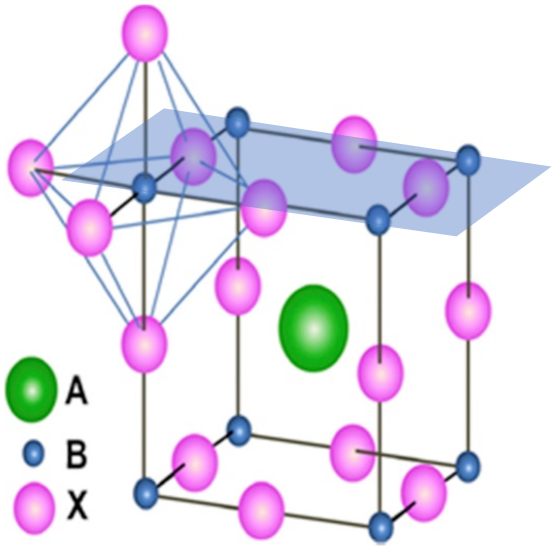

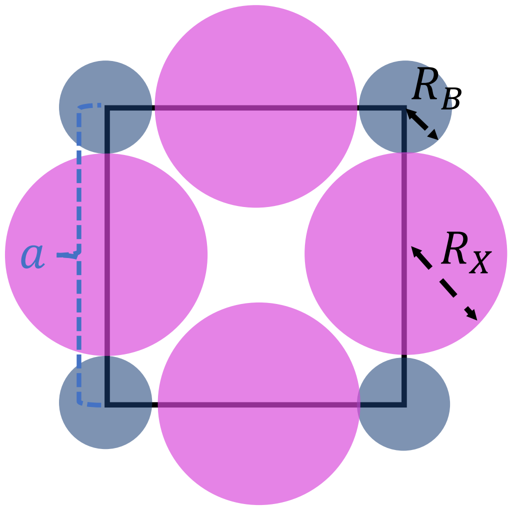

$$a = 2R_B + 2R_X$$

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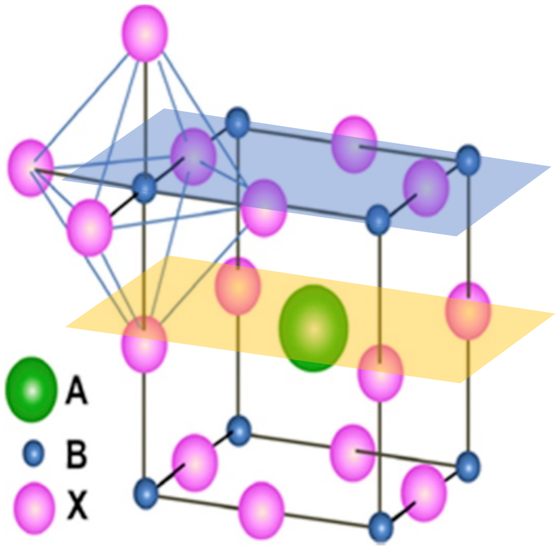
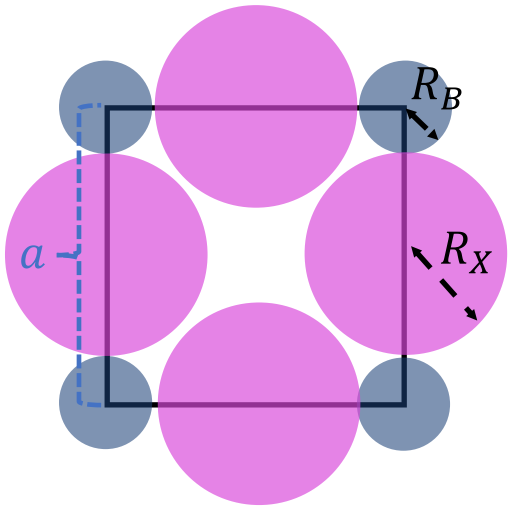
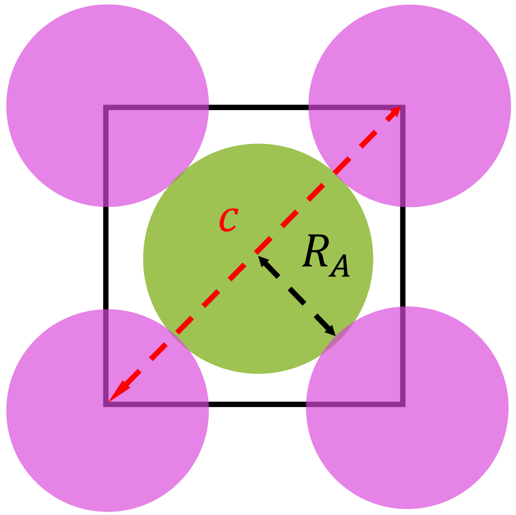




$$a = 2R_B + 2R_X$$

$$\frac{1}{cos45°} = \frac{c}{a}$$

$$t = \frac{c}{\sqrt{2}a}$$



$$c = 2R_A + 2R_X$$

Goldschmidt Tolerance Factor & Octahedral Factor

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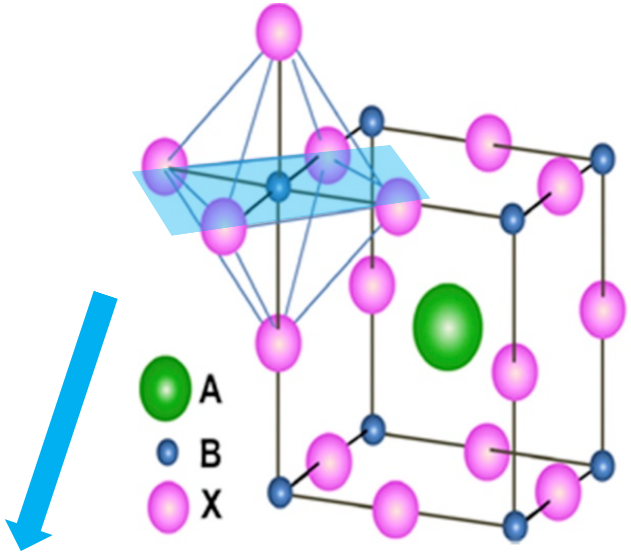
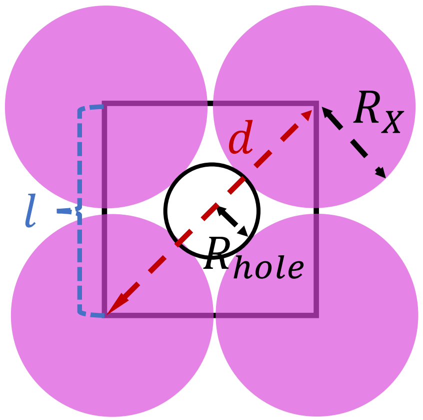




$$l = 2R_X$$

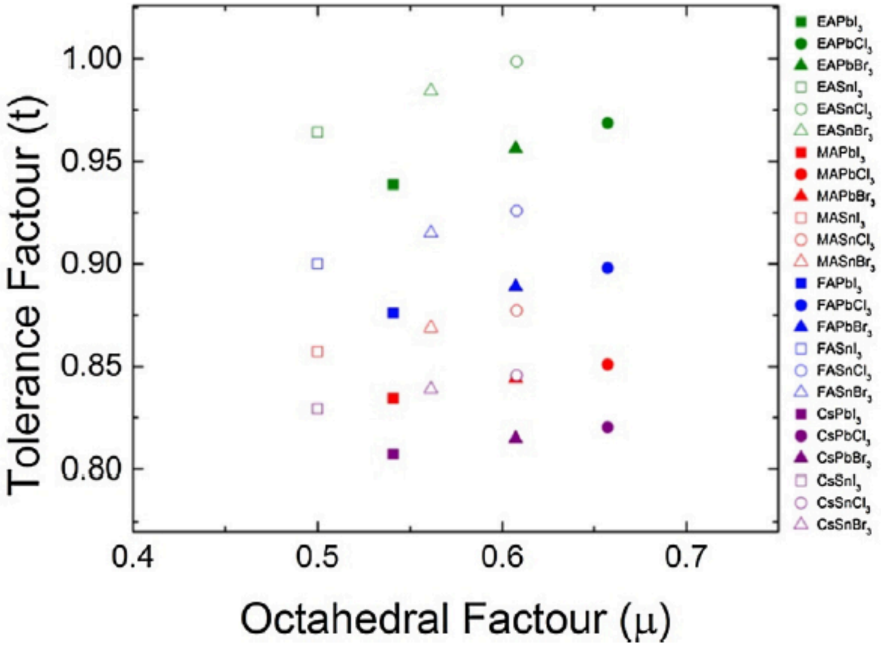
$$d = 2R_{hole} + 2R_X = \sqrt{2} \times l$$

$$2R_{hole} + 2R_X = \sqrt{2} \times 2R_X$$

$$R_{hole} = (\sqrt{2} - 1)R_X$$

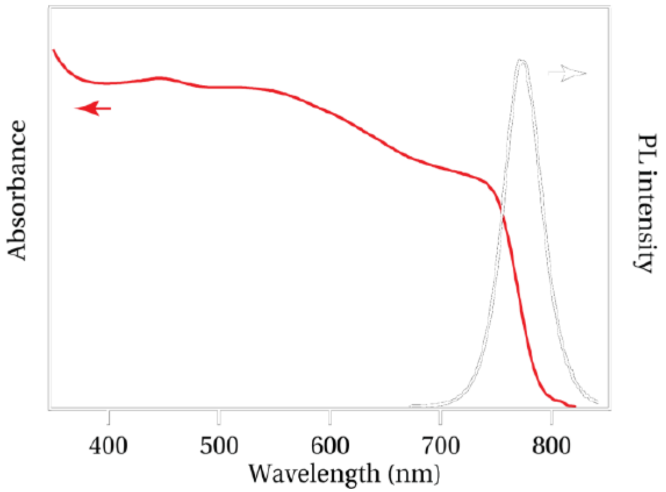
The B site cation can fit in the octahedral hole in the anion sublattice.
The radius of an octahedral hole formed within six close packed spheres of radius (R_{hole}) = $0.41R_X$

$$0.44 < \mu = \frac{R_B}{R_X} < 0.90$$

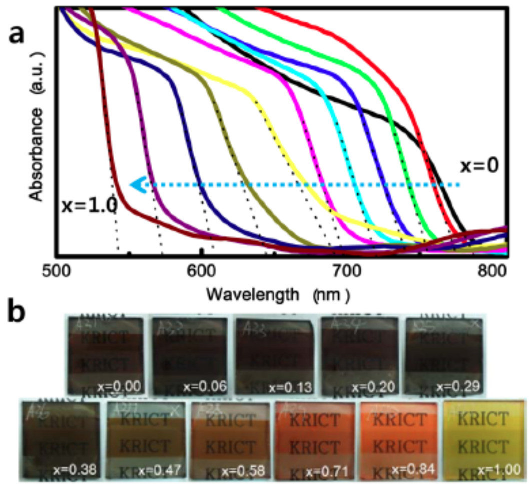


Q. Chen et al., *Nano Today,* **10**, 255–396 (2015).

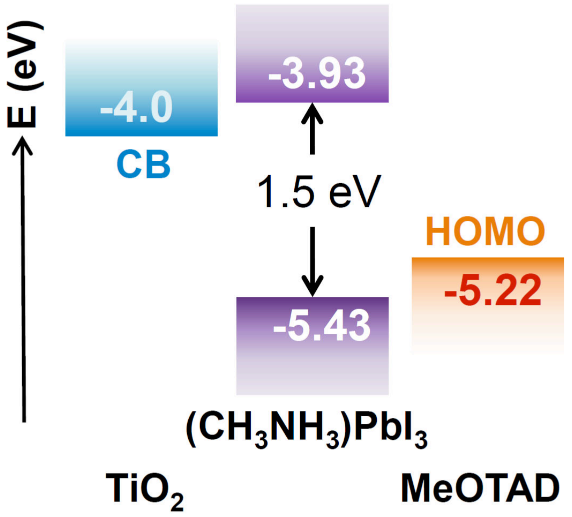
Organic-Inorganic Halide Perovskite



$MAPb(I_{1-x}Br_x)_3$

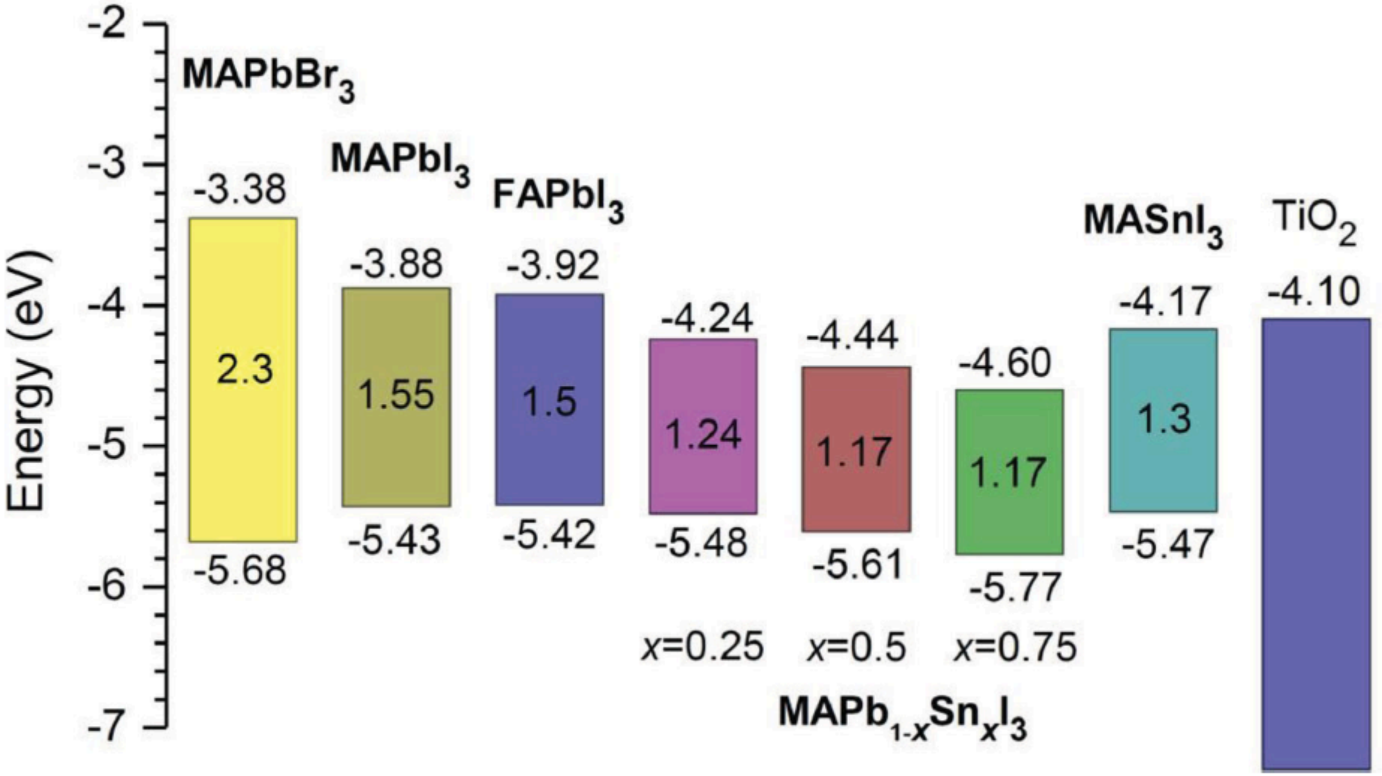


Nano Lett. 2013, 13, 1764−1769

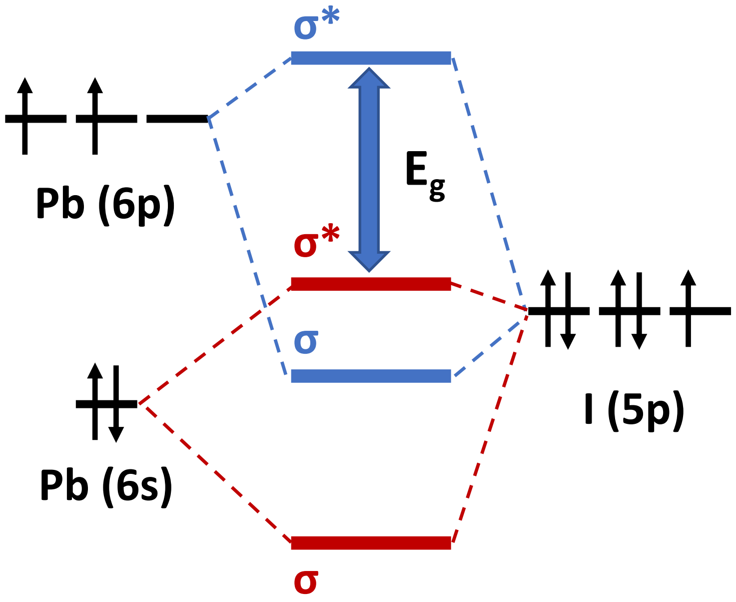


- High crystallinity and low defect density, even if solution processed
- Absorption coefficient of $10^4 – 10^5$ cm^{-1}
- Band gap of 1.6 eV and tunable band gap by compositional tuning (S-Q limit 33.7% with 1.34 eV)
- Proper energy levels to be compatible with existing ETM and HTM
- Ambipolar semiconductor with high charge carrier mobilities
- Low exciton binding energy with fast dissociation at room temperature, high dielectric constant

Band Gap Tuning

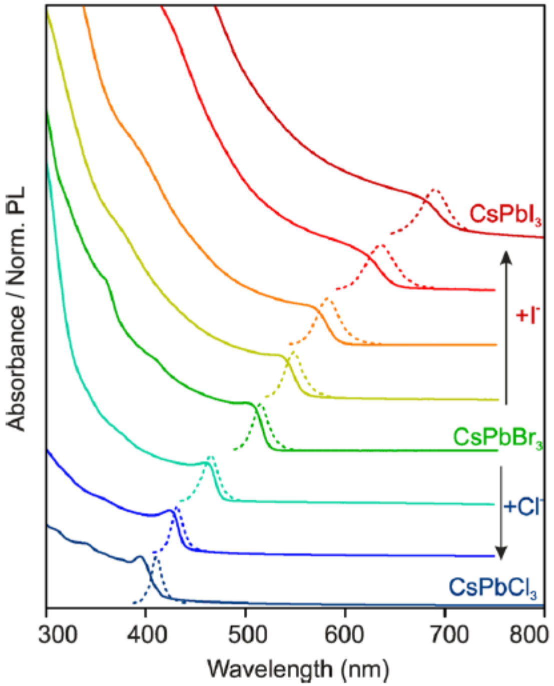


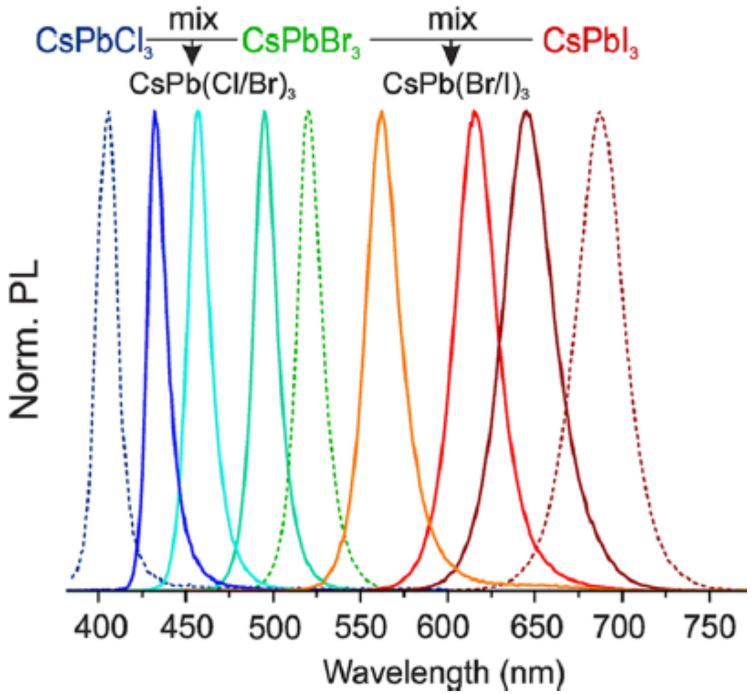
F. Hao et al., , *J. Am. Chem. Soc.*, **136**, 8094 (2014).



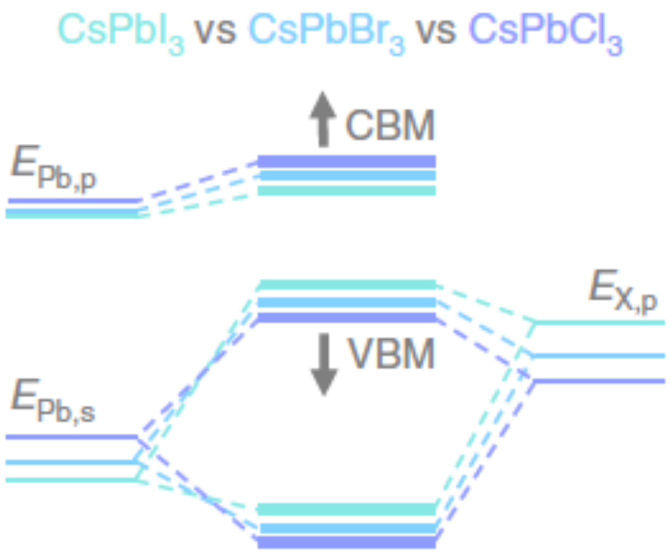
- **CB formed by the antibonding combination of empty Pb 6p (Sn 5p) orbitals.**
- **VB formed by the overlap of Pb 6s (Sn 5s) orbitals and X halogen np orbitals.**
- **The octahedral layer angle distortion or H bonding strength change leads to a change in the band gap.**

Band Gap Tuning with X Anion





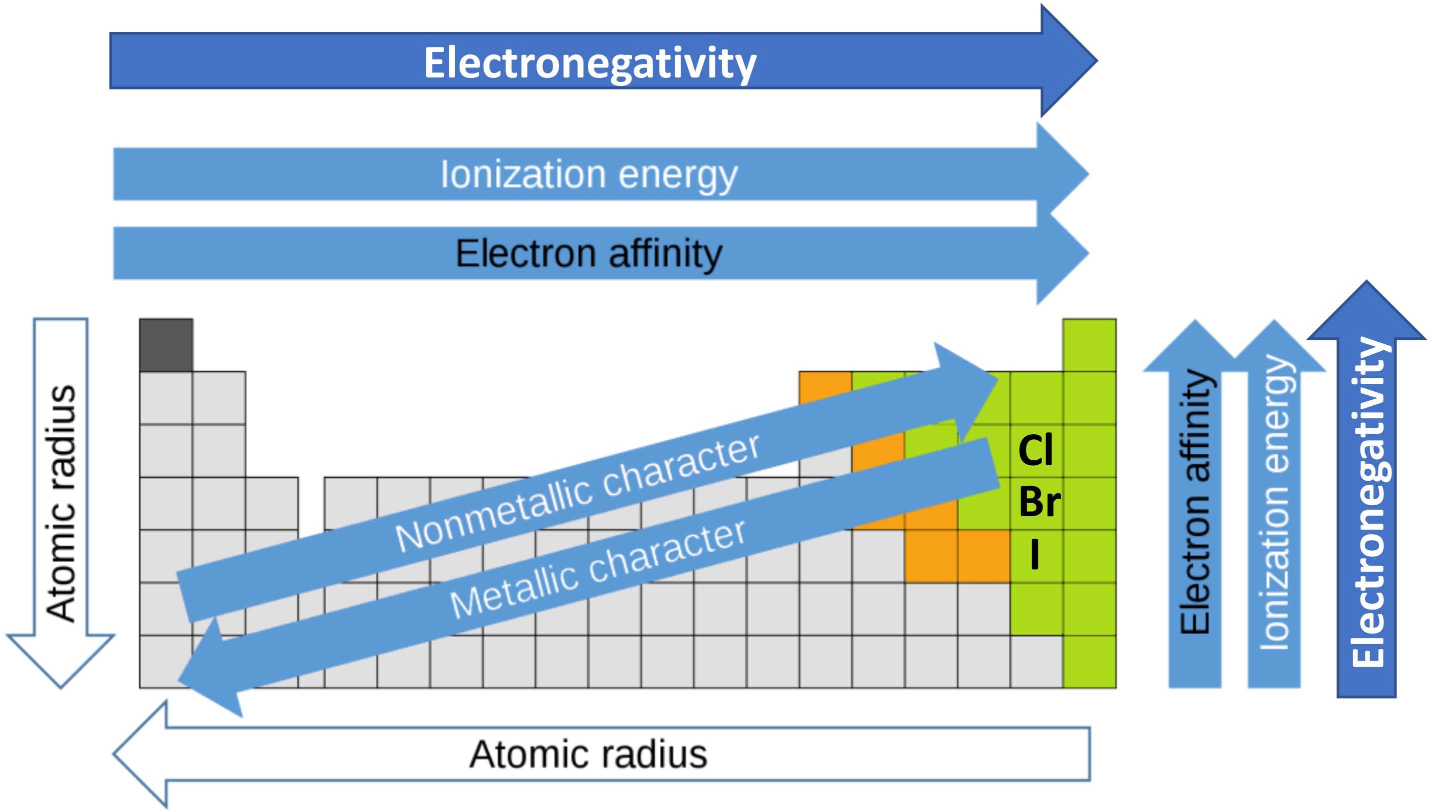
G. Nedelcu et al., , *Nano Lett.,* **15**, 5635 (2015).

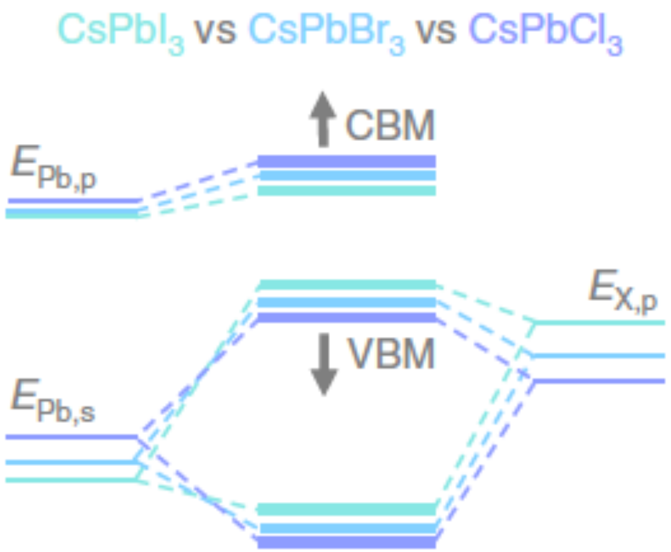


S. Tao et al., *Nature Commun.*, 10:2560 (2019).

- **The energy of the CBM is mostly influenced by the position of the Pb p orbital.**
- **A small shift in CBM is associated with that as the Pb-X distances decrease going from I to Br to Cl, an electron on a Pb atom is more confined and its energy increases (reason of the upward shift of Pb p and s orbitals).**
- **A significant downward shift of the X p orbital level going from I to Br to Cl, which simply reflects increasing electronegativity.**

Band Gap Tuning with X Anion

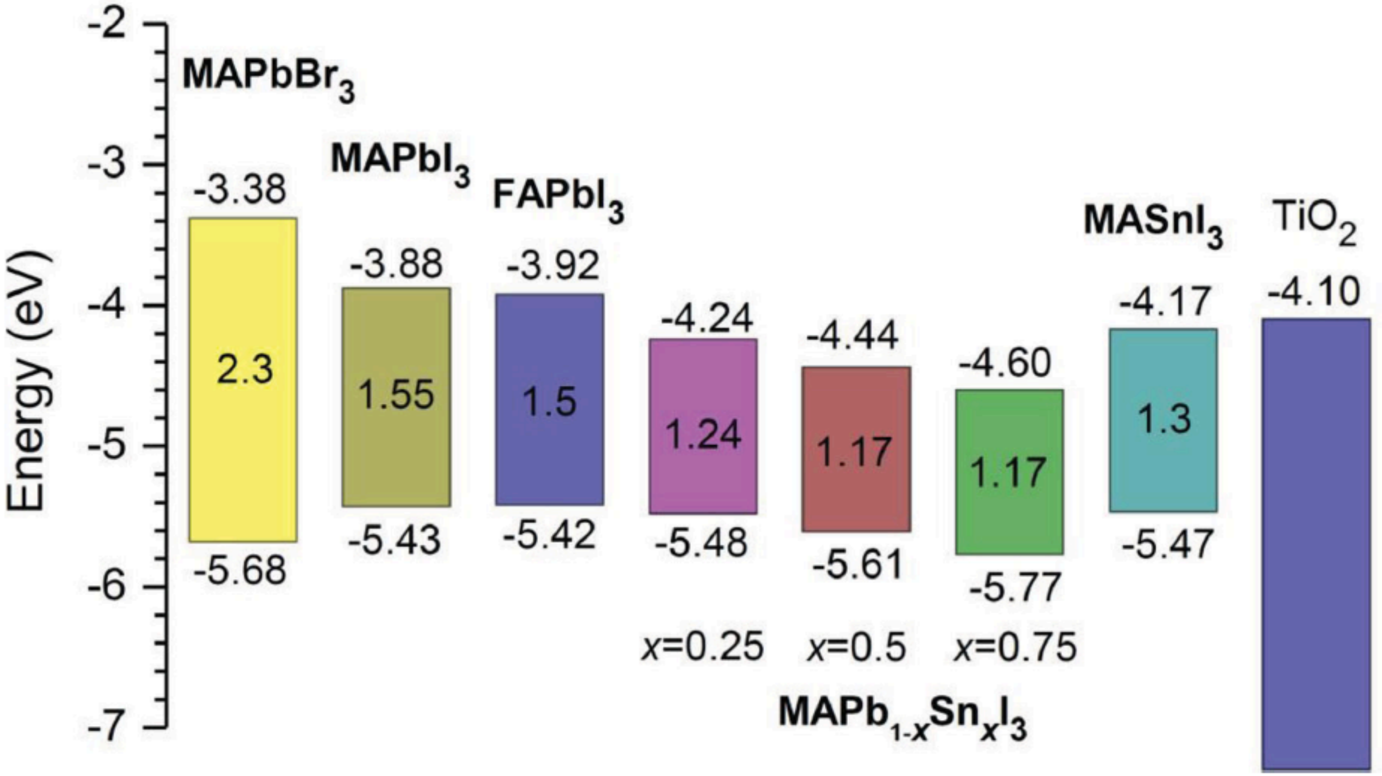




S. Tao et al., *Nature Commun.*, 10:2560 (2019).

Electronegativity is defined as an atom's ability to attract electrons towards it in a chemical bond.

Band Gap Tuning with B Cation



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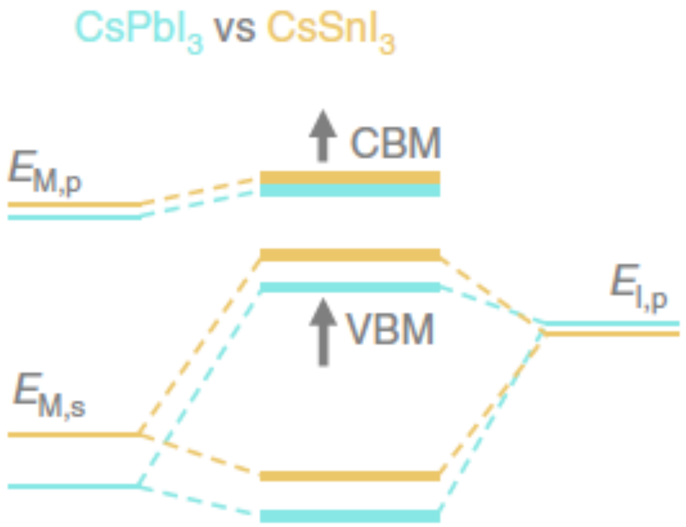
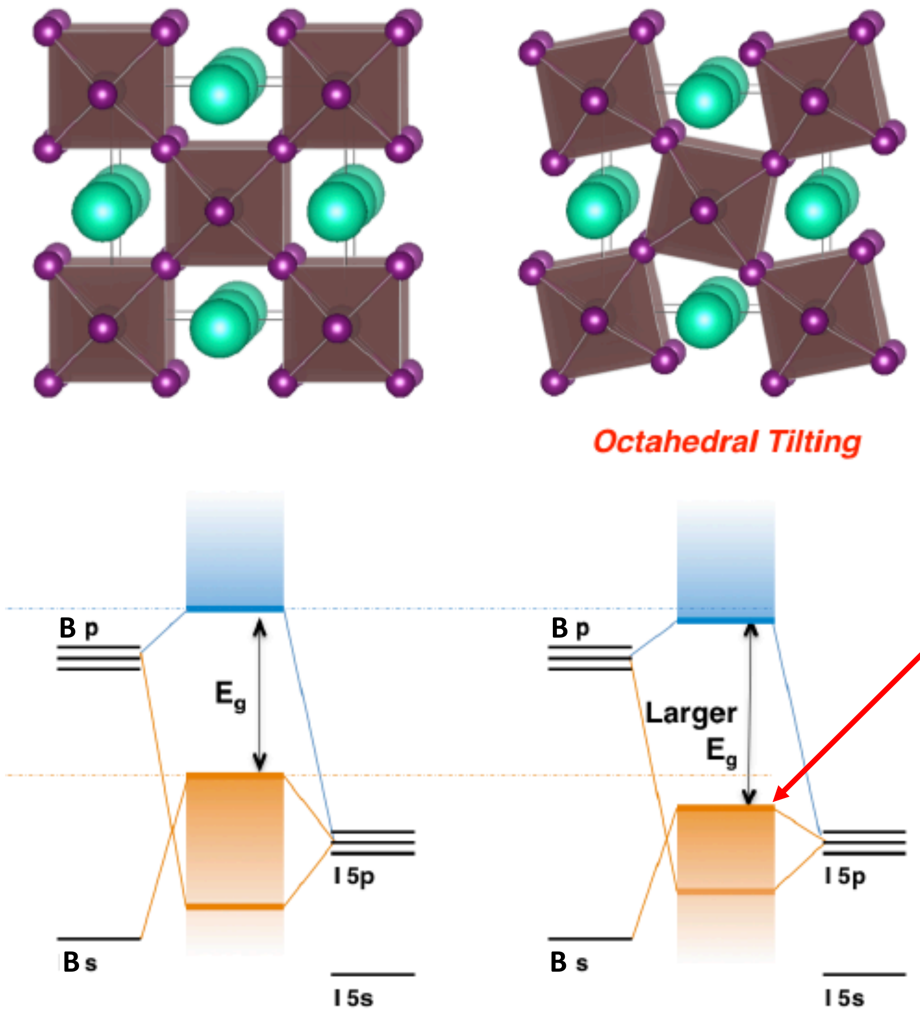


S. Tao et al., *Nature Commun.*, 10:2560 (2019).

- **Replacing Pb with Sn, the atomic levels shift upwards, which is consistent with the smaller electronegativity of Sn.**
- **The splitting between s and p states in a Sn atom is smaller than in a Pb atom: the VBM shifts upward more than the CBM.**

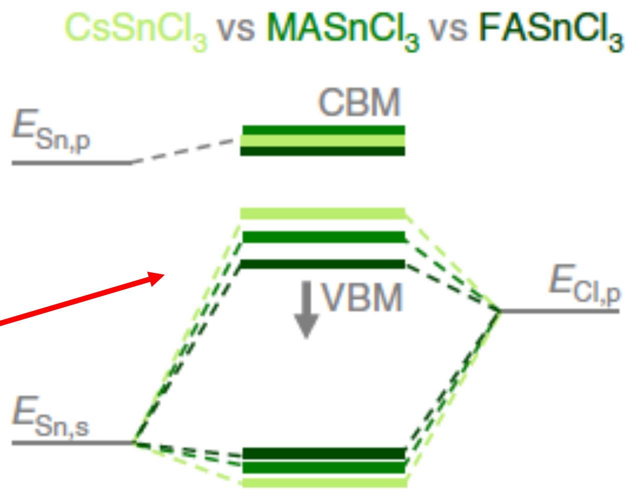
Band Gap Tuning with A Cation



R. Prasanna et al., *J. Am. Chem. Soc.*, **139**, 11117–11124 (2017).

more sensitive to hybridization

R_A: Cs^+ (1.81 Å) < MA^+ (2.70 Å) < FA^+ (2.79 Å)



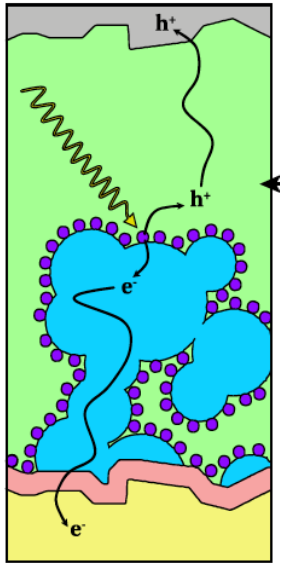
S. Tao et al., *Nature Commun.*, 10:2560 (2019).

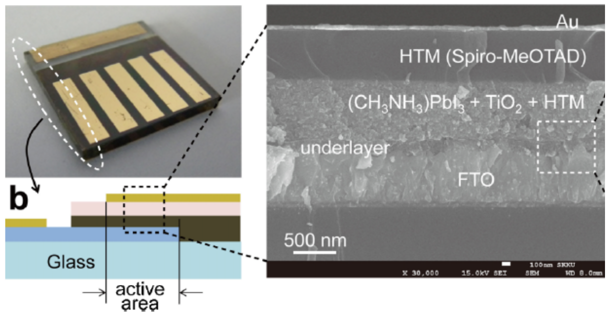
- **Structural deformations (octahedral tilting and distortion) of the octahedra reduce somewhat the hybridization strength between the B and X states: This shifts the VBM and CBM downward.**
- **Increasing the size of A cation lower the B levels (moderated confinement): CBM slight shifts downward.**

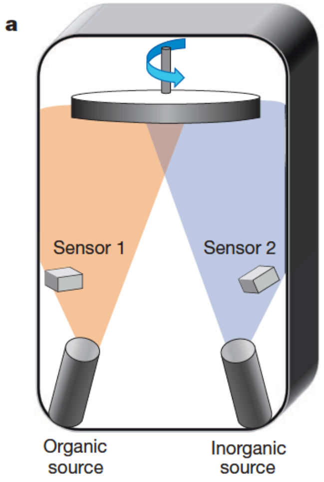
History

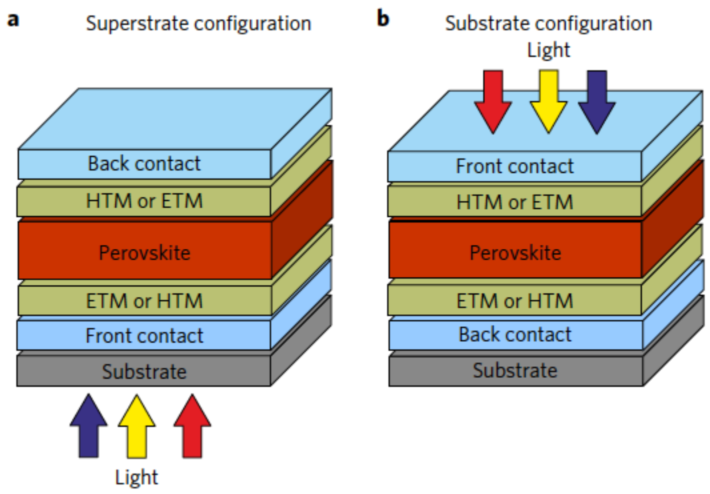
2009	2012	2013	2014	2015
3.5%	10%	15%	16.5%	20%
Perovskite Dye	**Solid state devices**	**Deposition methods**	**Solvent Engineering**	**Composition engineering**

Planar architectures

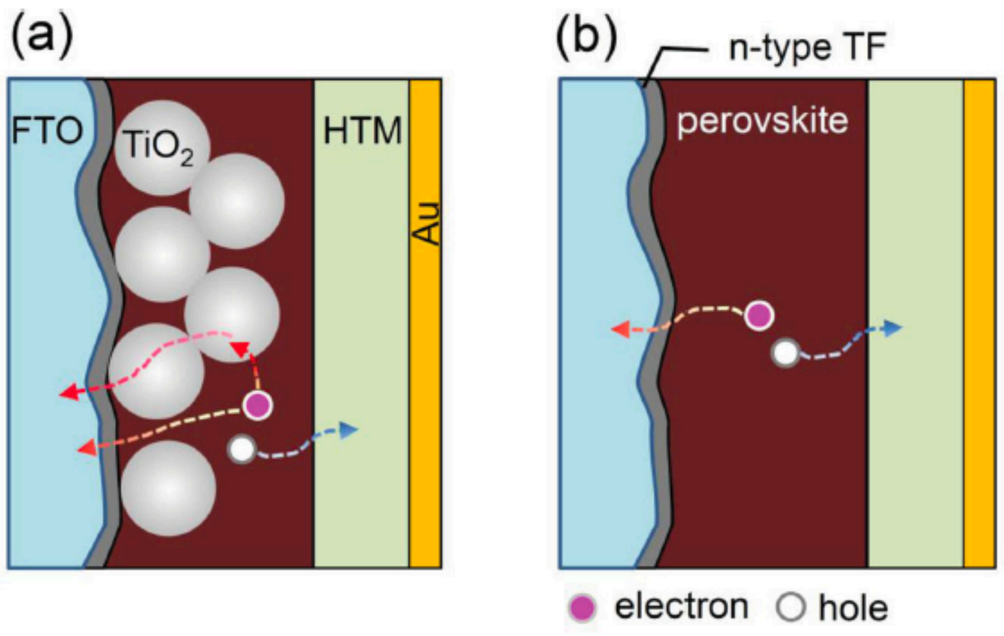








Operation Principle in PSC



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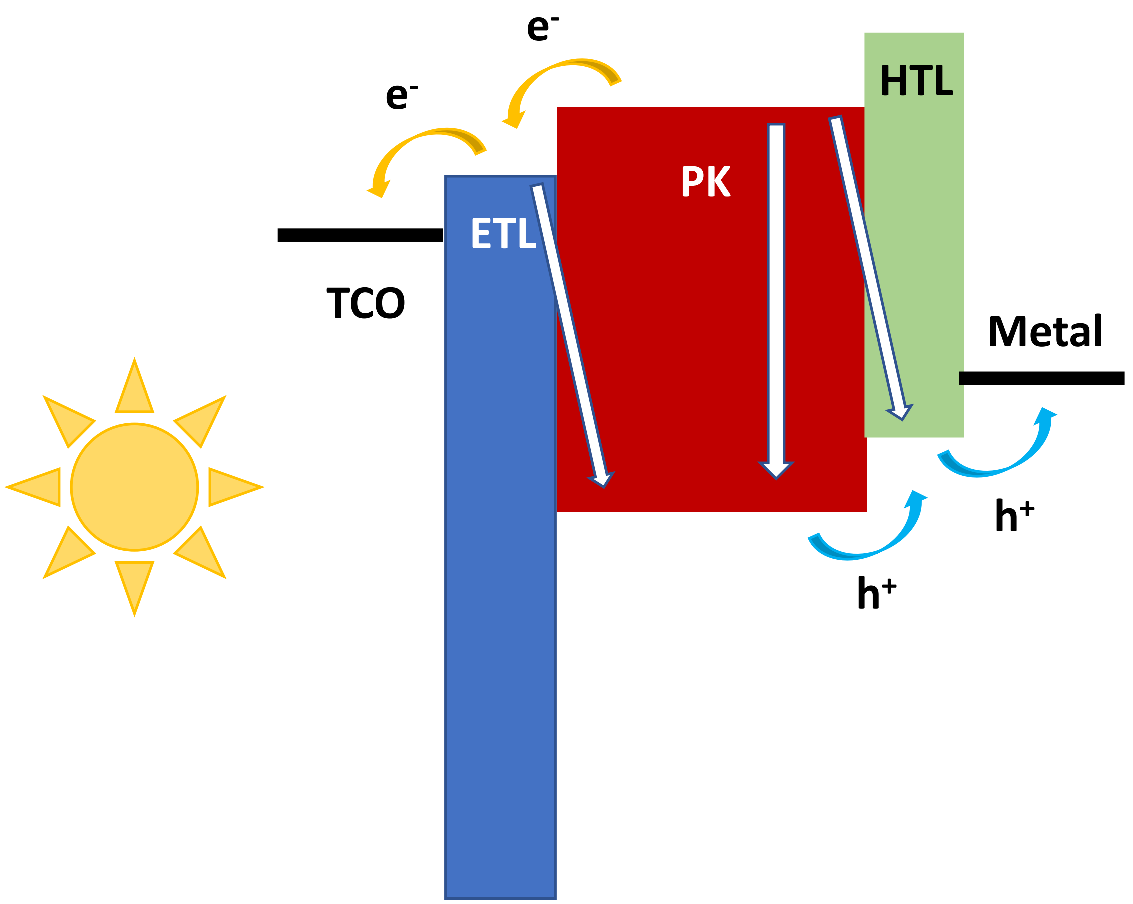
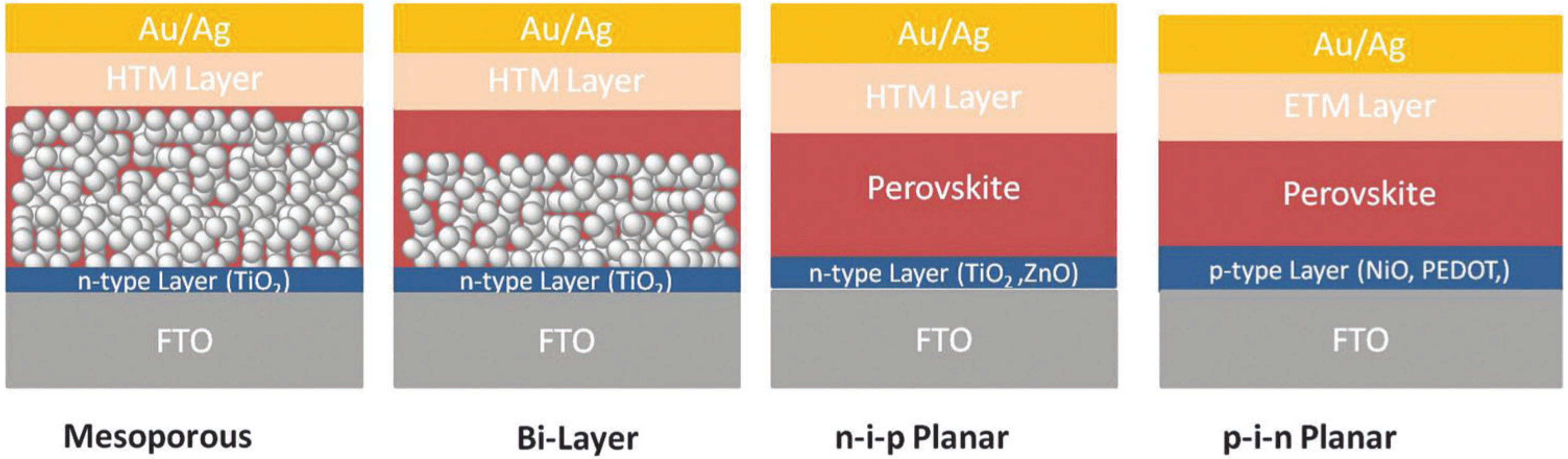


Device Structures

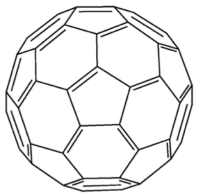


Chem. Soc. Rev., 2016, 45, 655-689

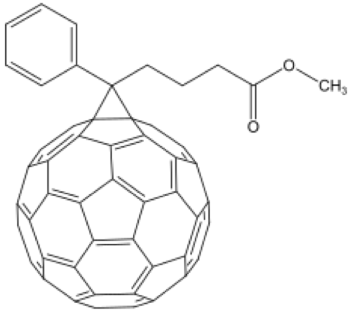
TCO: ITO, FTO, etc
Low W_F metal for hole and high W_F metal for electron
ETL (n-type): Inorganic Materials (TiO_2, SnO_2, ZnO, etc) or Organic Materials (PCBM, C60, etc)
HTL (p-type) : Inorganic Materials (NiOx, MoOx, etc) or Organic Materials (Spiro-OMeTAD, PTAA, PEDOT:PSS, etc)
SAM (p-type): MeO-2PACz, 2PACz

Device Structures

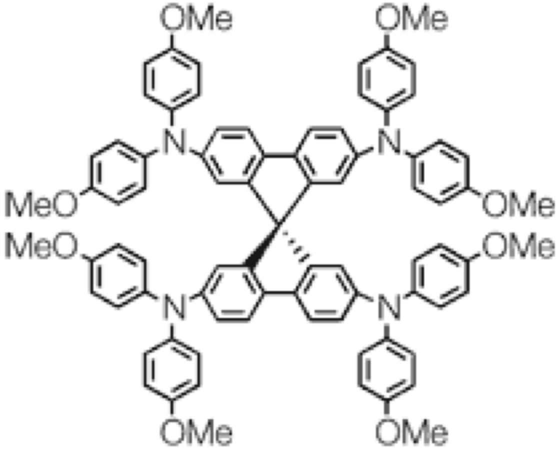
C60



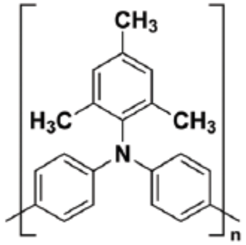
PCBM



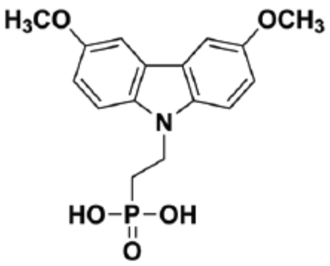
Spiro-OMeTAD



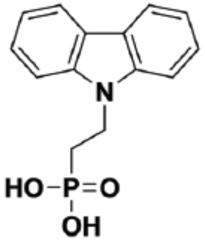
PTAA



MeO-2PACz



2PACz



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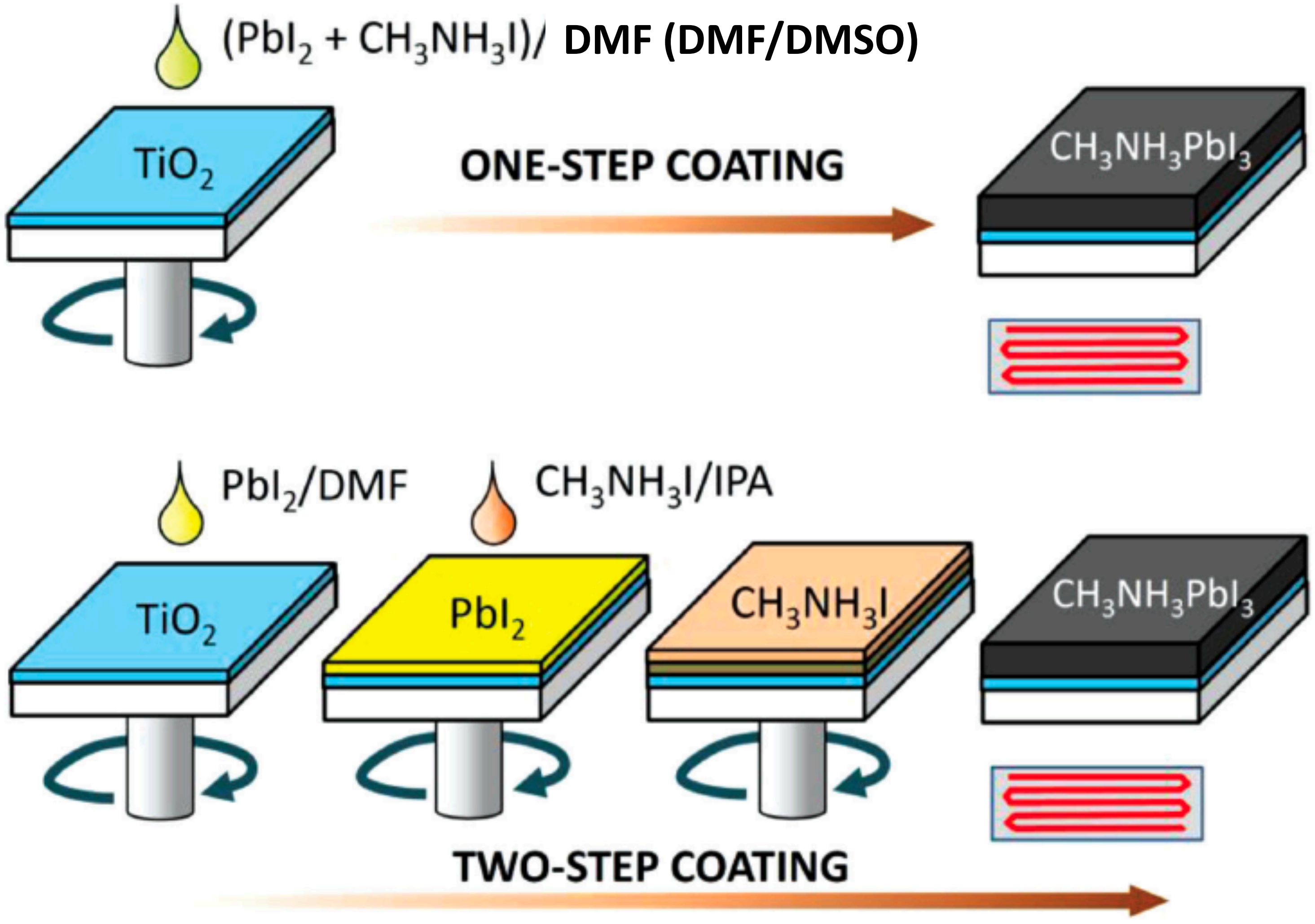
Conventional Solution Process



PbI_2, MAI as precursor

DMF: Dimethly Formamide
DMSO: Dimethlysulfoxide
IPA: 2-propanol

F. Hao et al., , *J. Am. Chem. Soc.*, **136**, 8094 (2014).

Antisolvent Method

Antisolvent is **a solvent in which your compound is less soluble.**
Ex) Chlorobenzene, Toluene, Green antisolvents: Diethyl carbonate, n-Ethane etc.

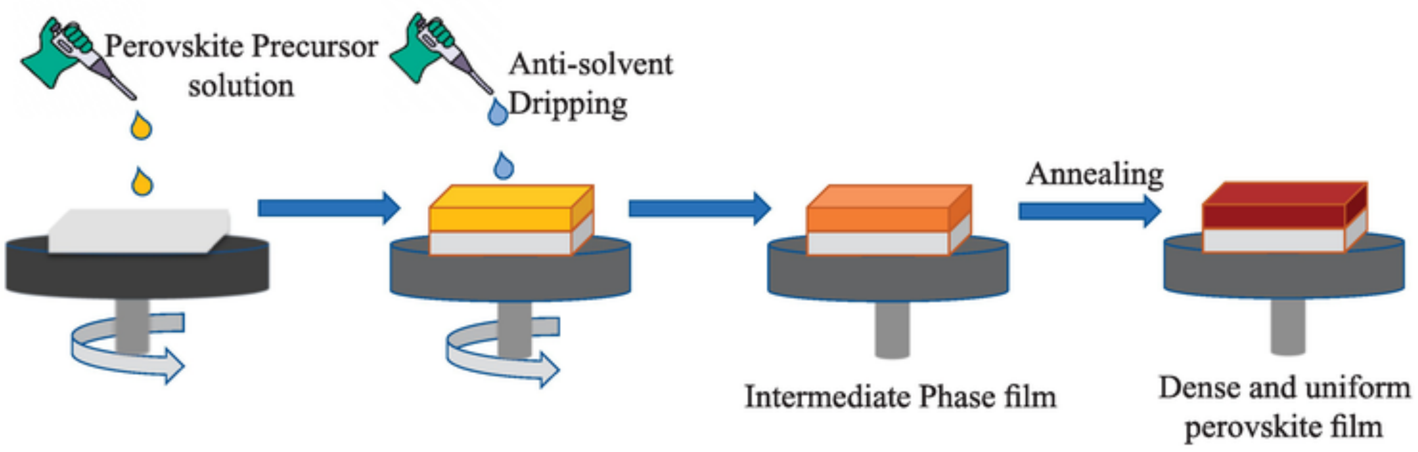
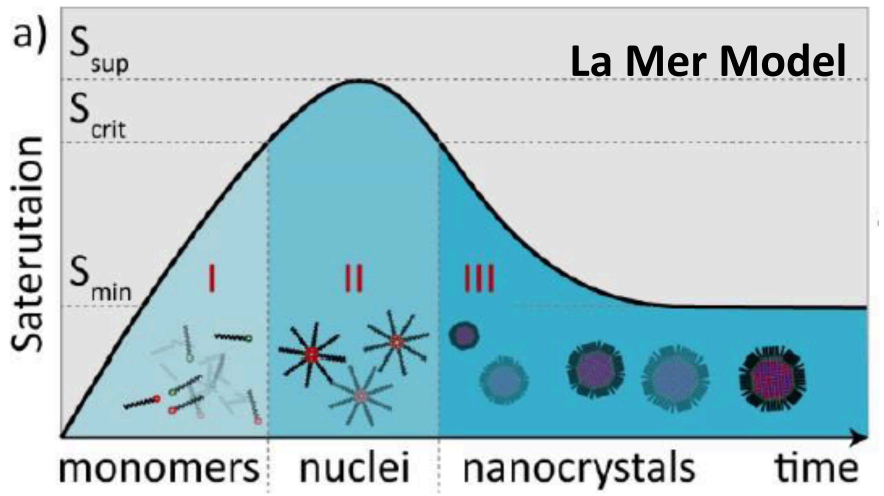


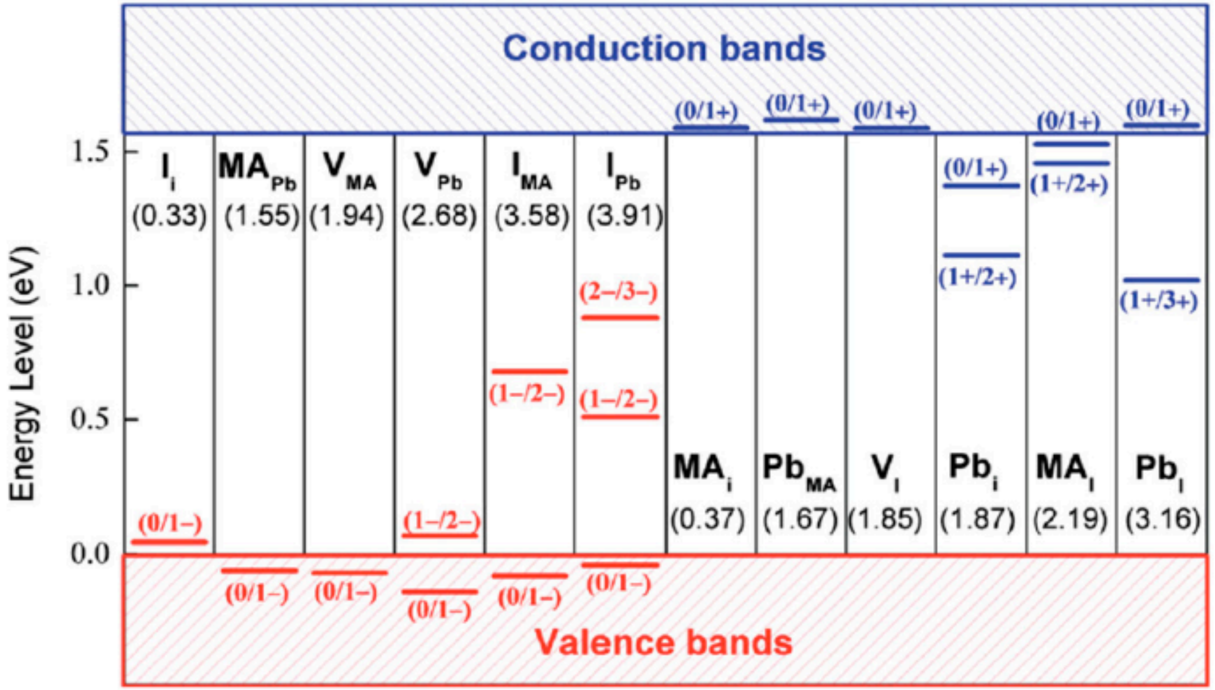
Image taken from "Thin Film Solution Processable Perovskite Solar Cells", IntechOpen, 2022.



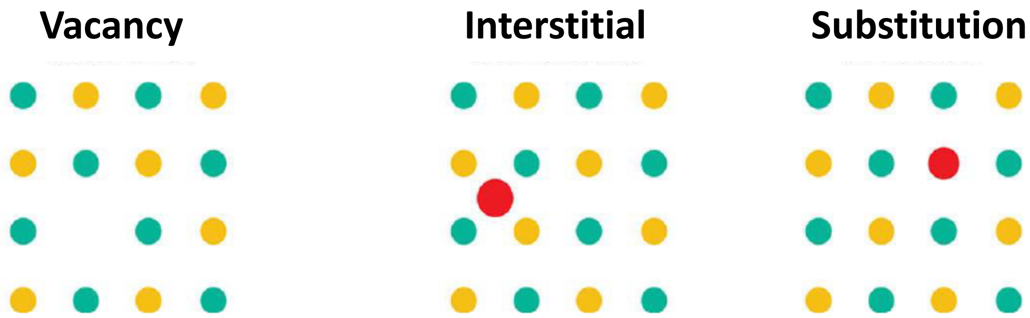
- The principle of antisolvent engineering is **extracting the DMF/DMSO solvent using an antisolvent**.
- This process leads to rapid oversaturation of the components, resulting in the formation of a target perovskite, after low temperature annealing.

Defect Tolerance

- Calculated transition energy levels of various type of point defects in $MAPbI_3$.
- Interstitials (i), vacancies (V), ion substitutions.
- Vacancy type defects produce shallow traps or resonance within the band.
- Some interstitials and substitutions associated with Pb and I form electronic states deep inside the band gap but have relatively high formation energies.

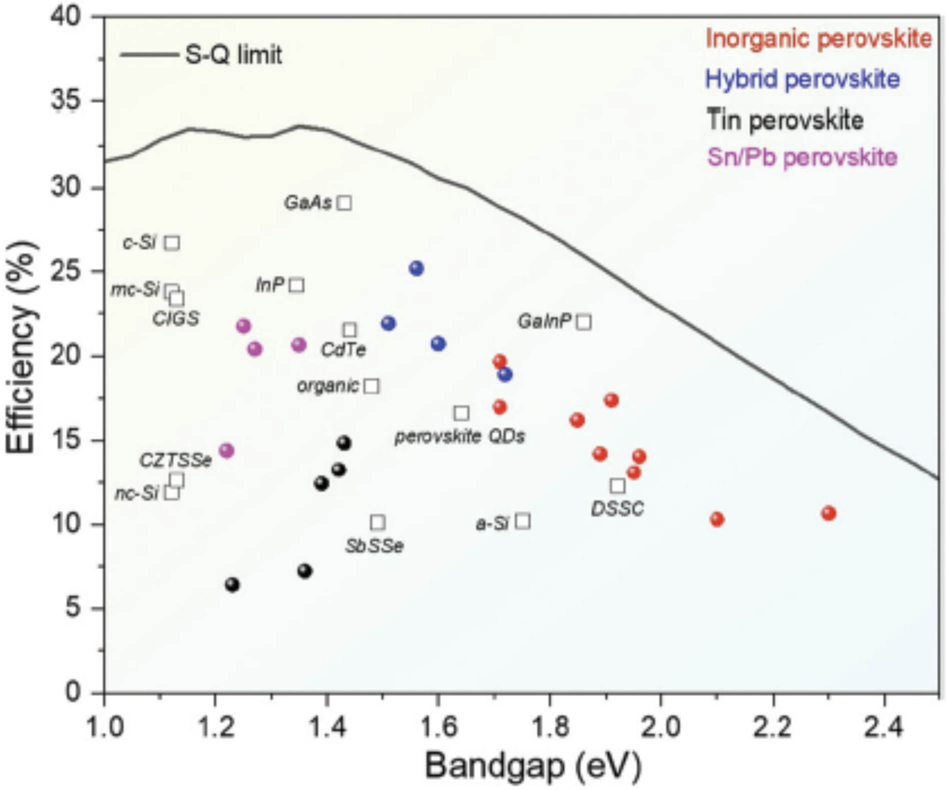


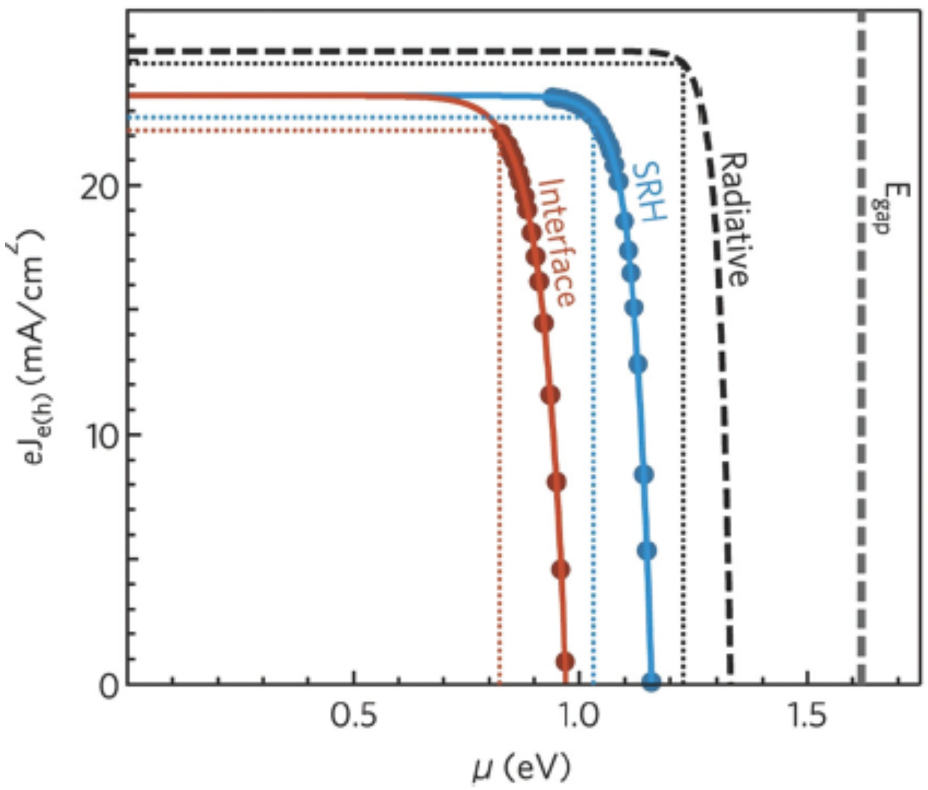
W-J. Yin et al., *Adv. Mater.*, **26**, 4653–4658 (2014).



A. Buin et al., *Nano Lett.*, **14**, 6281–6286 (2014).

Towards Higher Performance



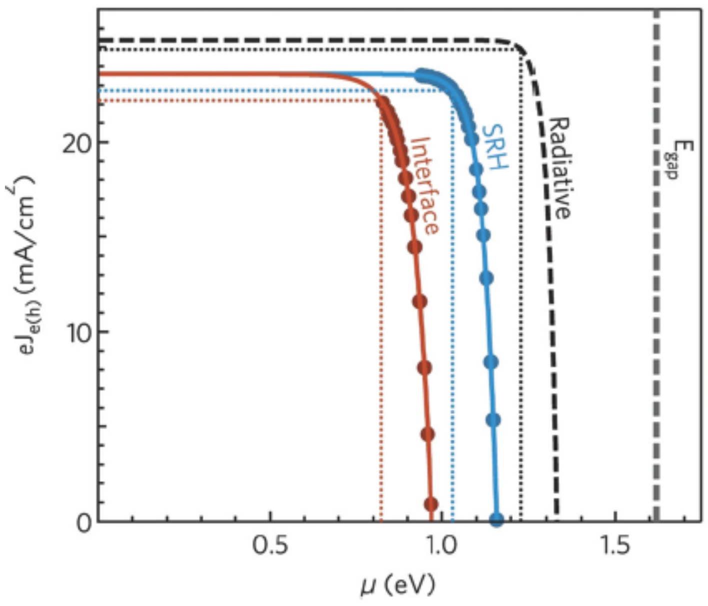


- Impressive efficiencies **over 25%** have been achieved.
- Room for further improvement.
- SRH non-radiative recombination by deep and shallow defects : film quality, crystal size, passivation.
- Interface recombination: energy alignment, charge extraction.
- Career management → enhanced V_{oc}, J_sc and *FF*.
- Light management → enhanced J_{sc}.

Image taken from Z. Guo et al., *Energy Environ. Sci.*, **15**, 3171 (2022)

Characterizing Recombination (Device)

- **From J-V curve and IQE**



$$EQE = IQE \times LHE$$

IQE is determined by charge management, e.g. charge separation/collection.

- **Ideality Factor**

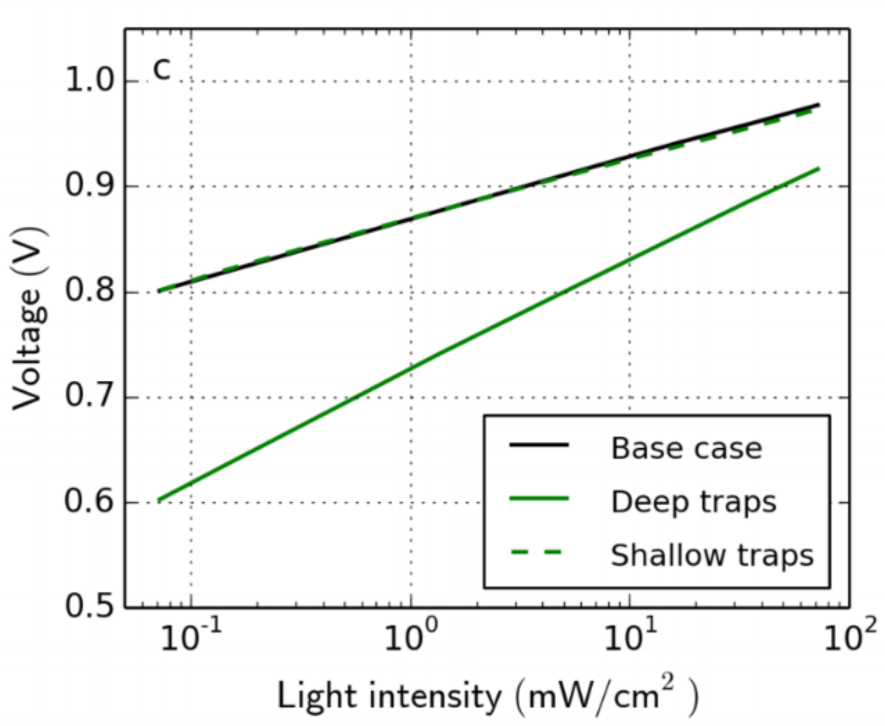


Image from https://www.fluxim.com

$$n = \frac{e}{k_B T} \cdot \frac{dV_{OC}}{d(lnL)}$$

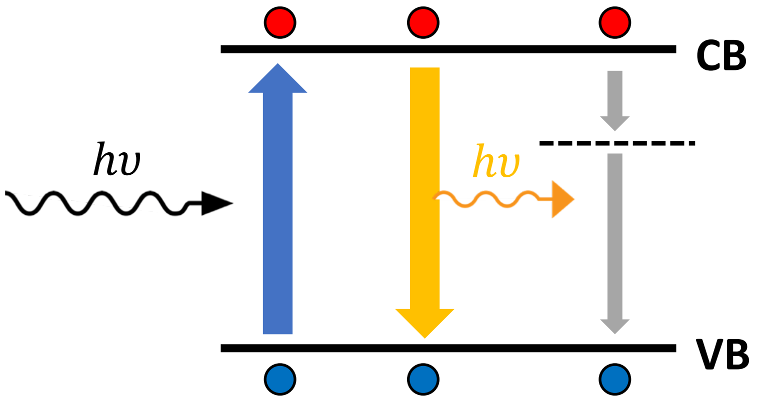
L is the incident photon flux

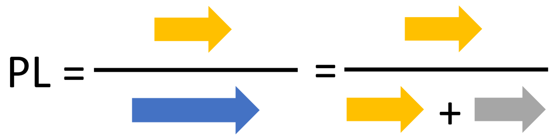
n = 1 is attributed to radiative recombination

n = 2 is attributed to dominant SRH recombination

Characterizing Recombination (Film)

- **Photoluminescence (PL)**





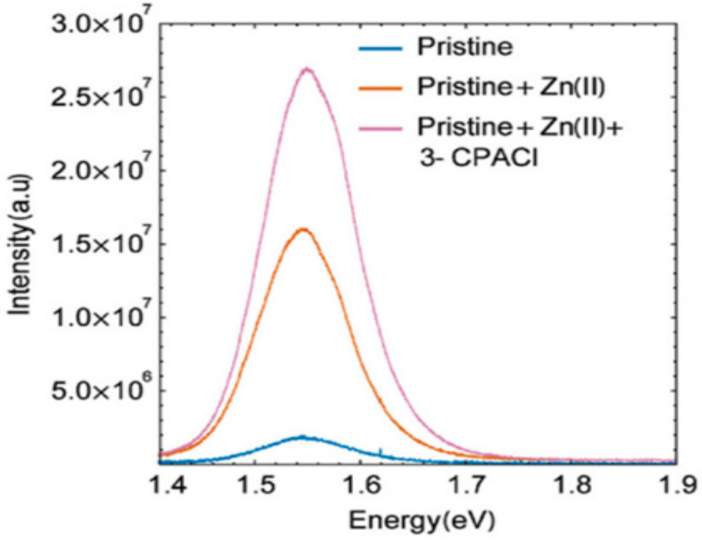
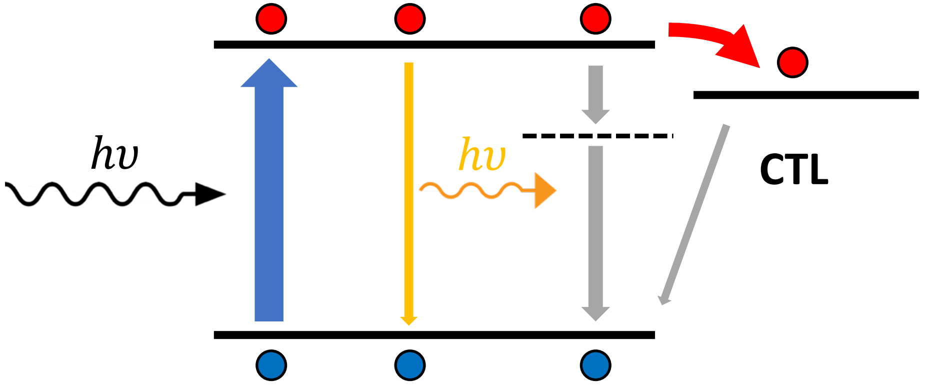
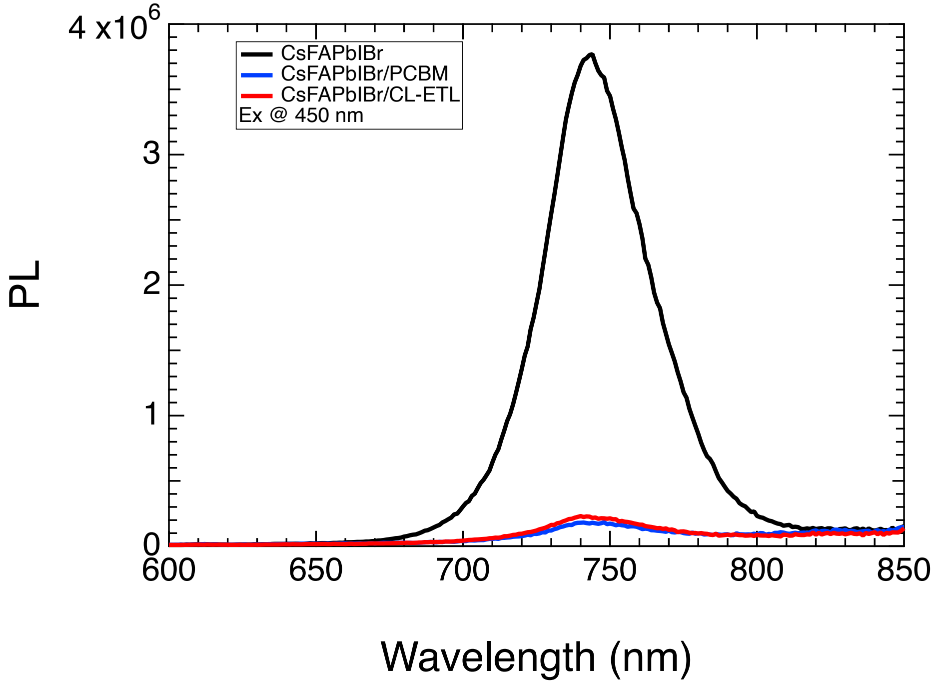


Image from L.A. Muscarella et al., *ACS Appl. Mater. Interfaces*, **11**, 17555 (2019)

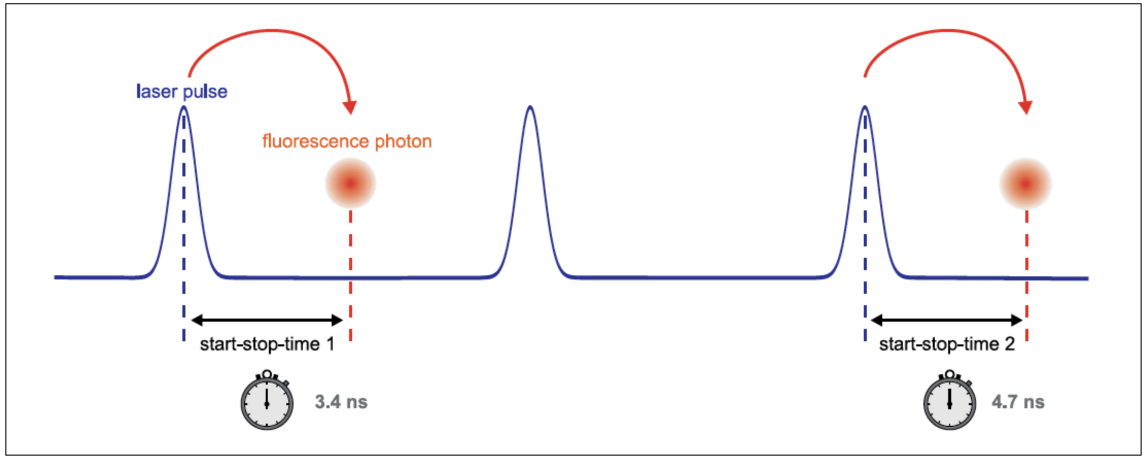
- **PL quenching with CTL**

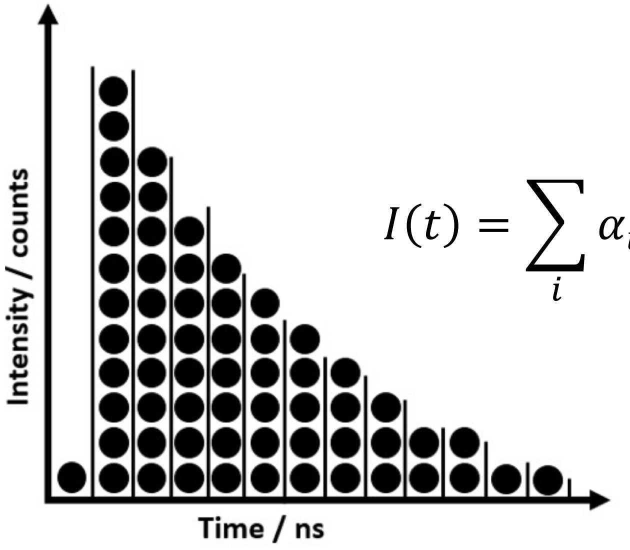




Characterizing Recombination (Film)

- **Time-resolved PL**





$$I(t) = \sum_i \alpha_i \exp(-\frac{t}{\tau_i})$$

Time-correlated single-photon counting (TCSPC)

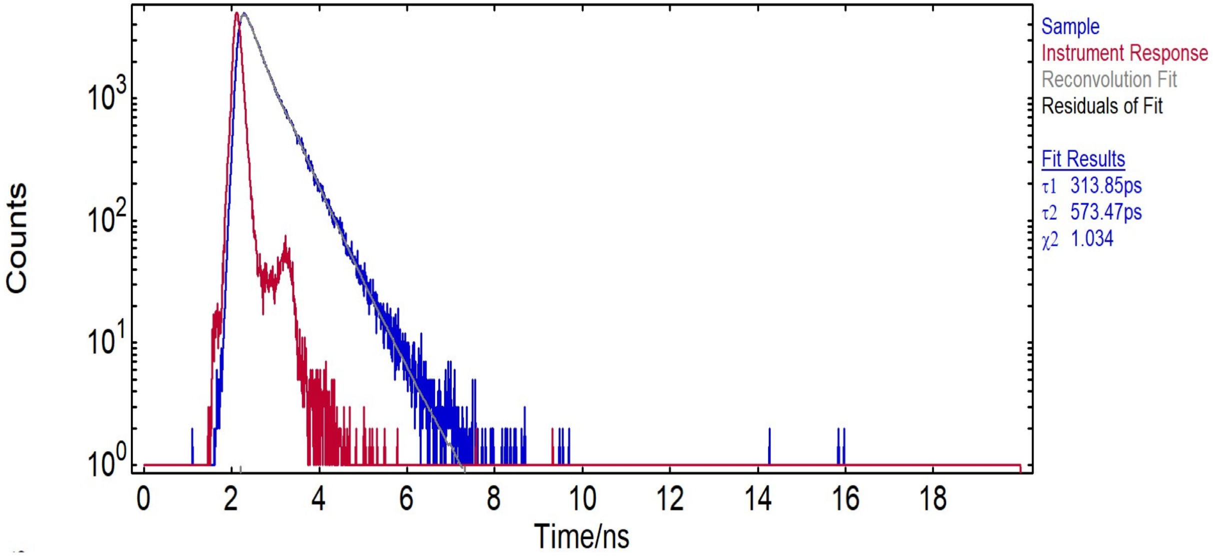
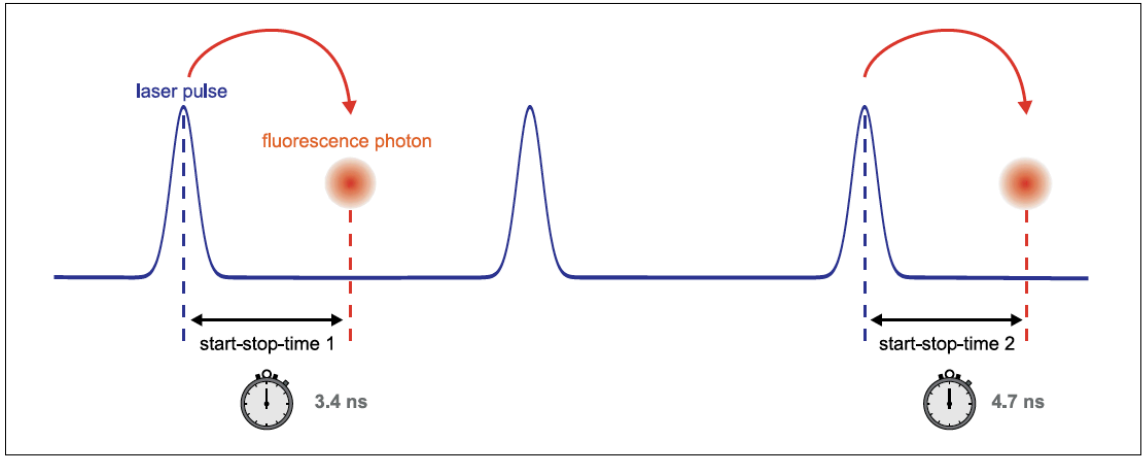
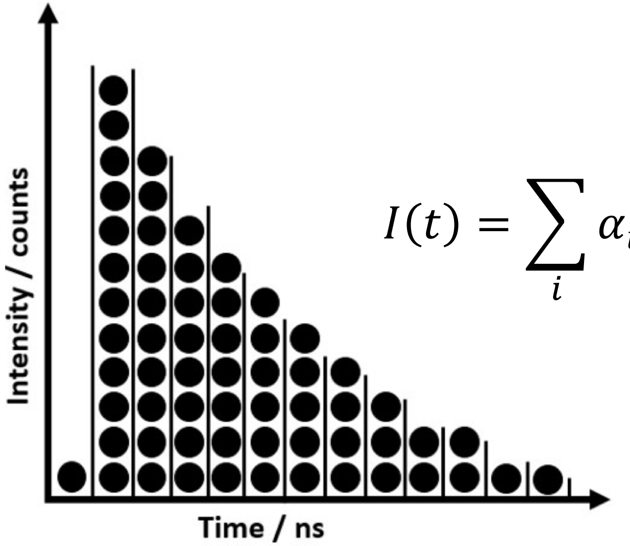


Image taken from https://www.edinst.com/blog/what-is-tcspc/

Characterizing Recombination (Film)

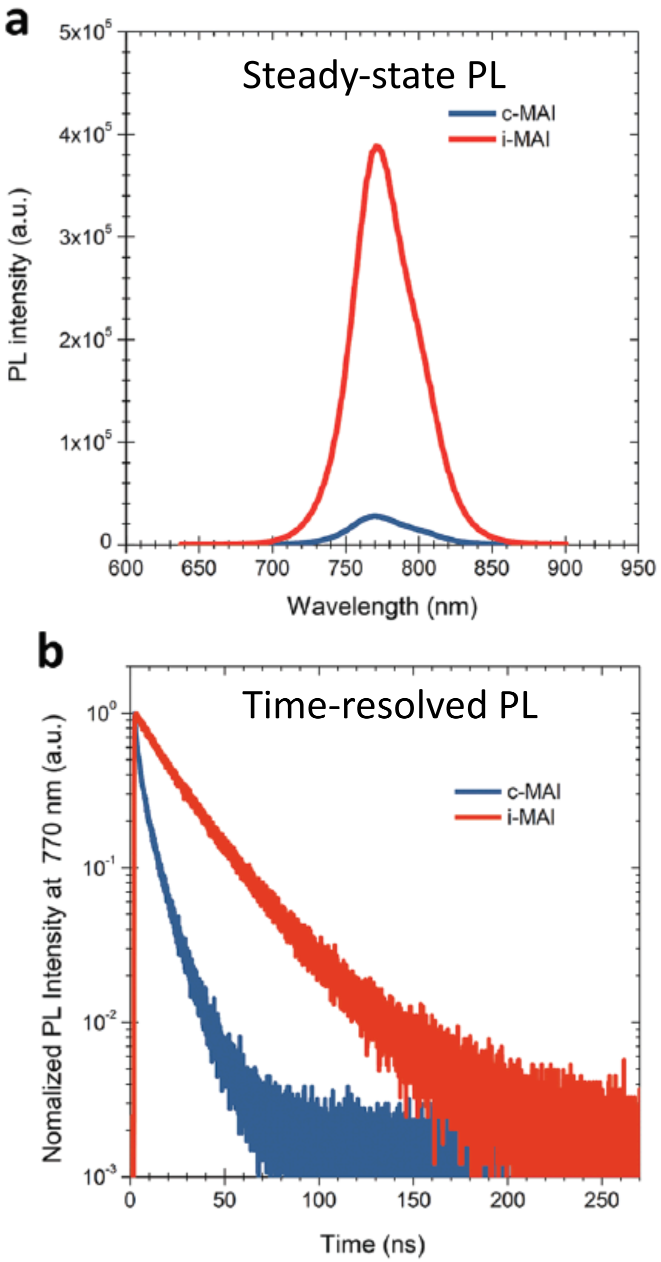
- **Time-resolved PL**





$$I(t) = \sum_i \alpha_i \exp(-\frac{t}{\tau_i})$$

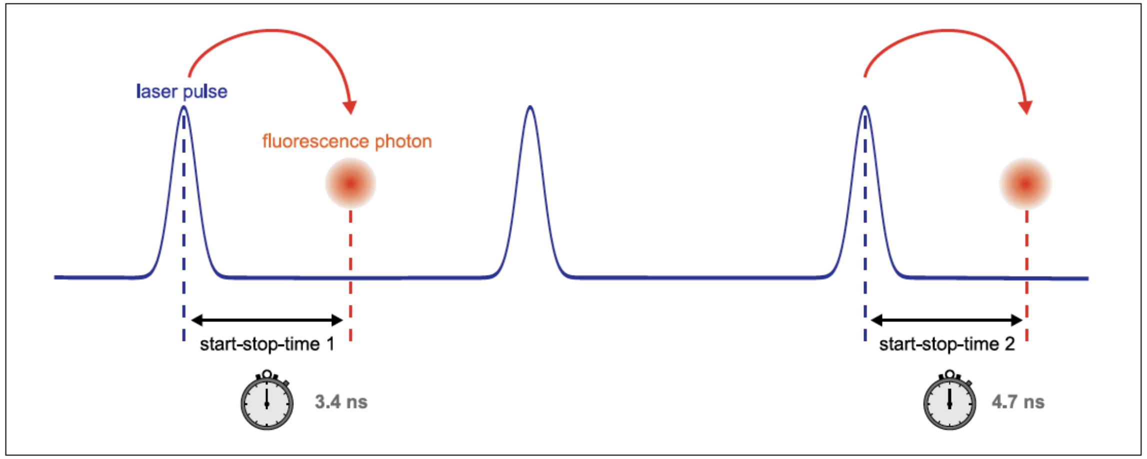
Time-correlated single-photon counting (TCSPC)

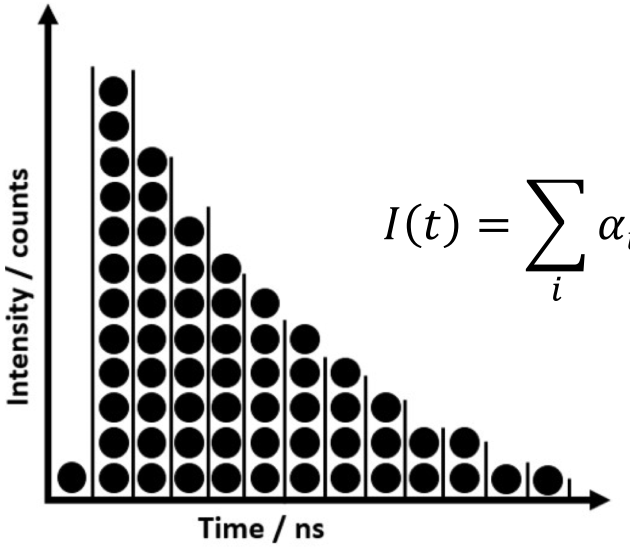


I. Levchuk et al., *Adv. Mater. Interfaces*, 1600593 (2016)

Characterizing Recombination (Film)

- **Time-resolved PL**

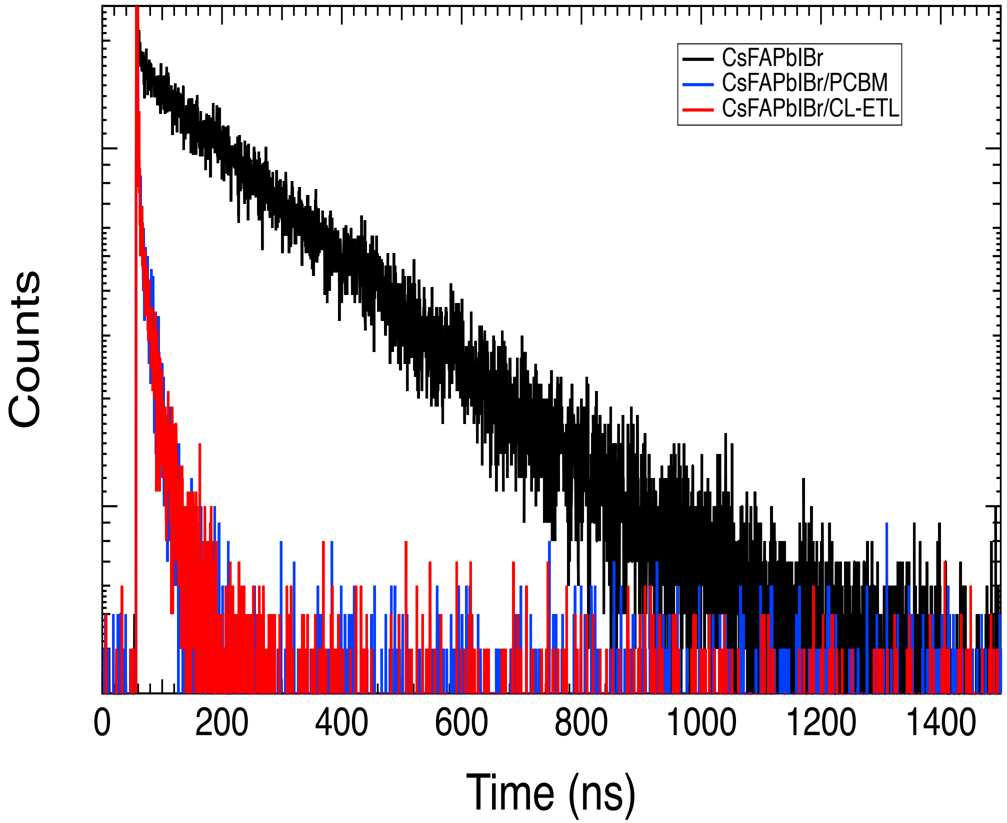




$$I(t) = \sum_i \alpha_i \exp(-\frac{t}{\tau_i})$$

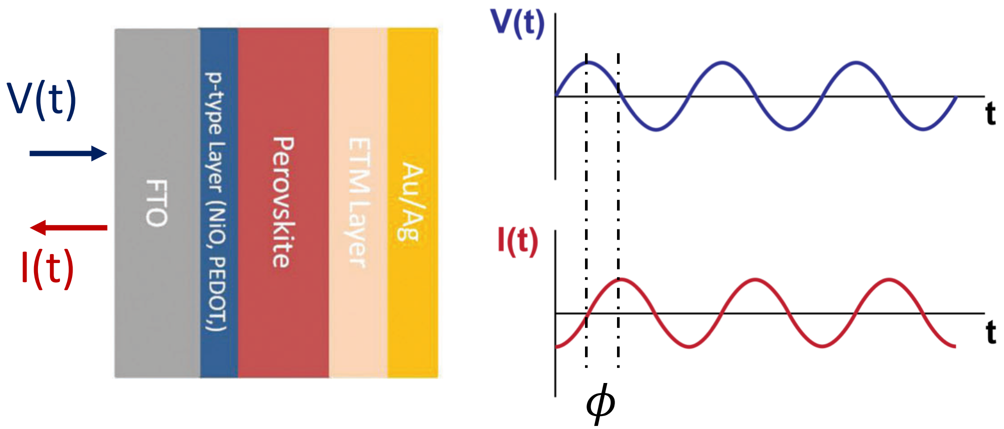
Time-correlated single-photon counting (TCSPC)

In general, the kinetics of the charge transfer to CTL is faster than the kinetics of radiative recombination.



Characterizing Recombination (Device)

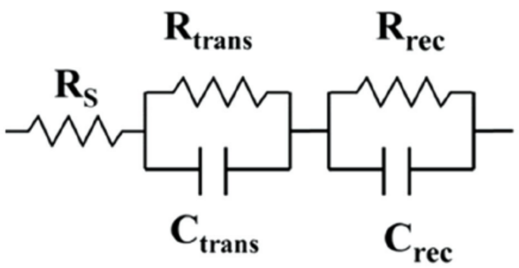
- **Electrochemical Impedance Spectroscopy (EIS)**



$$Apply \rightarrow \ \Delta V(t) = V_0 sin(\omega t), \qquad \omega = 2\pi f$$

$$Response \rightarrow \ \Delta I(t) = I_0 sin(\omega t - \phi)$$

equivalent electrical circuit



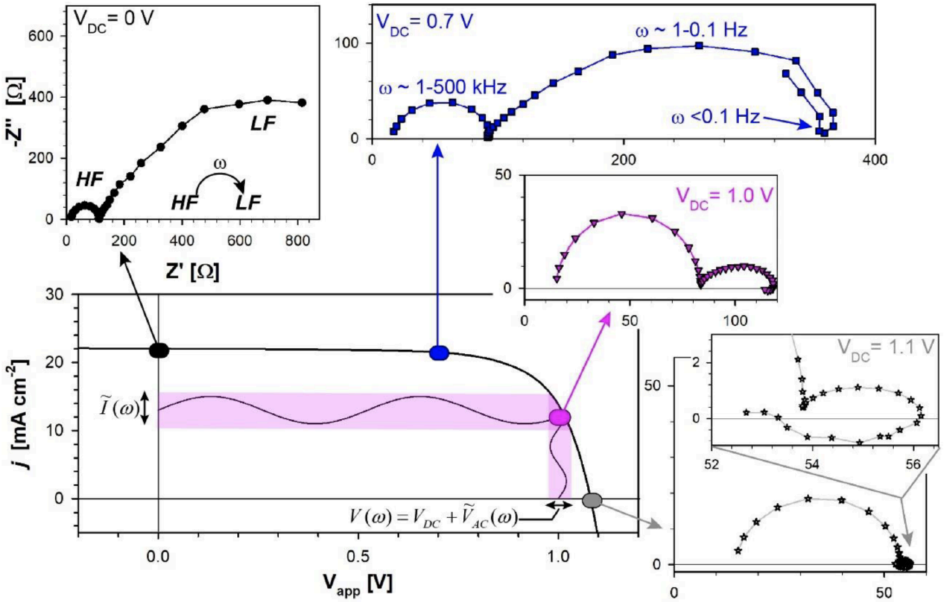


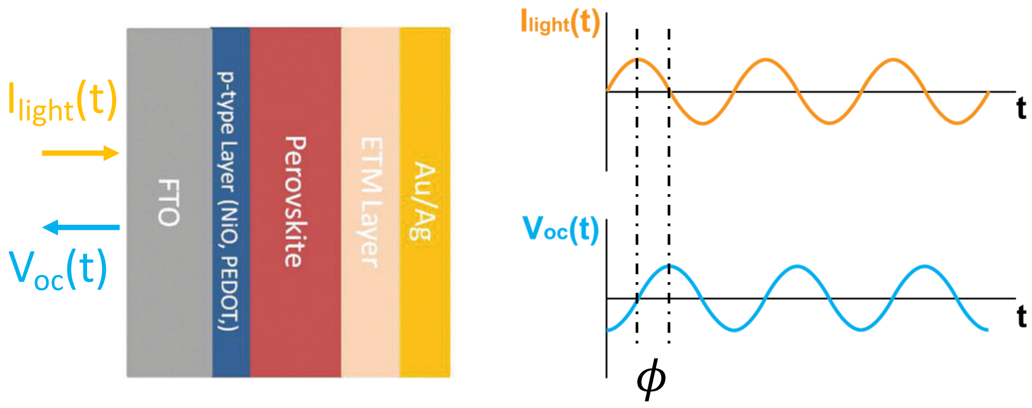
Image from A. Guerrero et al.,, *Chem. Rev.*, **121**, 14430 (2021)

$$impedance \ \equiv Z = \frac{\Delta V(t)}{\Delta I(t)} = \frac{V_0 sin(\omega t)}{I_0 sin(\omega t - \phi)} = Z_0 e^{i\phi} = Z_0(cos\phi + isin\phi) = Z' + iZ''$$

The **impedance at a given frequency** is related to the **processes occurring at the timescales** imposed by the frequency.

Characterizing Recombination (Device)

- **Intensity-Modulated Photovoltage Spectroscopy (IMVS)**



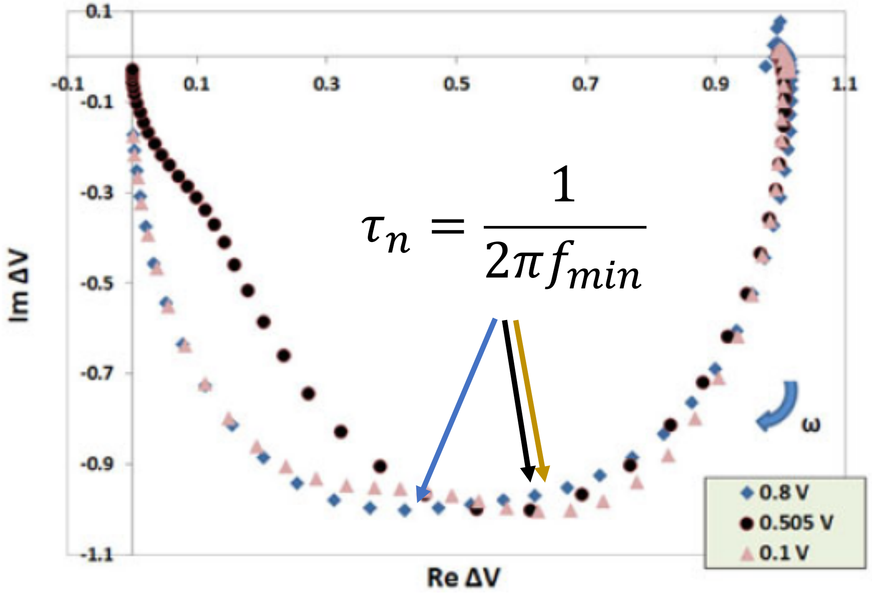
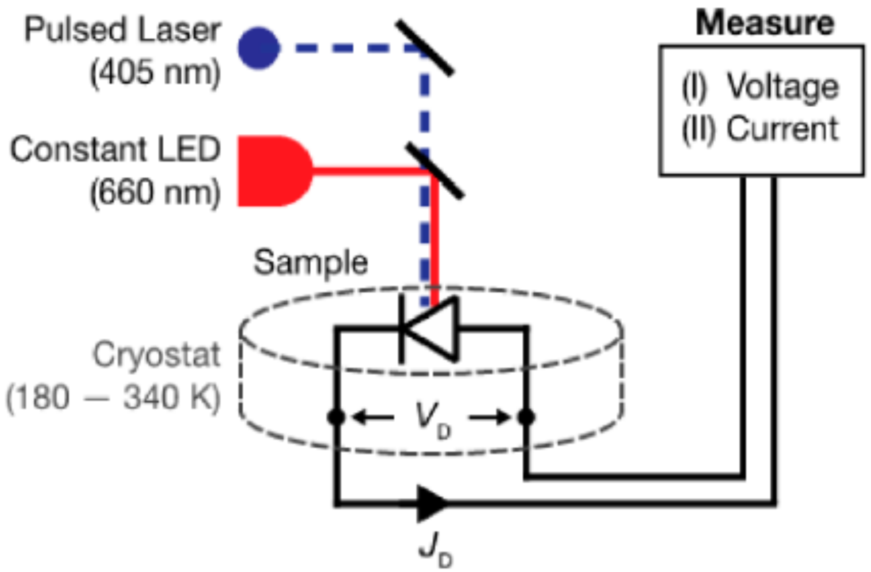


Image from K. Adhitya et al., *IEEE J. Photovoltaics*, **5**, 1414 (2015)

- **Transient Photovoltage Decay**



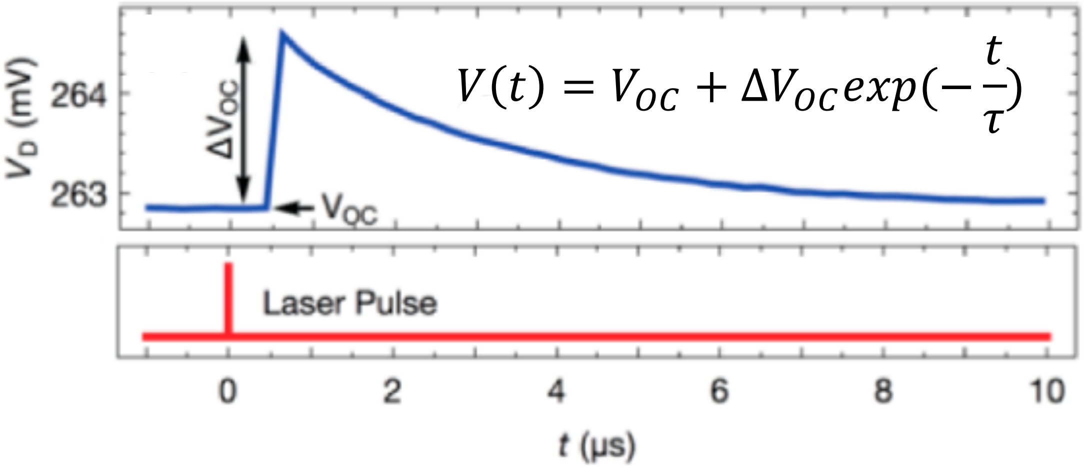
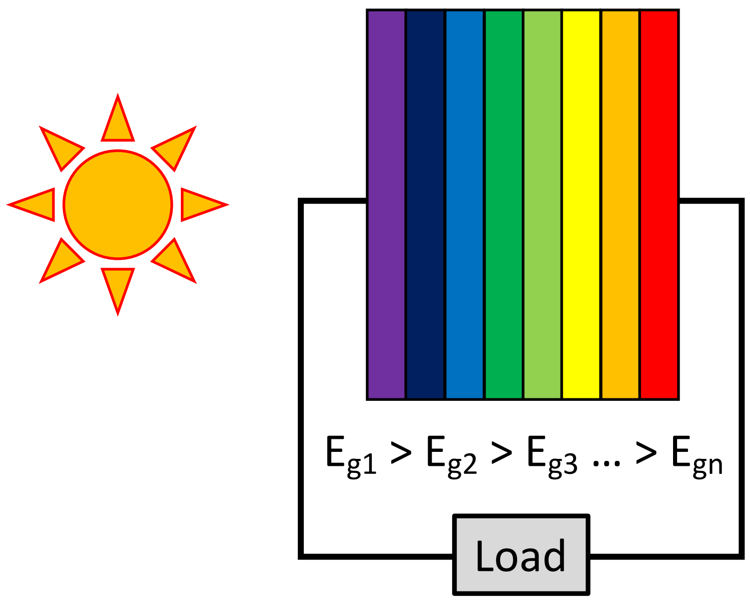


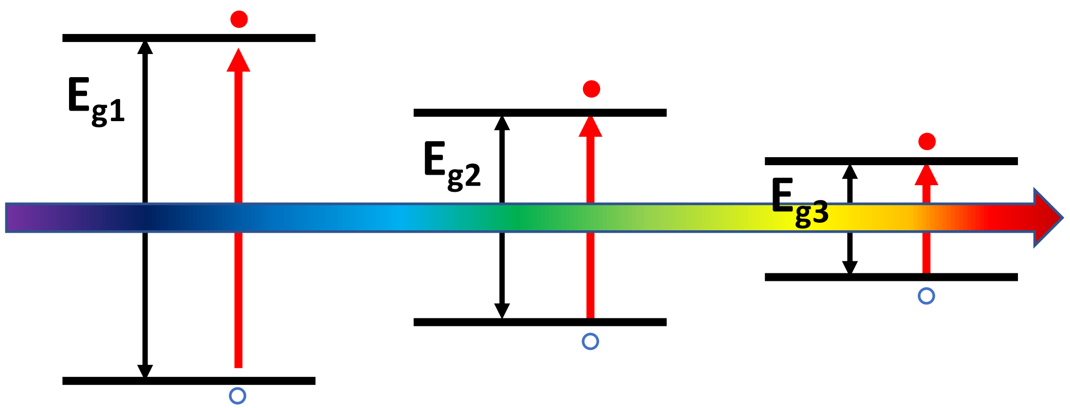
Image from W.M.M. Lin et al., *J. Phys. Chem. C*, **120**, 12900 (2016)

Beyond S-Q Limit

- Tandem Solar Cells
- Concentrated Solar Cells
- Intermediate Band Solar Cells
- Hot Carrier and Carrier Multiplication

Tandem Solar Cells





- **V = V (E_{g1}) + V (E_{g2}) + V (E_{g3})**
- **J is determined by the lower value**

Tandem solar cells: Semiconductors with different bandgaps connected electrically in series either in the same device or in different devices.

Efficiency can be significantly enhanced by using a stack of materials with different band gaps.

- **Efficiency >45% (dual junction)** is possible under standard AM 1.5 illumination.
- Challenges:
  - Current matching required for series connection of junctions. Sensitive to illumination conditions.
  - Difficult to maintain a high crystal quality due to lattice mismatch.
  - High cost.

Tandem Solar Cells

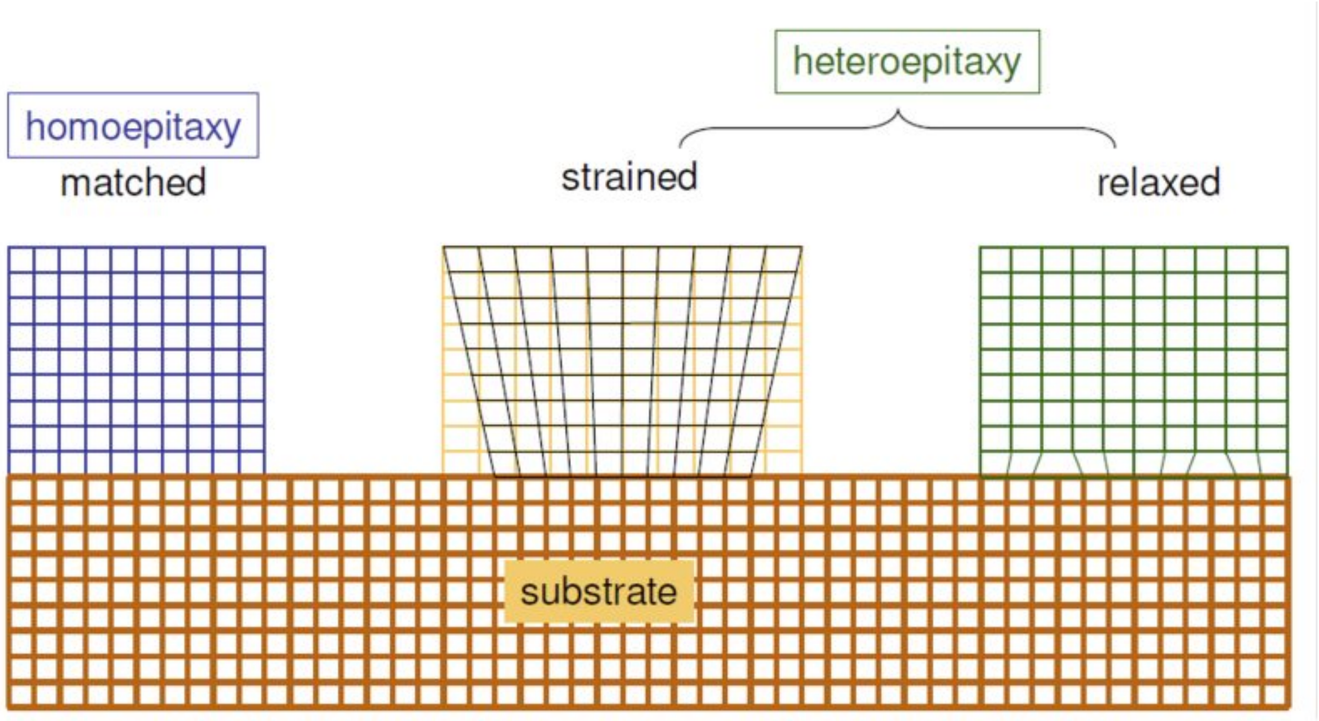


Image taken from https://www.mks.com/n/silicon-epitaxial-thin-films

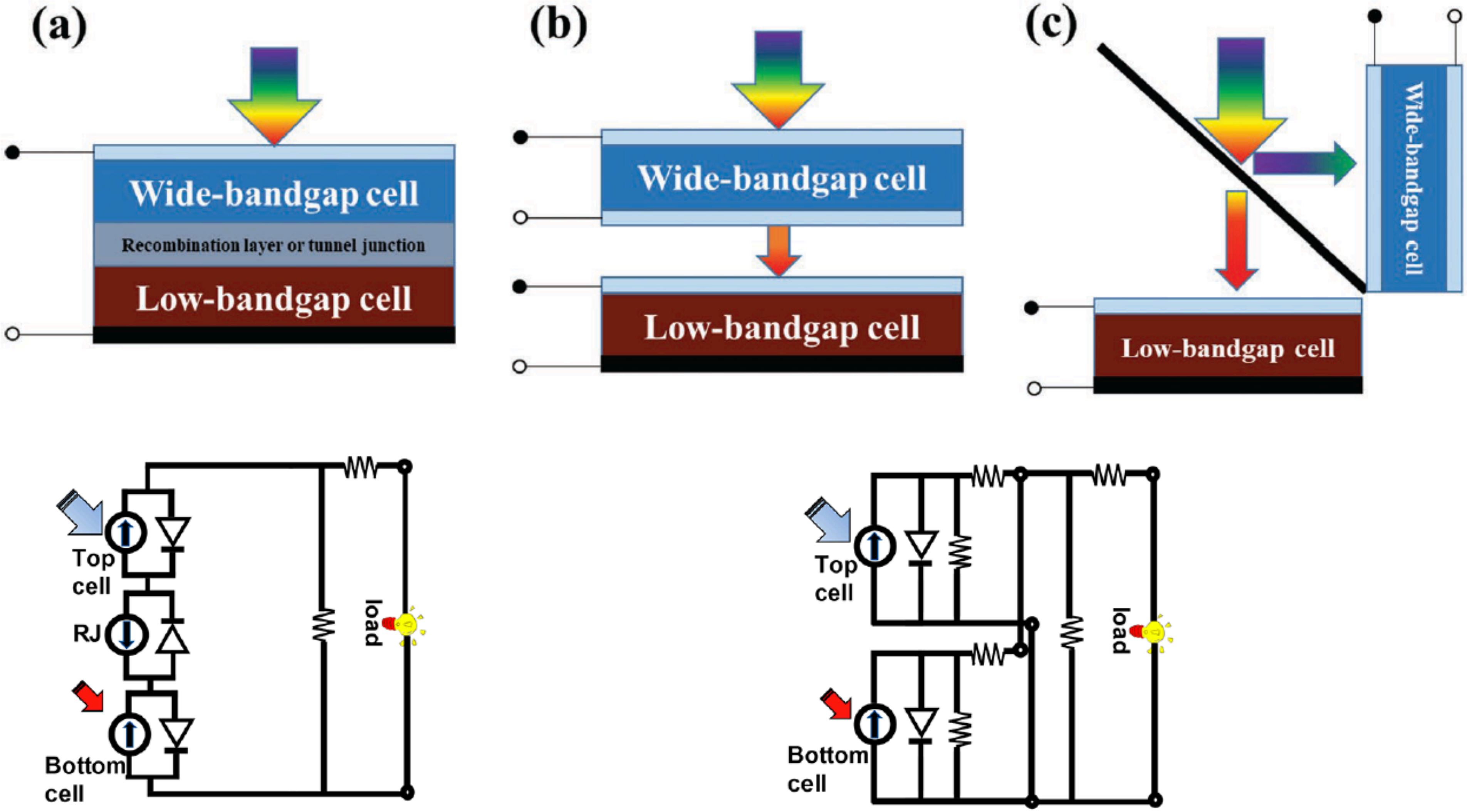
- Epitaxy is defined as the "regularly oriented growth of one crystalline substance on another".
- Lattice mismatch, ε < 9%, is necessary for obtaining epitaxy.

$$\varepsilon = \frac{a_f - a_s}{a_f}$$

a_f: lattice constant of the film

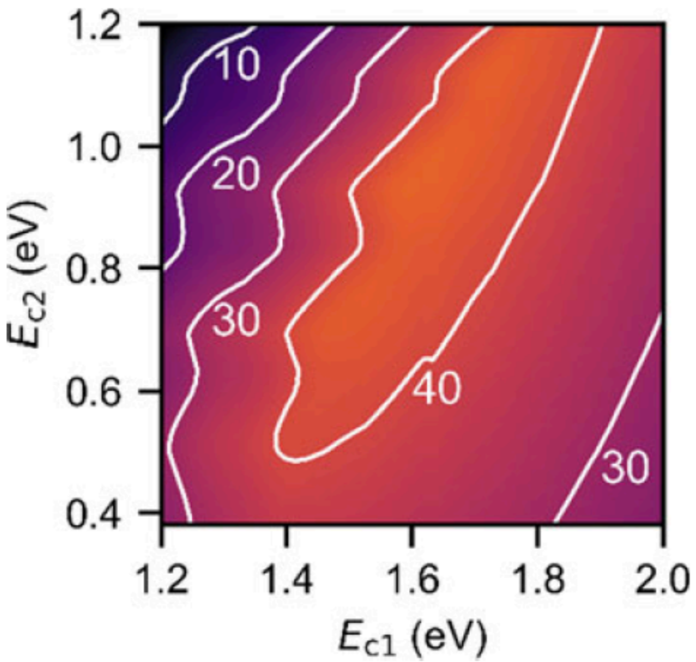
a_s: lattice constant of the substrate

Tandem Solar Cells

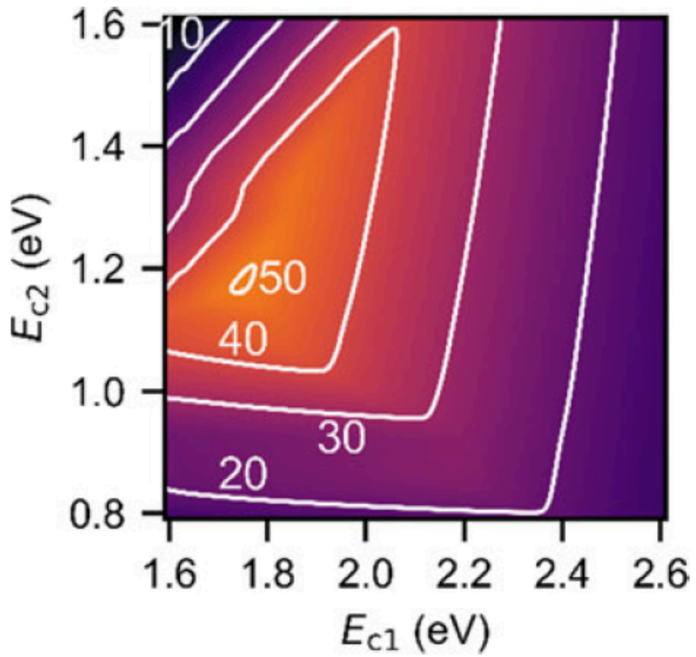


Images taken from Z. Wang et al., *Adv. Sci.* 6, 1801704 (2019) and H. Li et al., *Chem. Rev.*, **120**, 9835–9950 (2020).

Tandem Solar Cells



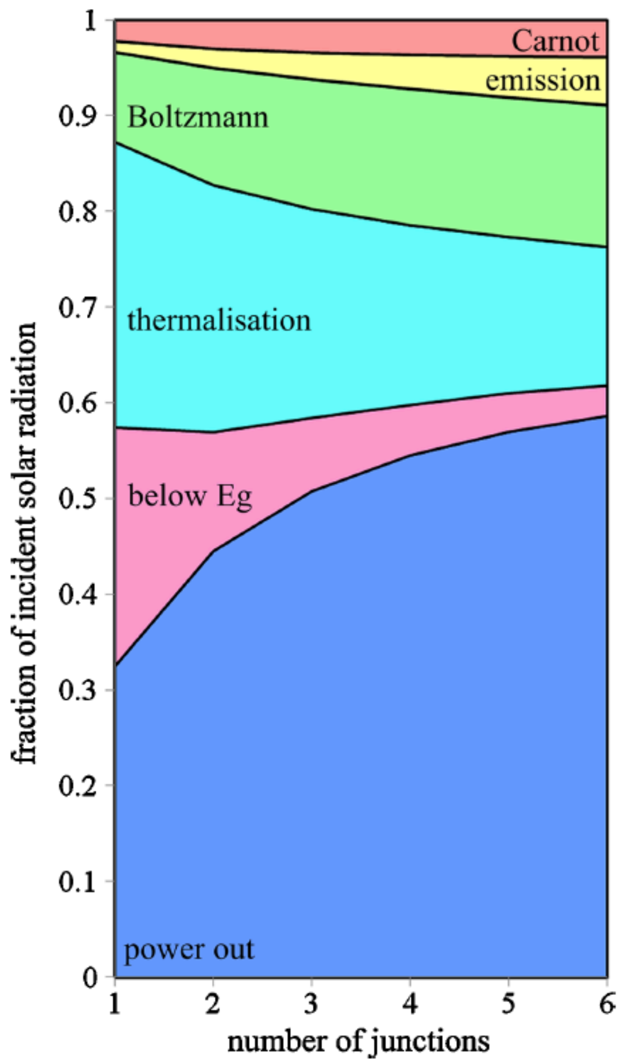
A **dual junction solar cell**:
At the point E_{c1} = 1.58 eV and E_{c2} = 0.94 eV, the conversion efficiency reaches its maximum of **45.4%**.



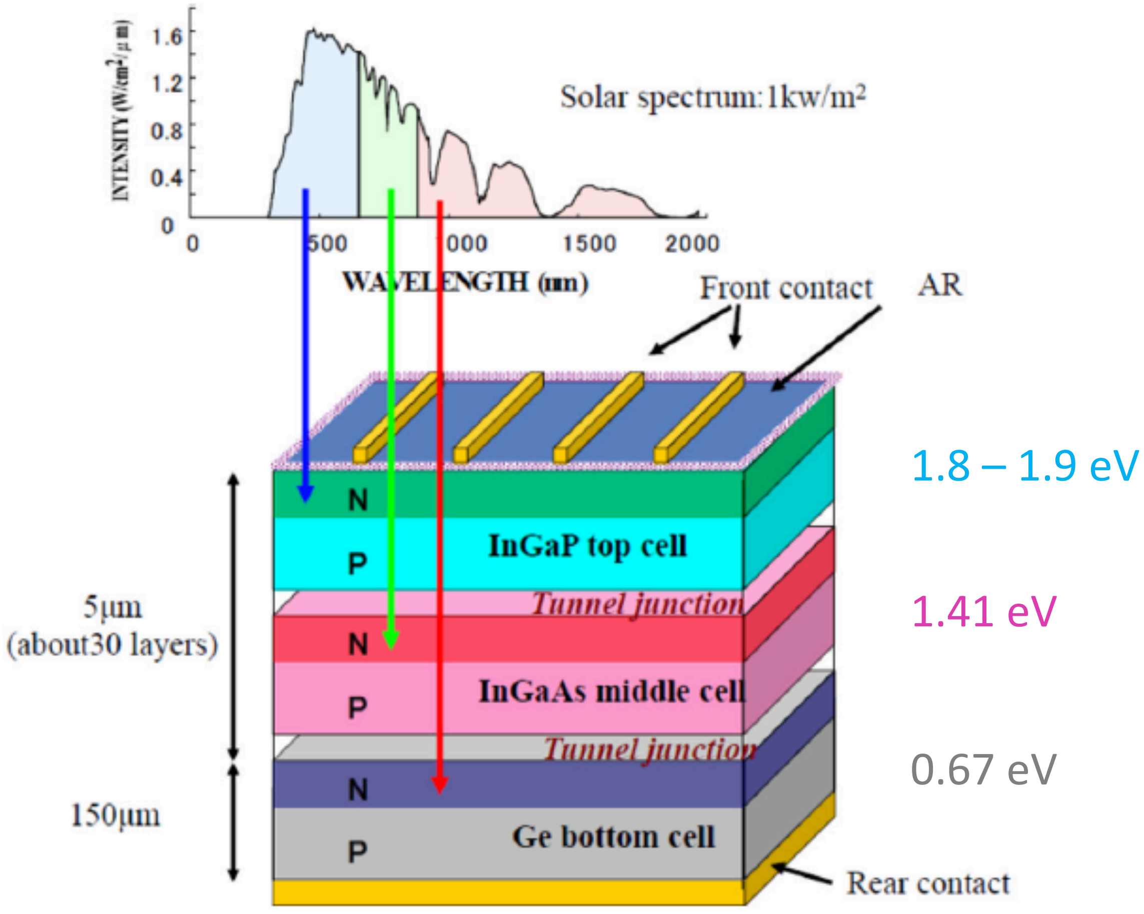
A **triple junction solar cell**:
With Ge (E_{c3} = 0.66 eV), at the point E_{c1} = 1.76 eV and E_{c2} = 1.18 eV, the conversion efficiency reaches its maximum of **50.3%**.

Image taken from Energy Conversion Efficiency of Solar Cells, Springer

III-V Semiconductors: Multijunction Solar Cells



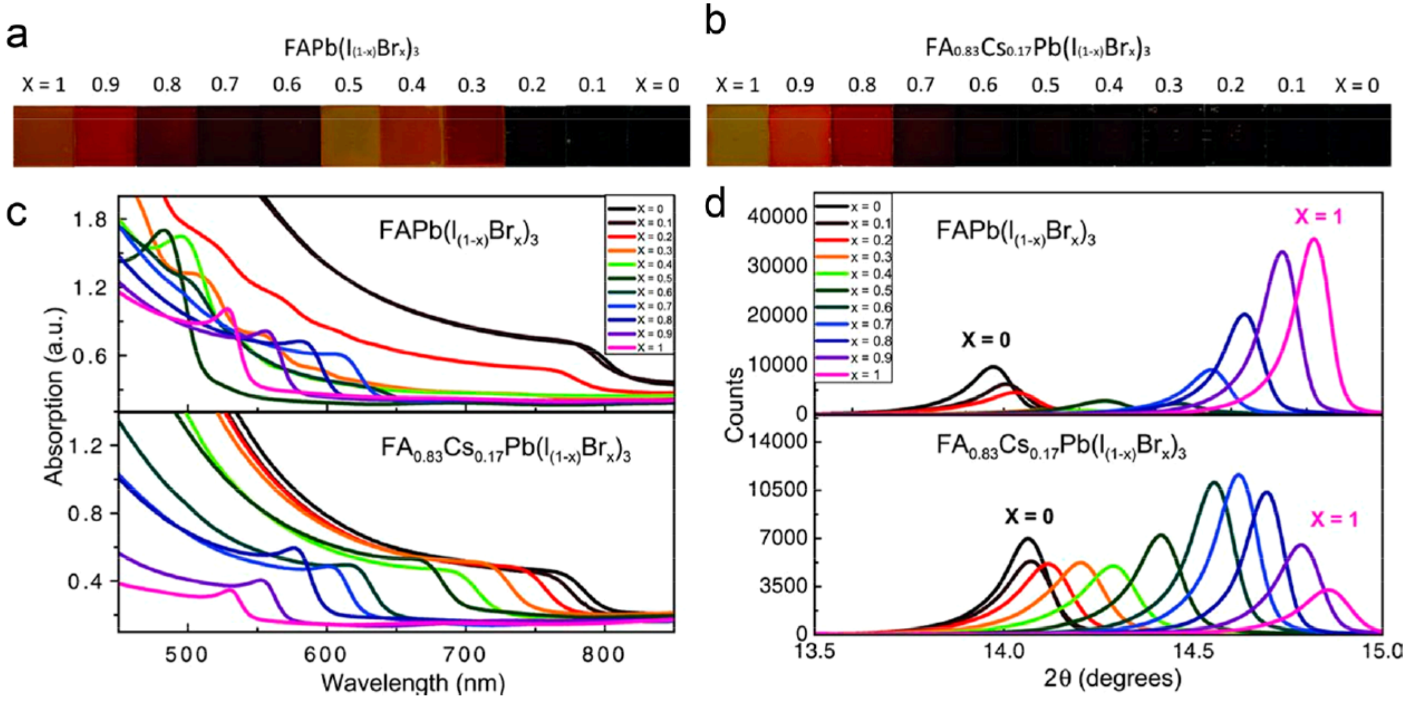
Hirst et al., *Prog. Photovolt: Res. Appl.*, **19**, 286–293 (2011)



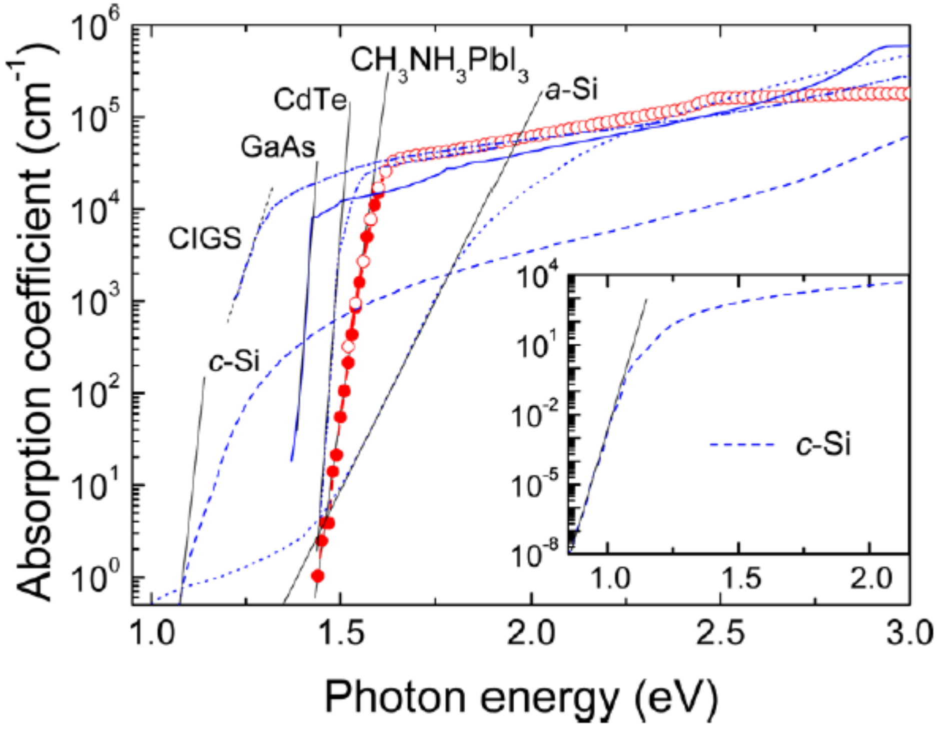
Yamaguchi et al., *J. Appl. Phys.*, **129**, 240901 (2021)

Halide Perovskite is Ideal for Tandem Solar Cells?

- **Optical bandgap: 1.57 eV**
- **Band gap Tuning**
- **No optically detectable deep states.**
- **Highest reported V_{oc} values:**
  c-Si = 0.75 V, GaAs = 1.12 V, $CH_3NH_3PbI_3$ = 1.05 V.



D. P. McMeekin, *Science*, **351**, 151–155 (2016).



S. De Wolf et al., *J. Phys. Chem. Lett.*, **5**, 1035–1039 (2014).

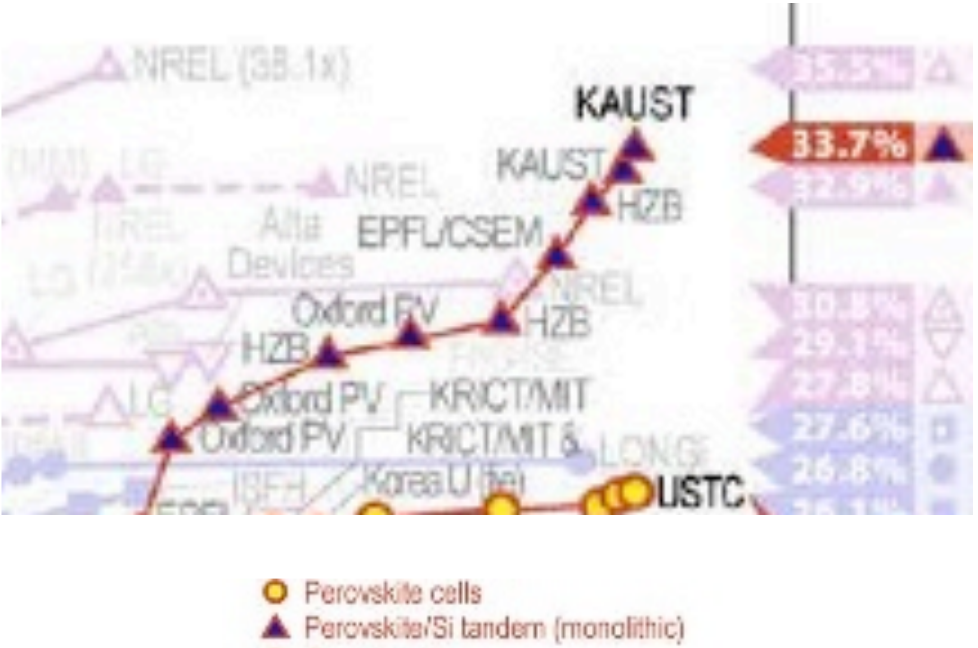
▪ Jun-Ho YUM, junho.yum@epfl.ch

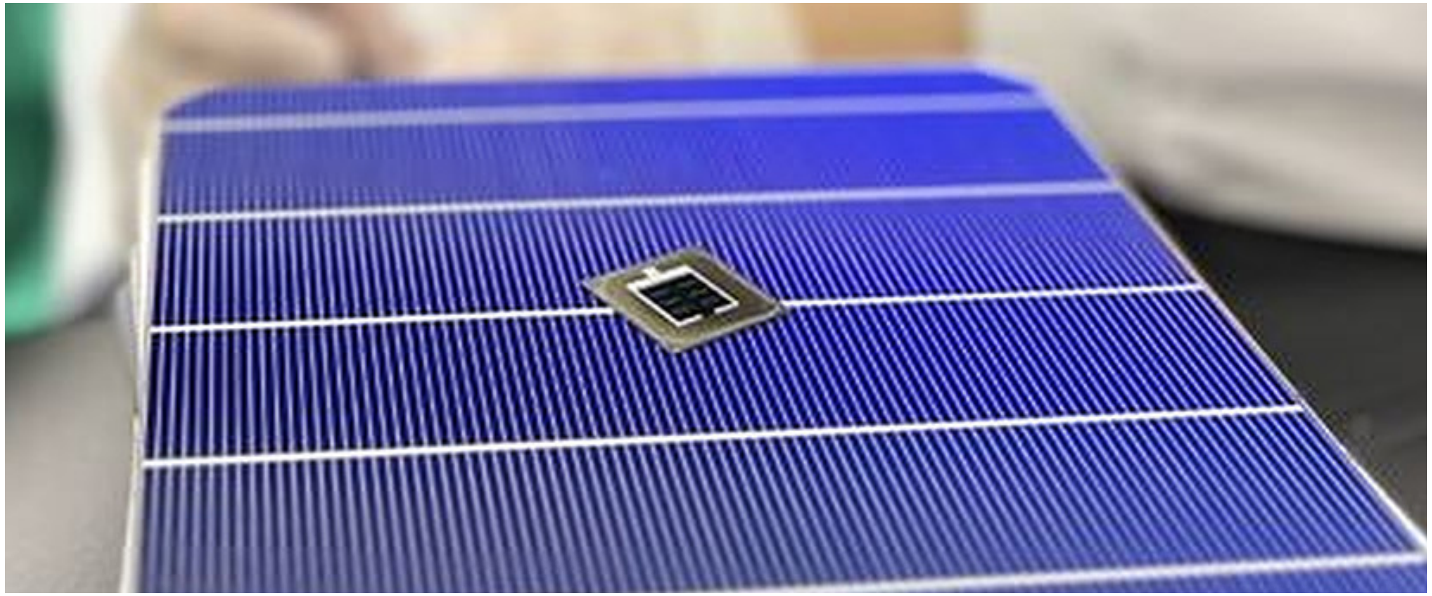
Perovskite/Si Tandem Solar Cell

Tandem cells at 33.7%

KAUST have set a new world efficiency record for its perovskite/silicon tandem solar cells.

https://www.pv-magazine.com/2023/05/30/kaust-claims-33-7-efficiency-for-perovskite-silicon-tandem-solar-cell/



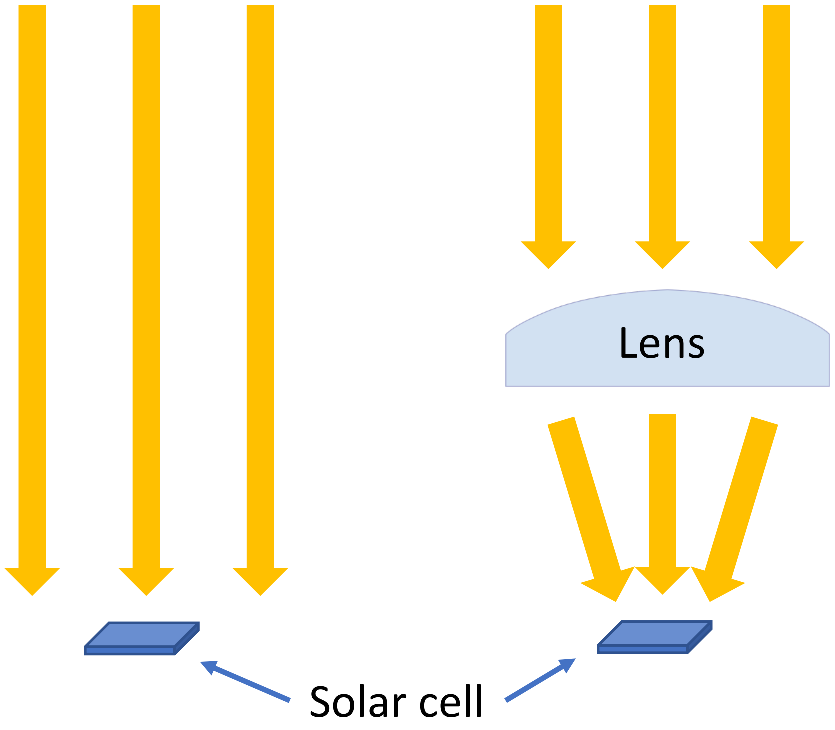


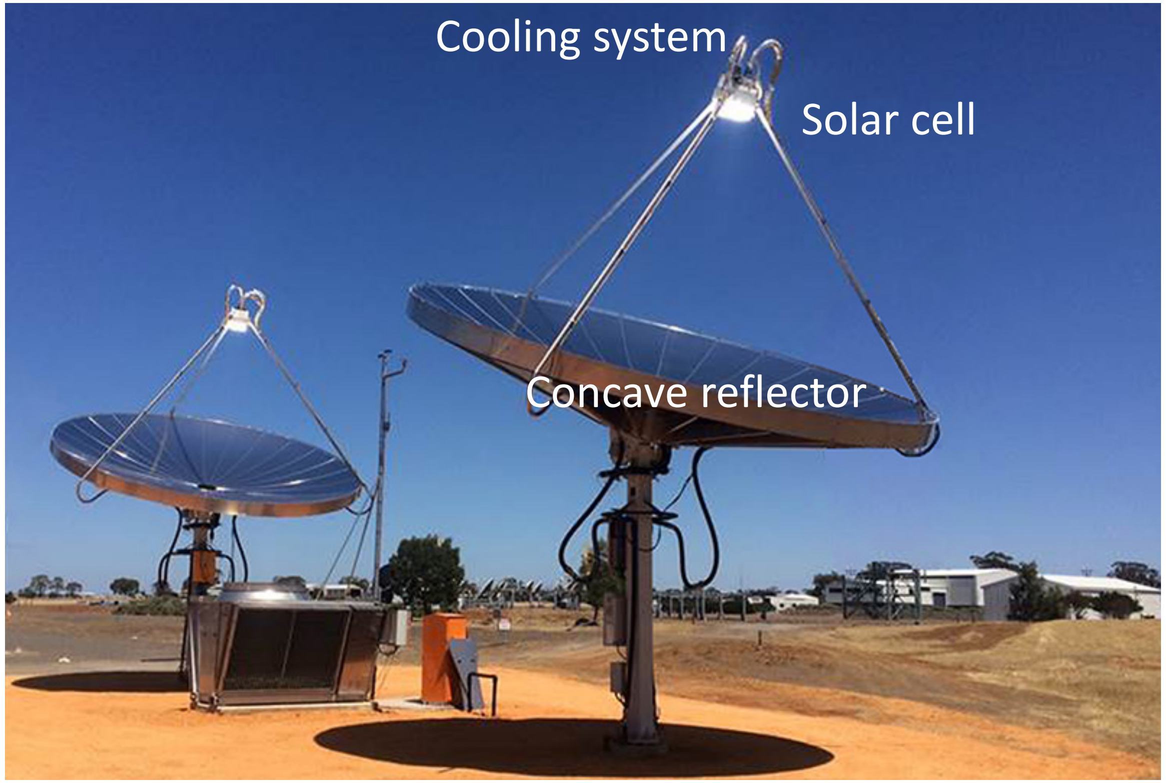
A PCE of 35% is anticipated by increasing the band gap of PSC to 1.7 eV.

Concentrated Solar Cells

Without concentration of sunlight

With concentration of sunlight





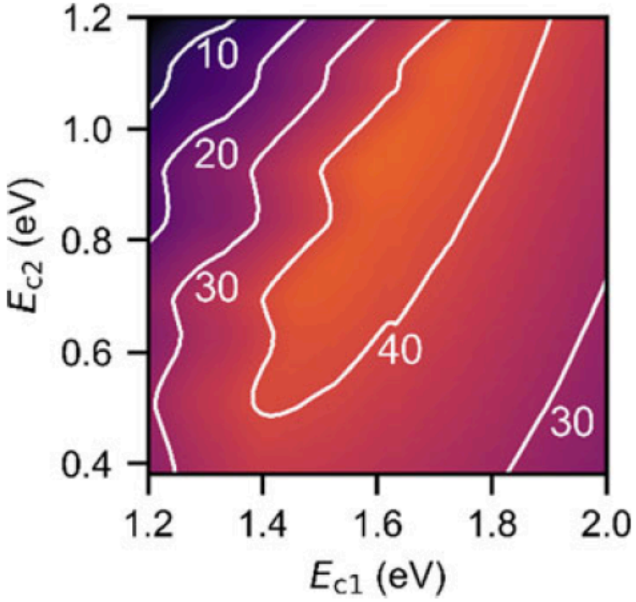
Concentrated Solar Cells

J_{SC} is proportional to incident optical power density

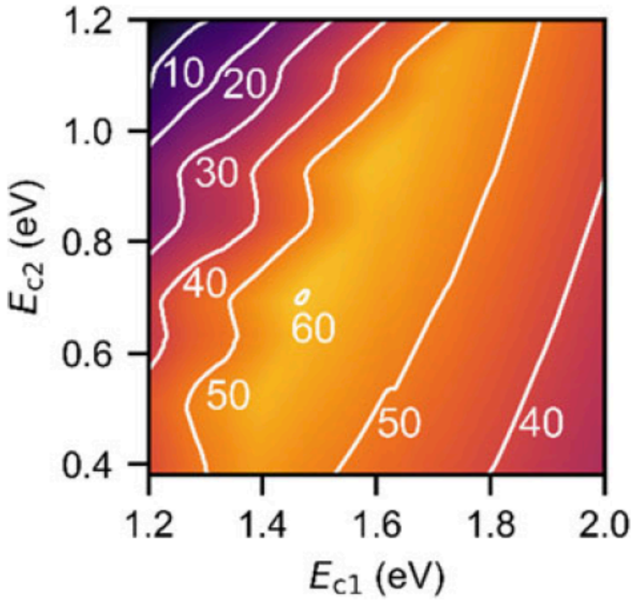
V_{OC} increases logarithmically with J_{SC}.

$$V_{OC}(C \times J_{SC}) = \frac{k_B T}{q} \times \ln\left(C \times \frac{J_{SC}}{J_0}\right) = V_{OC}(J_{SC}) + 0.26 \times \ln(C)$$

$C = concentration\ factor$

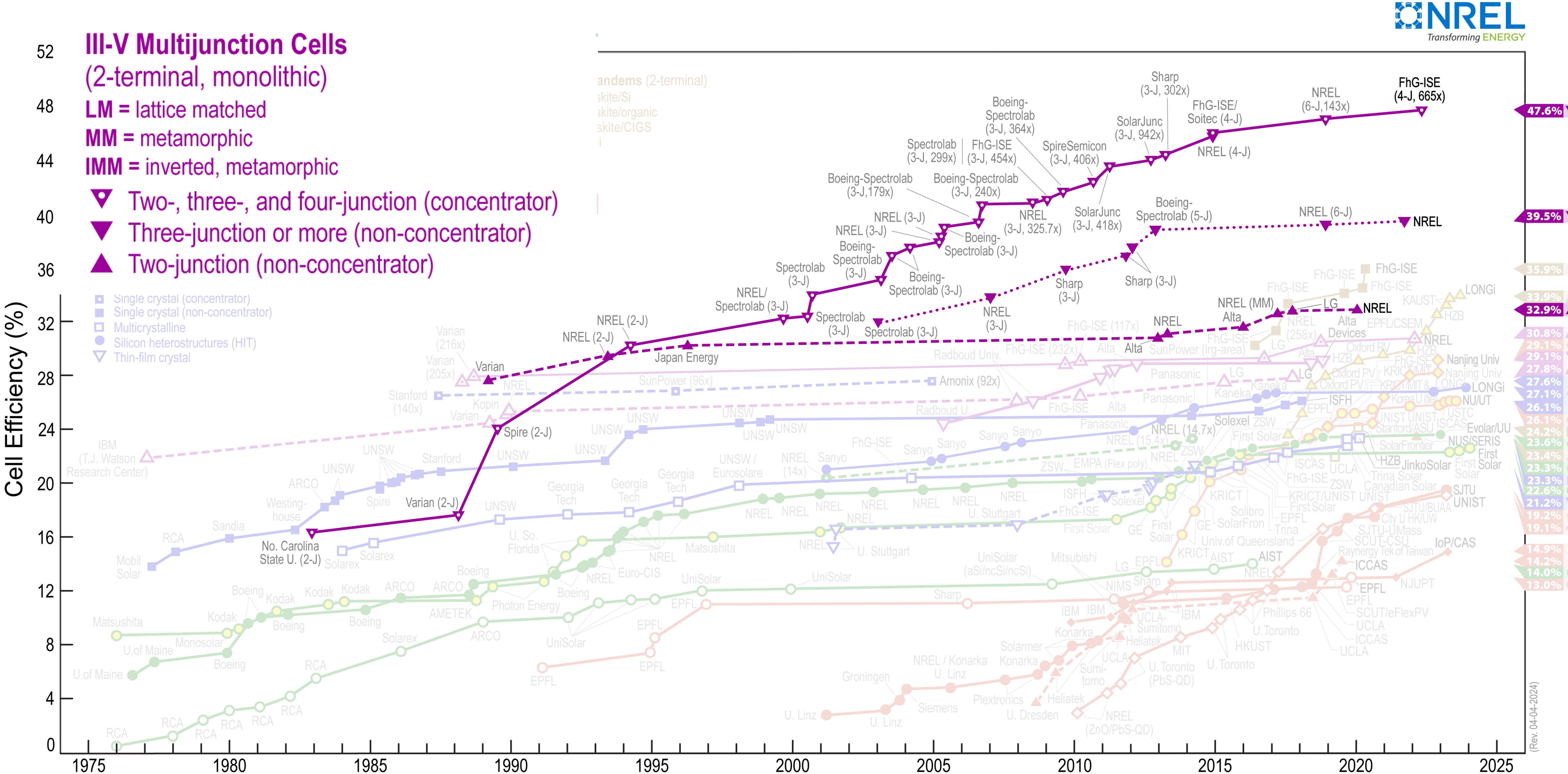


The conversion efficiency of the dual-junction solar cell under **unconcentrated light (45.4%)**.

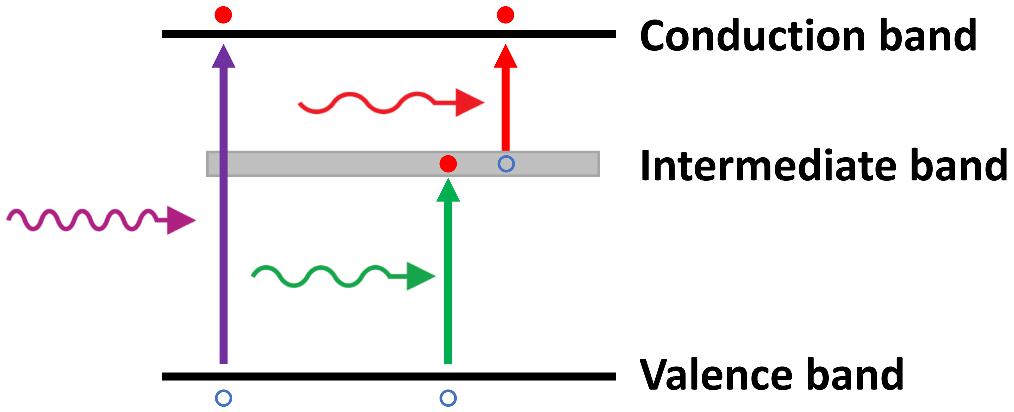


The conversion efficiency of the dual-junction solar cell under **concentrated light (C = 1000)** and it reaches the maximum of **60%** at E_{c1} = 1.44 eV and E_{c2} = 0.70 eV.

III-V Semiconductors: Multijunction Solar Cells

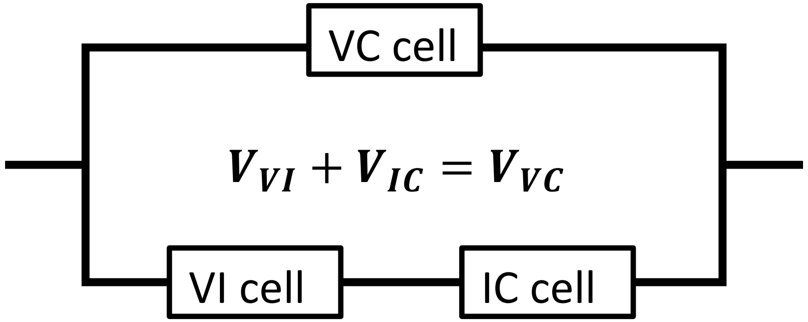


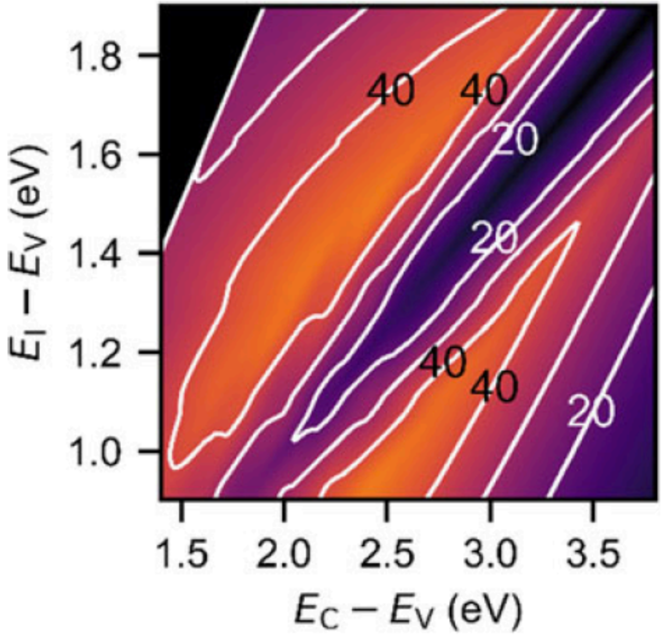
Intermediate-band Solar Cells



Less sensitive to illumination condition due to the direct absorption via inter-band transition and a stepwise absorption via the intermediate band.

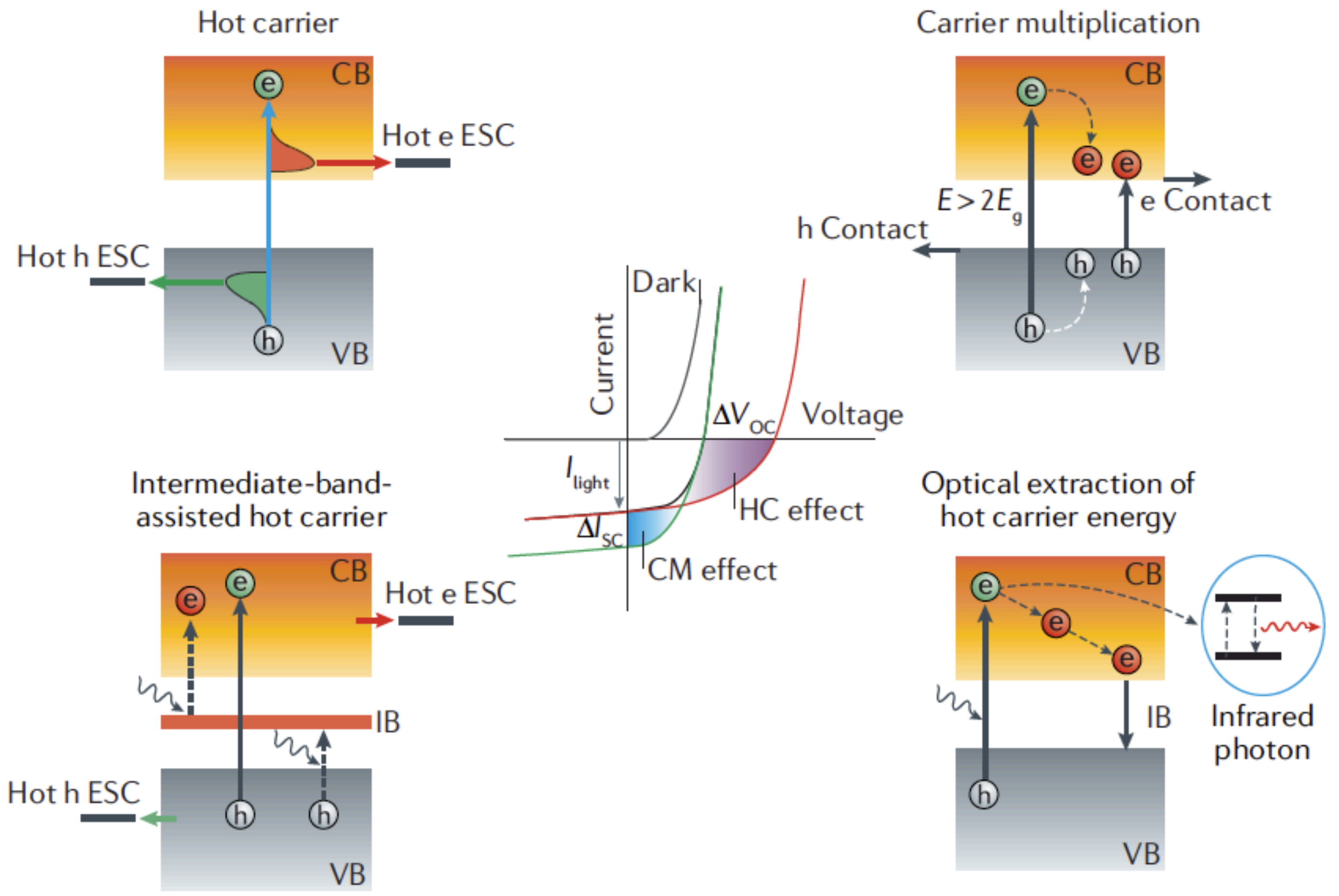
$$I_{total} = I_{VC} + I_{IC}$$

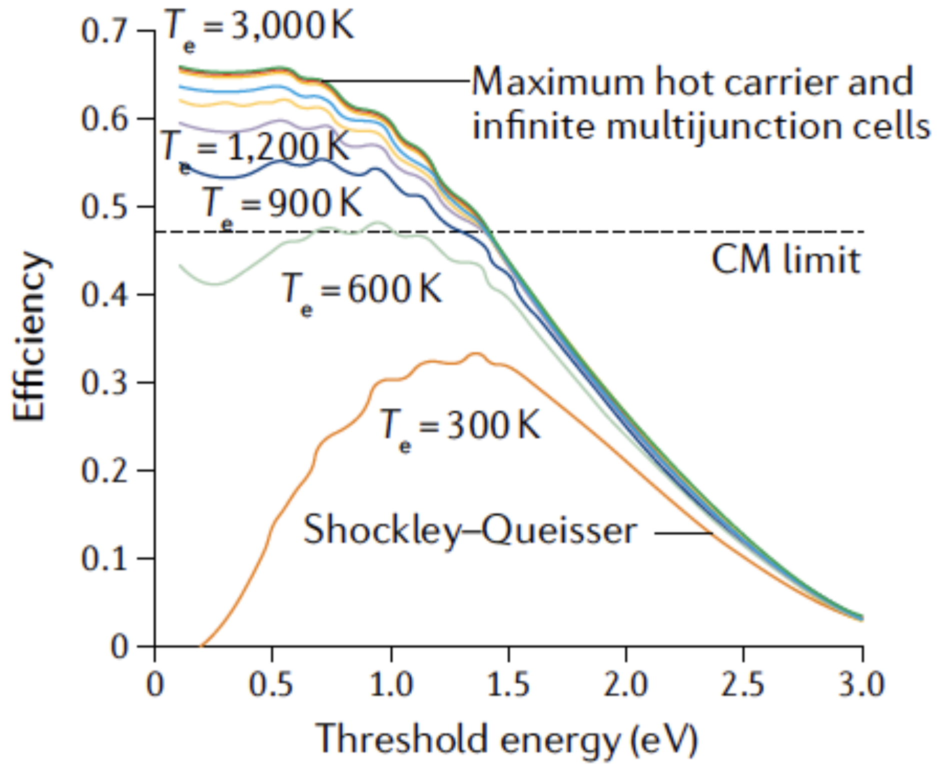




A maximum conversion efficiency of **49.4%** is reached for a band-gap energy of 2.43 eV between the CB and the VB, and an energy gap of 1.49 eV between the valence band maximum (VBM) and the intermediate-band quasi-Fermi level.

Hot Carrier Generation and Carrier Multiplication





ESC: energy- selective contacts

Images taken from K. K. Paul et al., *Nature Reviews Physics*, **3**, 178 (2021)