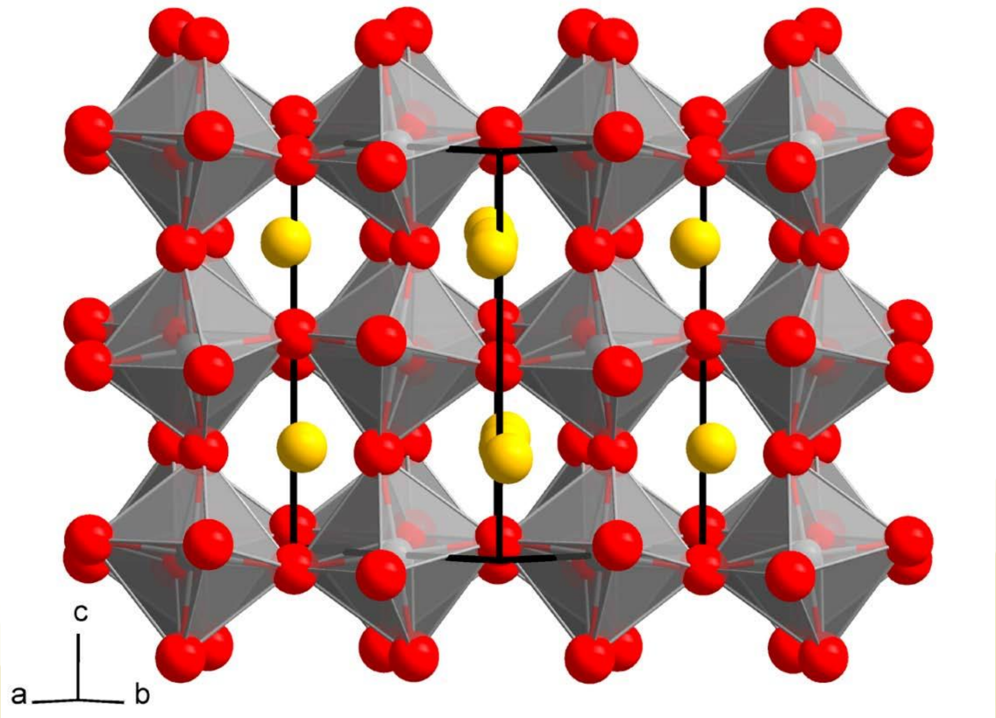
Perovskites: crystal structure, important compounds and properties

Origin And History of Perovskite compounds

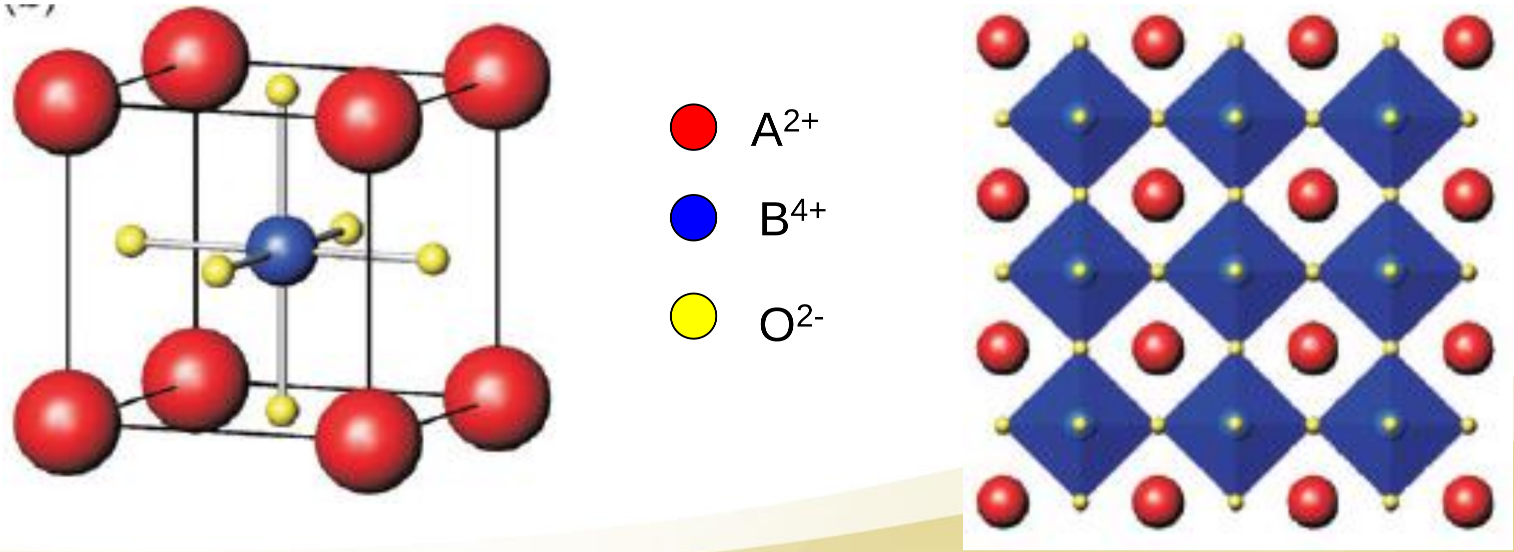
Perovskite is **calcium titanium oxide or calcium titanate,** with the chemical formula **$CaTiO_3$**. The mineral was discovered by Gustav Rose in 1839 and is named after Russian mineralogist **Count Lev Alekseevich Perovski** (1792–1856)."



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

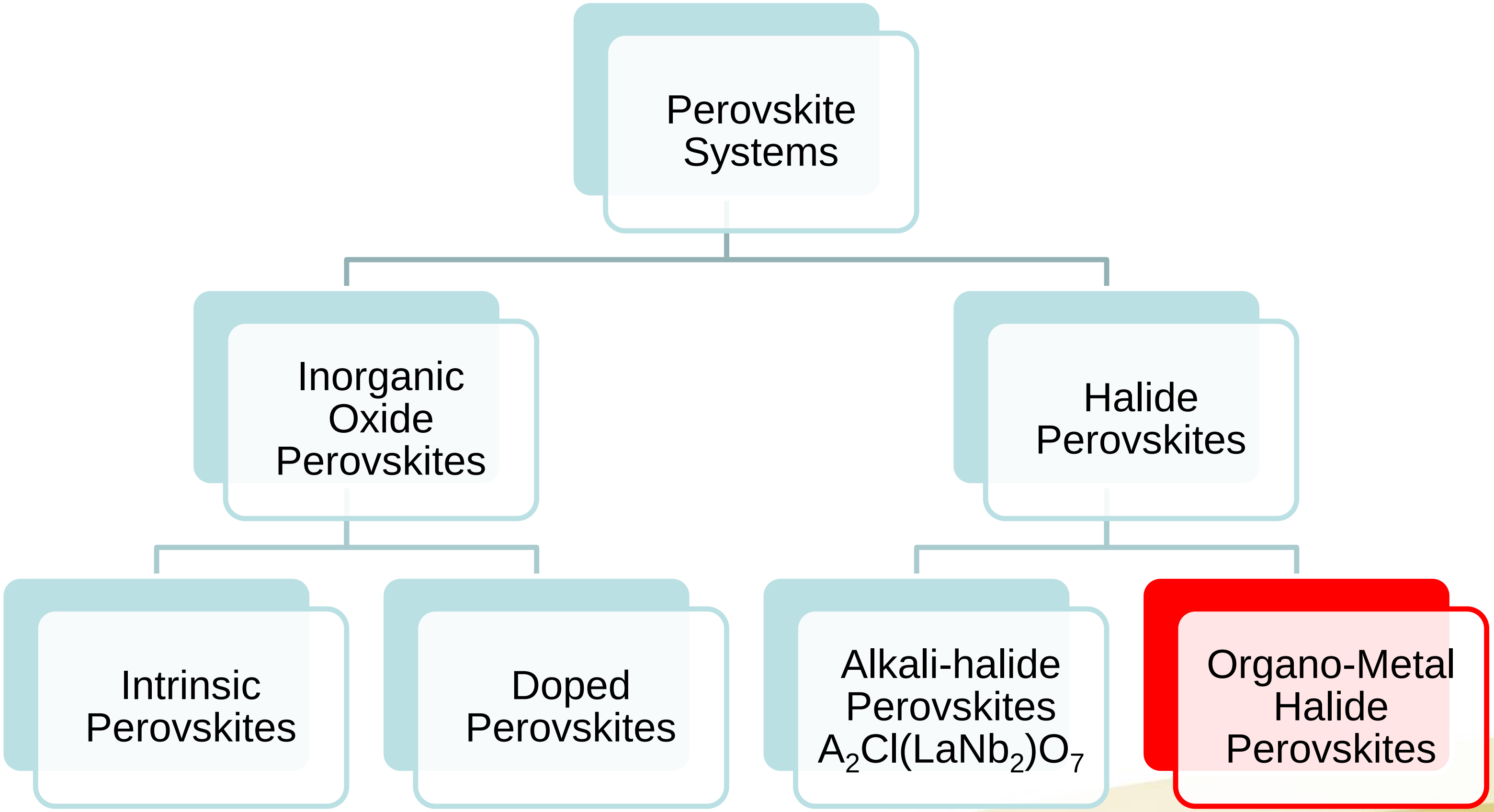
Origin And History of Perovskite compounds

- Very stable structure, large number of compounds, variety of properties, many practical applications.
- Key role of the BO_6 octahedra in ferromagnetism and ferroelectricity.
- Extensive formation of solid solutions → material optimization by composition control and phase transition engineering.



Ideal cubic perovskite structure (ABO_3)

Classification of Perovskite System



Useful salts with perovskite structure

Reference compound	Properties	Existing and potential applications	Notes
$BaTiO_3$	Ferroelectricity, piezoelectricity, high dielectric constant	Multilayer ceramic capacitors (MLCCs), PTCR resistors, embedded capacitance	Most widely used dielectric ceramic T_C = 125° C
$(Ba,Sr)TiO_3$	Non-linear dielectric properties	Tunable microwave devices	Used in the paraelectric state
$Pb(Zr,Ti)O_3$	Ferroelectricity, piezoelectricity	Piezoelectric transducers and actuators, ferroelectric memories (FERAMs)	PZT: most successful piezoelectric material
$Bi_4Ti_3O_{12}$	Ferroelectric with high Curie temperature	High-temperature actuators, FeRAMs	Aurivillius compound T_C = 675° C
$(K_{0.5}Na_{0.5})NbO_3$, $Na_{0.5}Bi_{0.5}TiO_3$	Ferroelectricity, piezoelectricity	Lead-free piezoceramics	Performances not yet comparable to PZT but rapid progress
$(Pb,La)(Ti,Zr)O_3$	Transparent ferroelectric	Optoelectronic devices	First transparent ferroelectric ceramic
$BiFeO_3$	Magnetoelectric coupling, high Curie temperature	Magnetic field detectors, memories	Most investigated multiferroic compound. T_C = 850° C
$PbMg_{1/3}Nb_{2/3}O_3$	Relaxor ferroelectric	Capacitors, actuators	High permittivity, large electrostrictive coefficients, frequency-dependent properties
$SrRuO_3$	Ferromagnetism	Electrode material for epitaxial ferroelectric thin films	
$(La, A)MnO_3$ A = Ca, Sr, Ba	Ferromagnetism, giant magnetoresistance, spin-polarized electrons	Magnetic field sensors, spin electronic devices	
$SrTiO_3$	Incipient ferroelectricity, thermoelectric power, metallic electronic conduction when n-doped, mixed conduction when p-doped, photocatalyst	Alternative gate dielectric material, barrier layer capacitors, substrate for epitaxial growth, photoassisted water splitting	Multifunctional material
$LaGaO_3$ $BaIn_2O_5$	Oxyde-ion conduction	Electrolyte in solid oxide fuel cells (SOFCs)	$BaIn_2O_5$ is an oxygen deficient perovskite with brownmillerite structure.
$BaCeO_3$, $BaZrO_3$	Proton conduction	Electrolyte in protonic solid oxide fuel cells (P-SOFCs)	High protonic conduction at 500-700° C
$(La,Sr)BO_3$ (B = Mn, Fe, Co)	Mixed conduction, catalyst	Cathode material in SOFCs, oxygen separation membranes, membrane reactors, controlled oxidation of hydrocarbons,	Used for SOFC cathodes
$LaAlO_3$ $YAlO_3$	Host materials for rare-earth luminescent ions,	Lasers Substrates for epitaxial film deposition	

1st Solar Cell Reports

214th ECS Meeting, Abstract #27, © The Electrochemical Society

Novel Photoelectrochemical Cell with Mesoscopic Electrodes Sensitized by Lead-halide Compounds (2)

Akihiro Kojima[a]*, Kenjiro Teshima[c], Tsutomu Miyasaka[b,c], and Yasuo Shirai[a]

Lead-halide perovskite compounds ($CH_3NH_3PbBr_3$) are known to construct self-organized semiconductor crystal structure (Fig.1). The perovskite compounds are expected to be constructed in nano-porous structures of TiO_2 electrode. In this study, we attempted to form the self-organized perovskite type crystal structure in the TiO_2 nano-porous structure and discussed about possibility to apply for visible-light sensitized photo electrochemical cells.

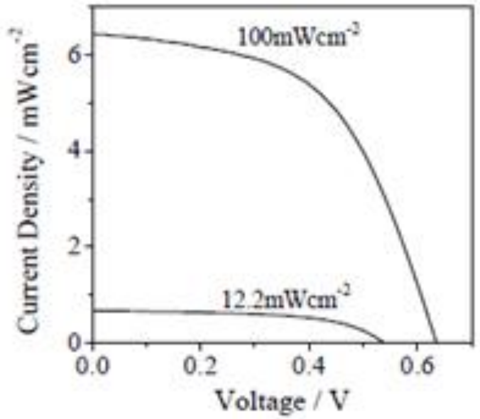


Fig.3 I-V curves of the cell sensitized by lead-halide perovskite compound

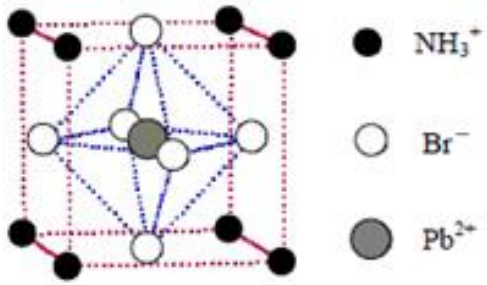


Fig.1 $CH_3NH_3PbBr_3$ perovskite structure

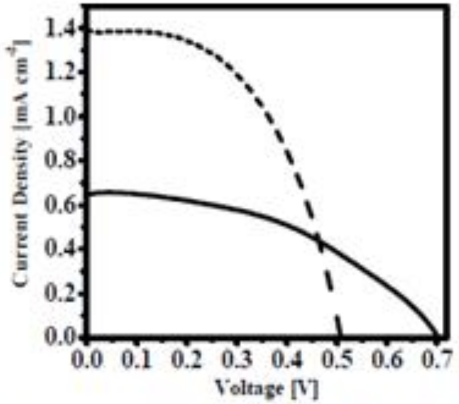


Fig.1 Current-voltage characteristics of polypyrrole based solid-state photocells using $CH_3NH_3PbBr_3$ (line) and $CH_3NH_3PbI_3$ (dot-line) as sensitizer for TiO_2 electrode.

Table.1 Photovoltaic performance of the cell sensitized by lead-halide perovskite compound

Intensity mWcm-2	Jsc mAcm-2	Voc V	FF	Eff. %
100	6.44	0.64	0.53	2.19
12.2	0.68	0.54	0.58	1.73

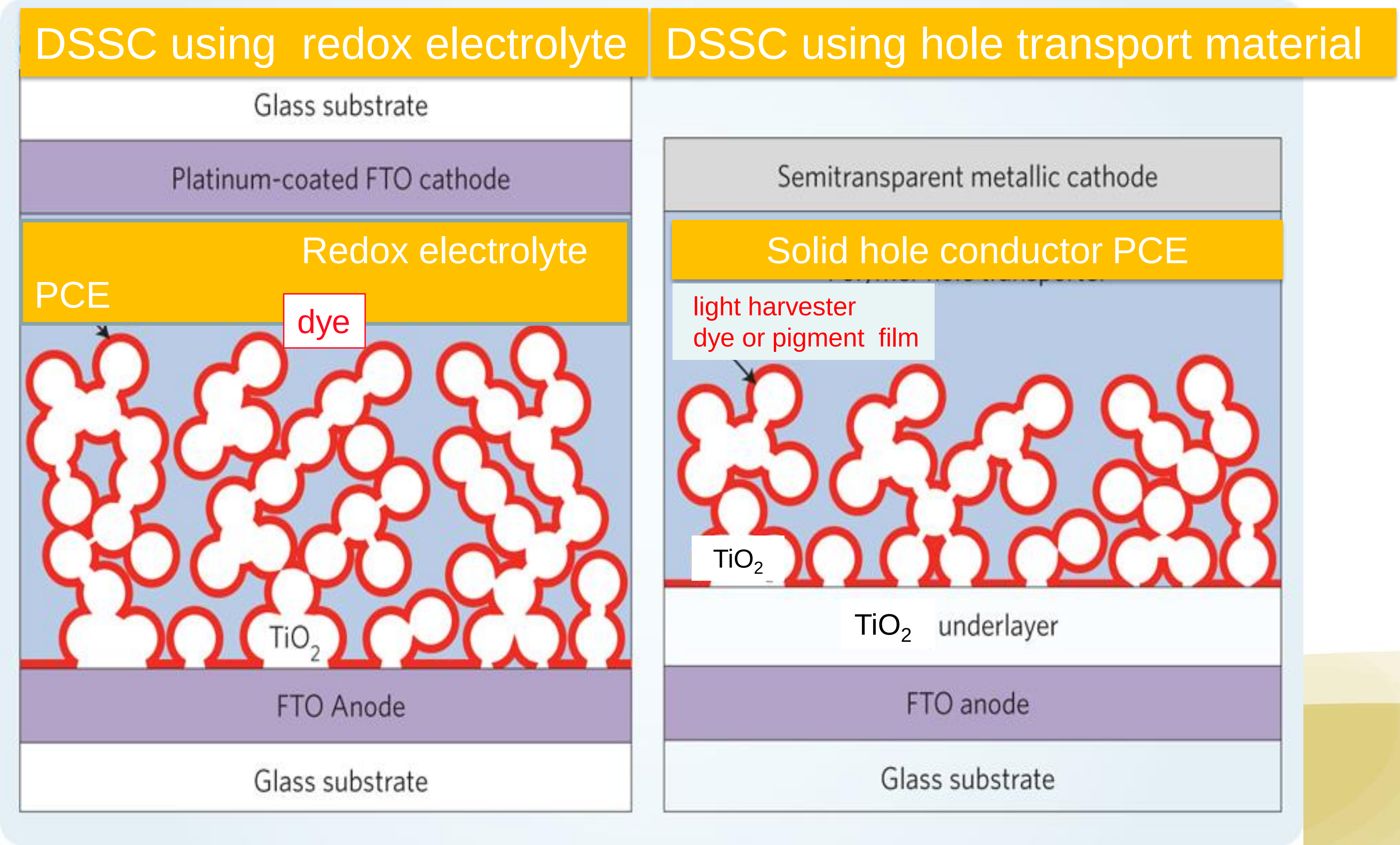
← Electrolyte (2006)

Solid-State (2008) →

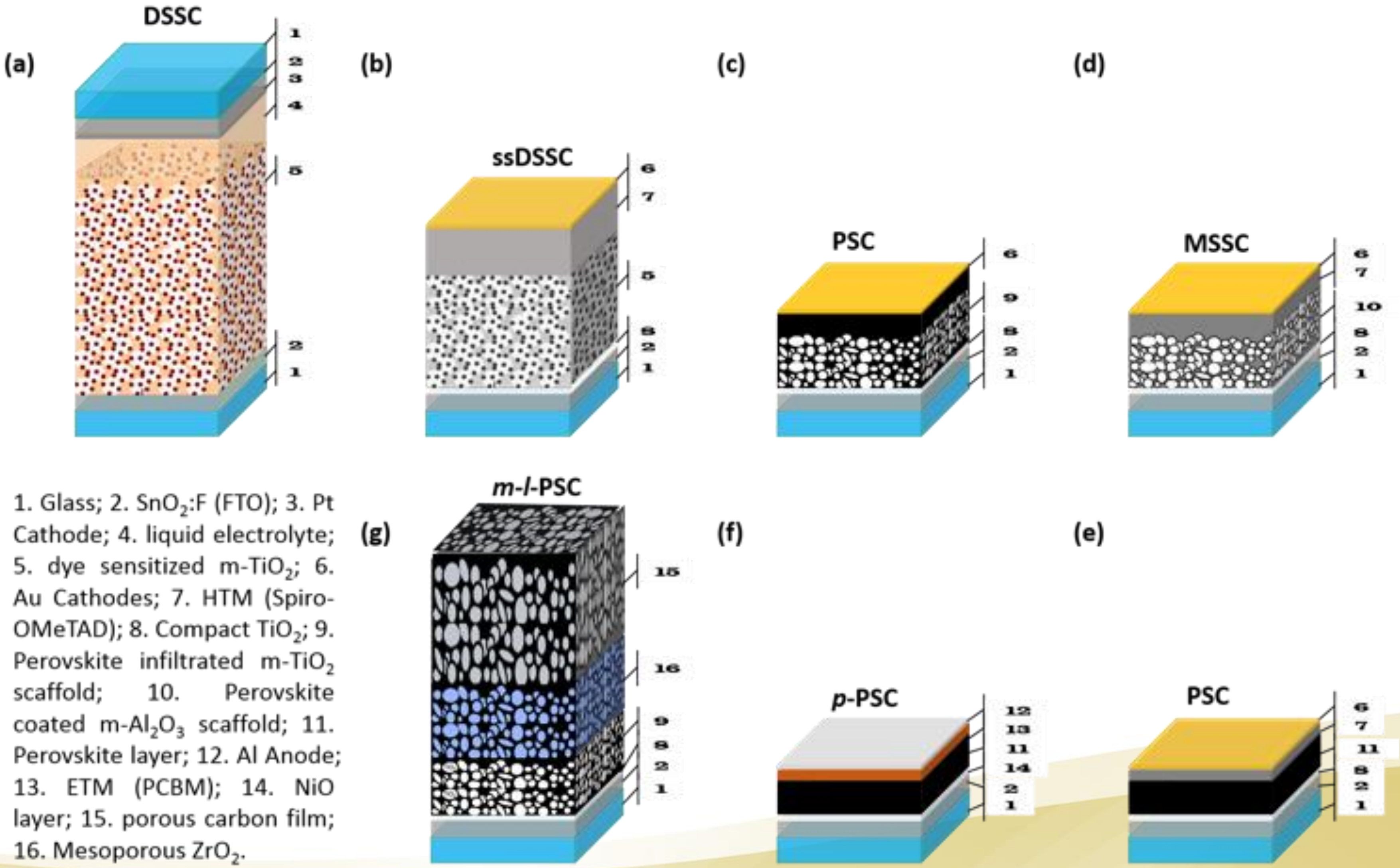
Table.1 Photovoltaic performance of $CH_3NH_3PbX_3$ sensitized solid-state photocell with polypyrrole based conductive polymer as charge transport layer

sensitizer	J_{sc} (mA/cm²)	V_{oc} (V)	FF	Eff. (%)
$CH_3NH_3PbBr_3$	0.65	0.70	0.45	0.21
$CH_3NH_3PbI_3$	1.39	0.51	0.52	0.37

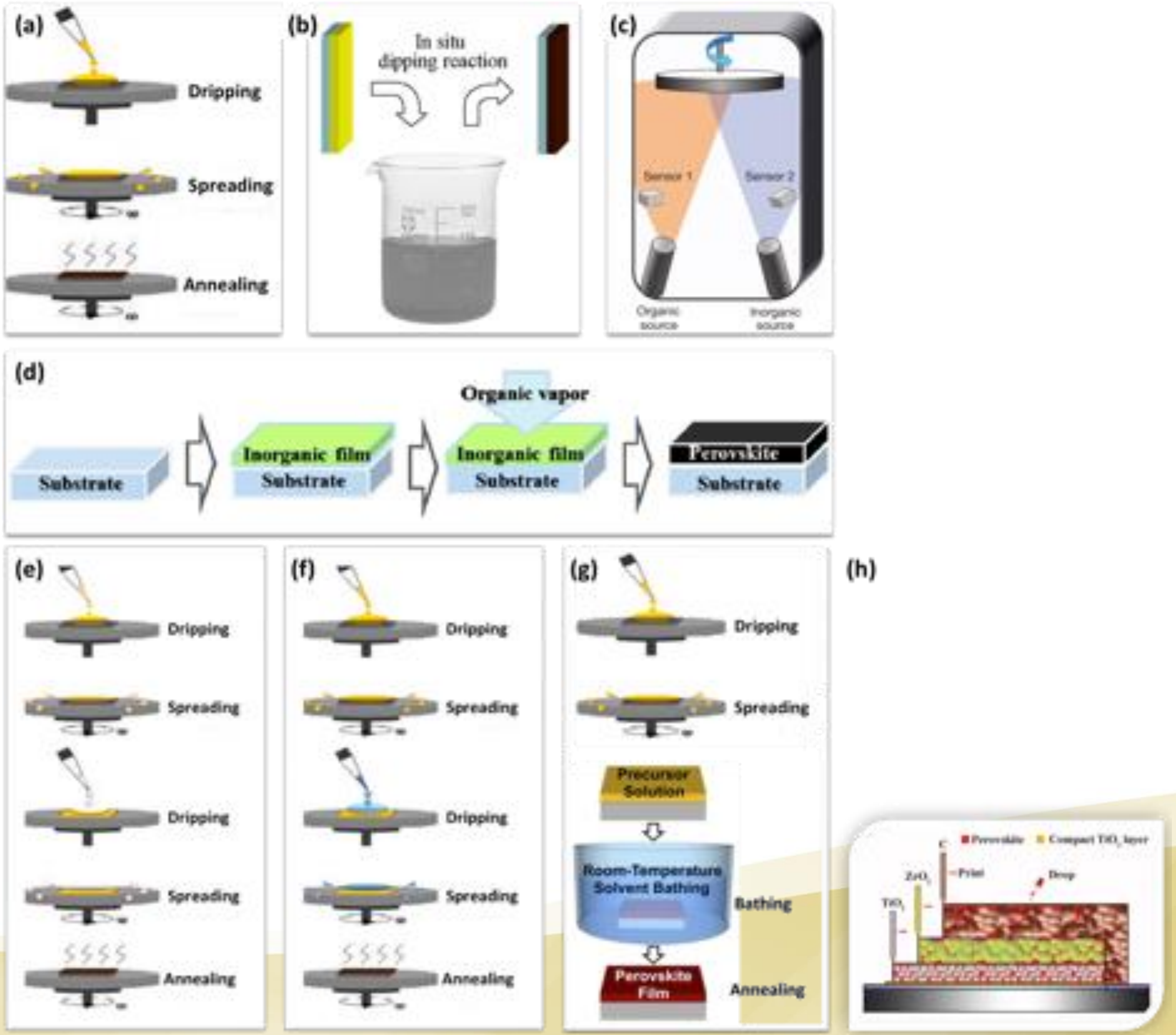
Solid-State DSC



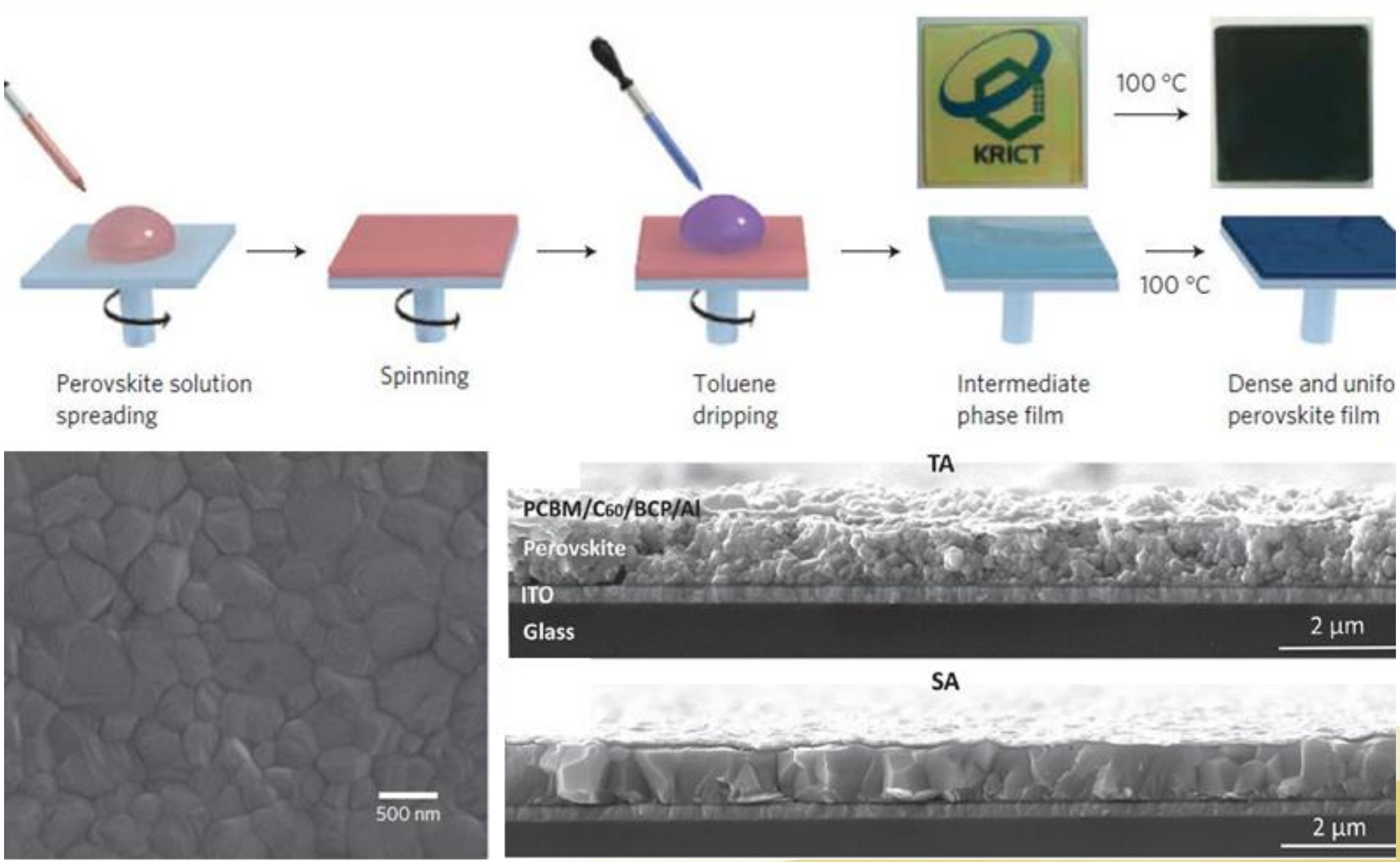
Evolution of device structures



Various device fabrication methods



‘Anti-solvent’ the key to optimum morphology



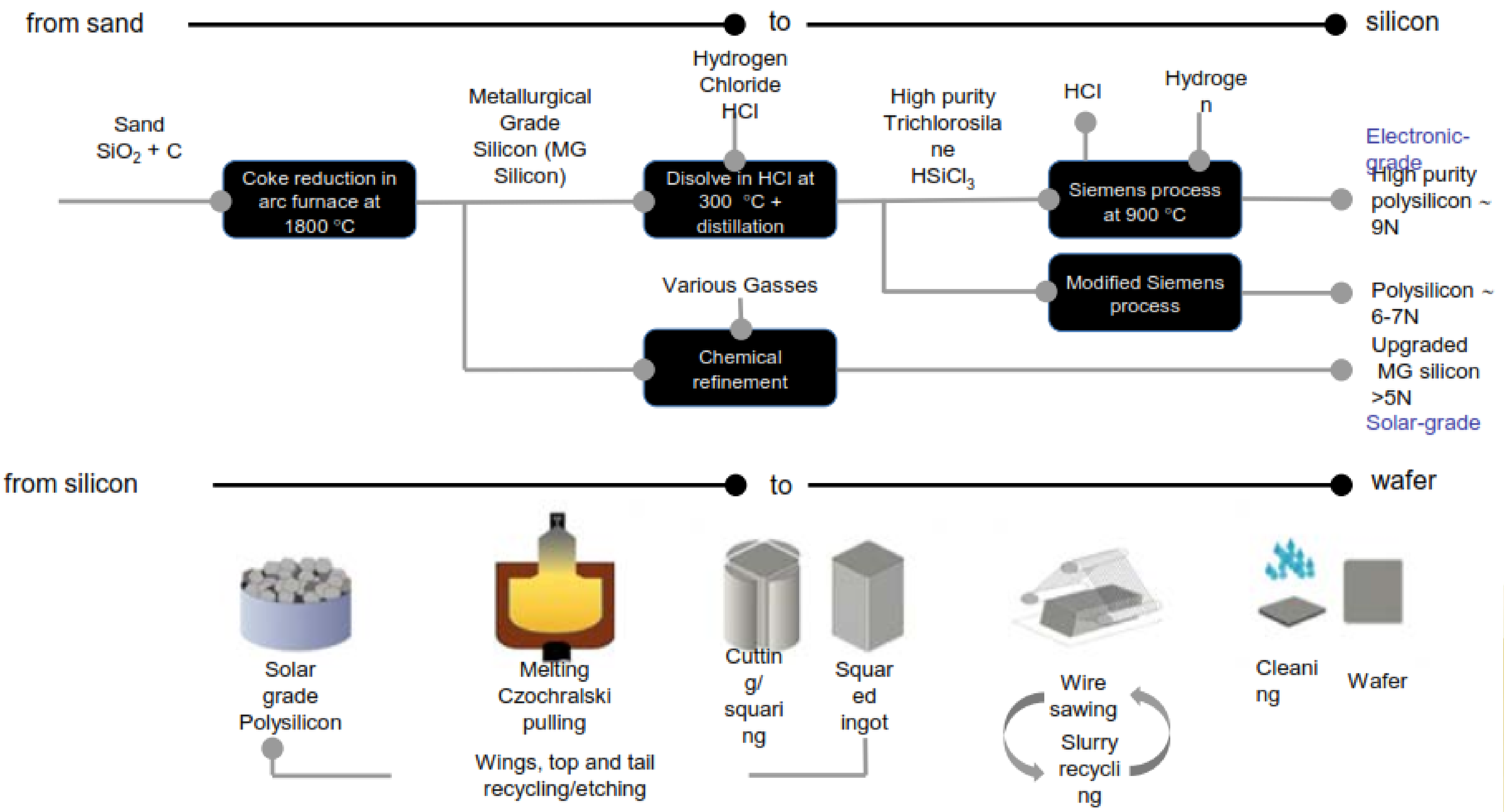
a) N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, S. I. Seok, Nat Mater 2014, 13, 897-903.

b) M. Xiao, F. Huang, W. Huang, Y. Dkhissi, Y. Zhu, J. Etheridge, A. Gray-Weale, U. Bach, Y.-B. Cheng, L. Spiccia, Angew. Chemie Int. Ed. 2014, 53, 9898–9903.

Perovskite vs silicon technology

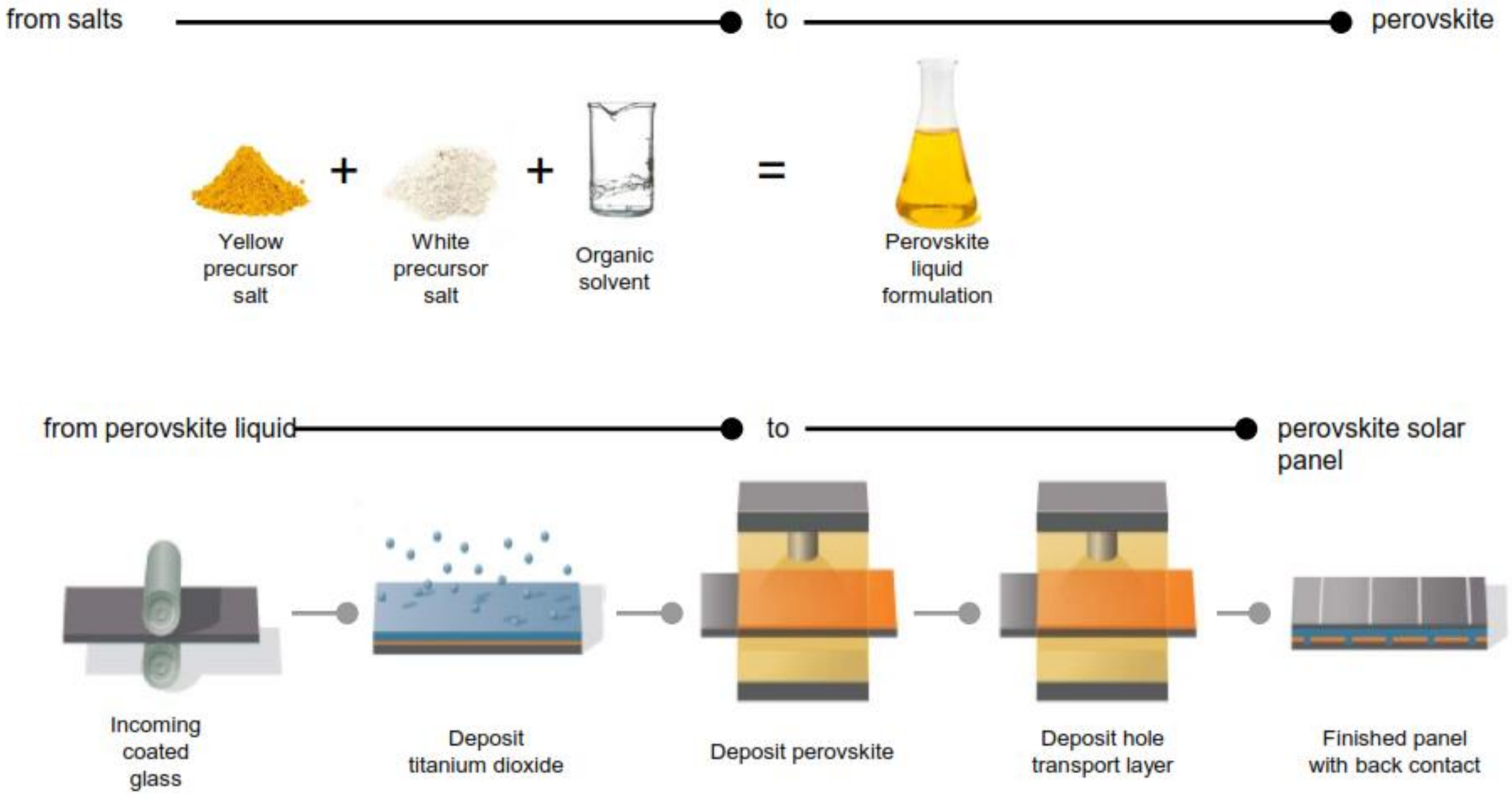
Production of silicon and silicon wafers

Expensive, high-energy process, generating high levels of waste material

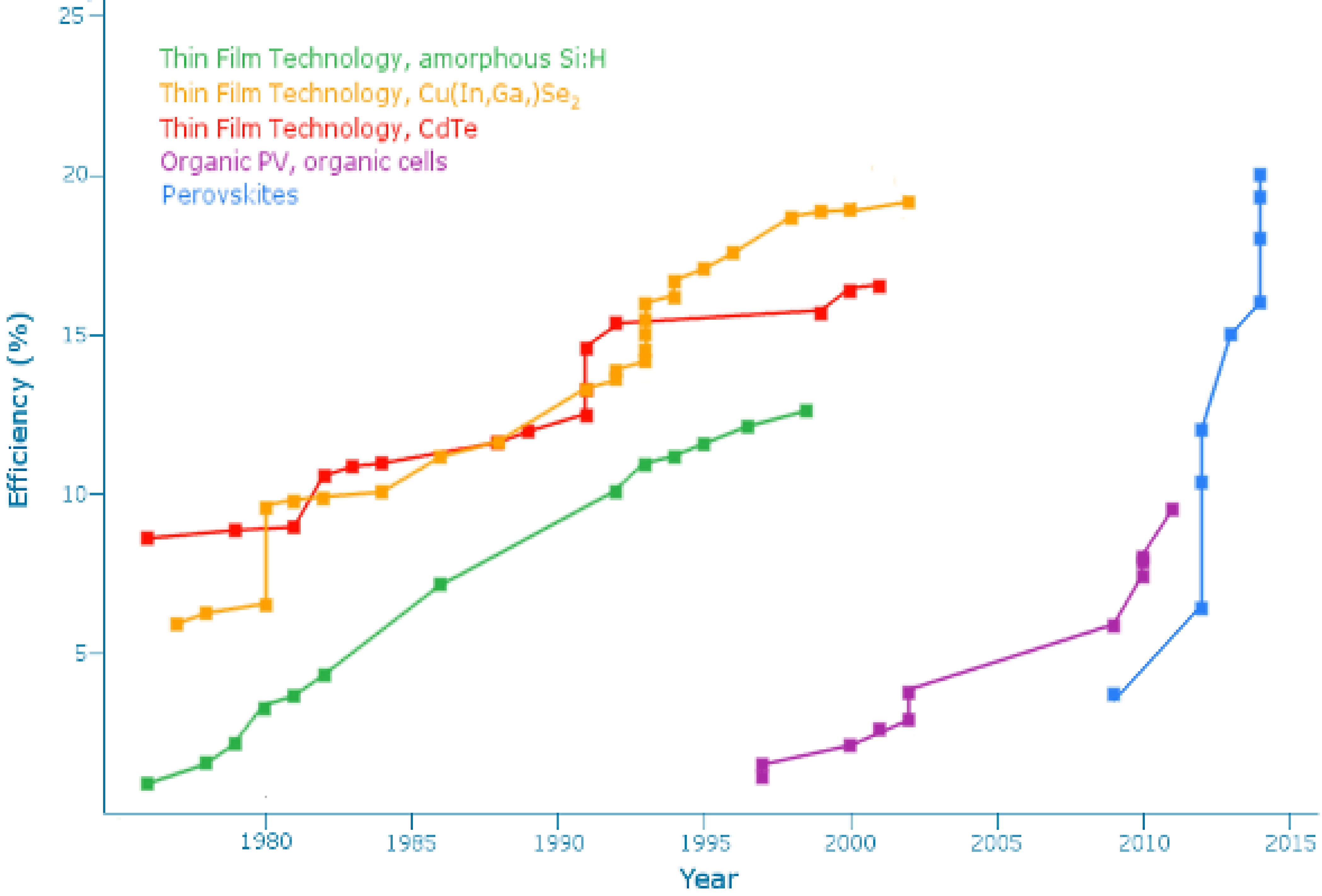


Production of perovskite cell

Simpler, lower cost, lower embodied energy, massively reduced environmental impact

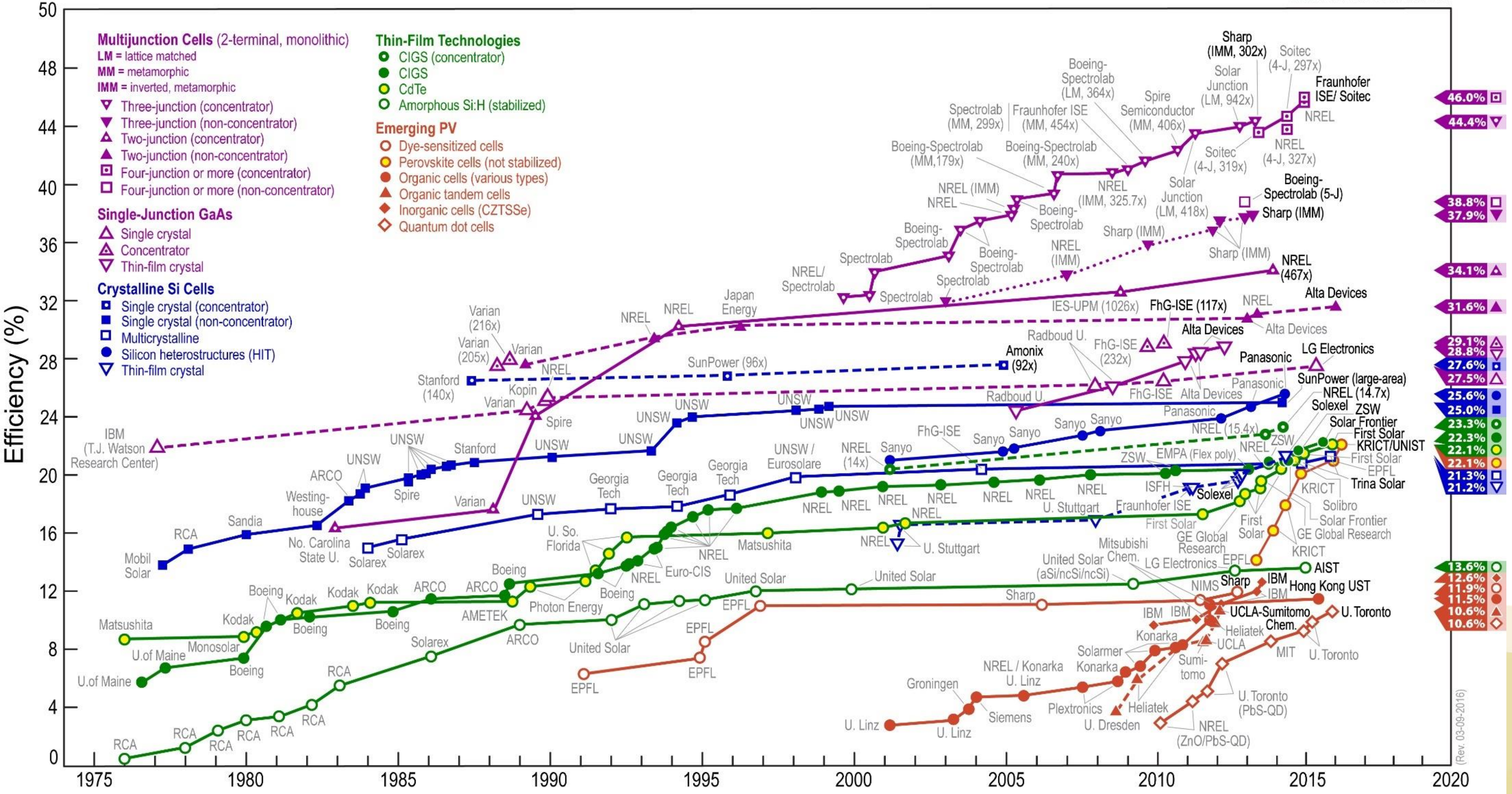


Characteristics	CdTe	CIGS	c-Si	Perovskite
Raw materials cost	Low	Medium	Low	Low
Finished material cost	Low	High	High	Low
Fabrication cost	Medium	Medium	High	Low
Energy payback period	Medium	High	High	Low
LCOE	Medium	High	High	Low
Efficiency	Medium	Medium	High	High
Toxicity	Medium	Medium	Low	High
Abundance	Low	Low	High	High

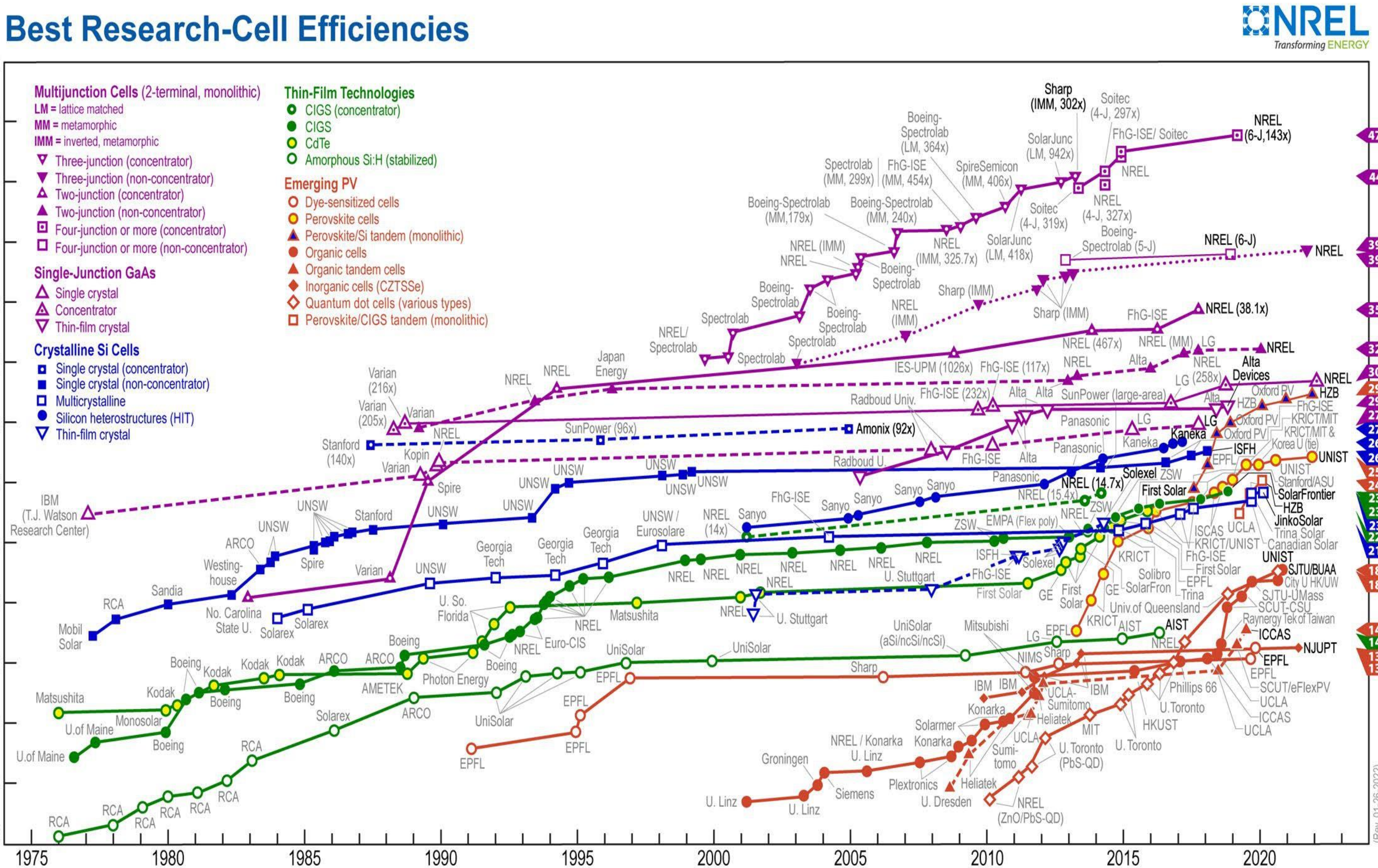


Thin Film Technology, amorphous Si:H
Thin Film Technology, Cu(In,Ga,)Se2
Thin Film Technology, CdTe
Organic PV, organic cells
Perovskites
Efficiency (%)
25
20
15
10
5
1980
1985
1990
1995
2000
2005
2010
2015
Year

Best Research-Cell Efficiencies



Рекорды КПД фотоэлементов.

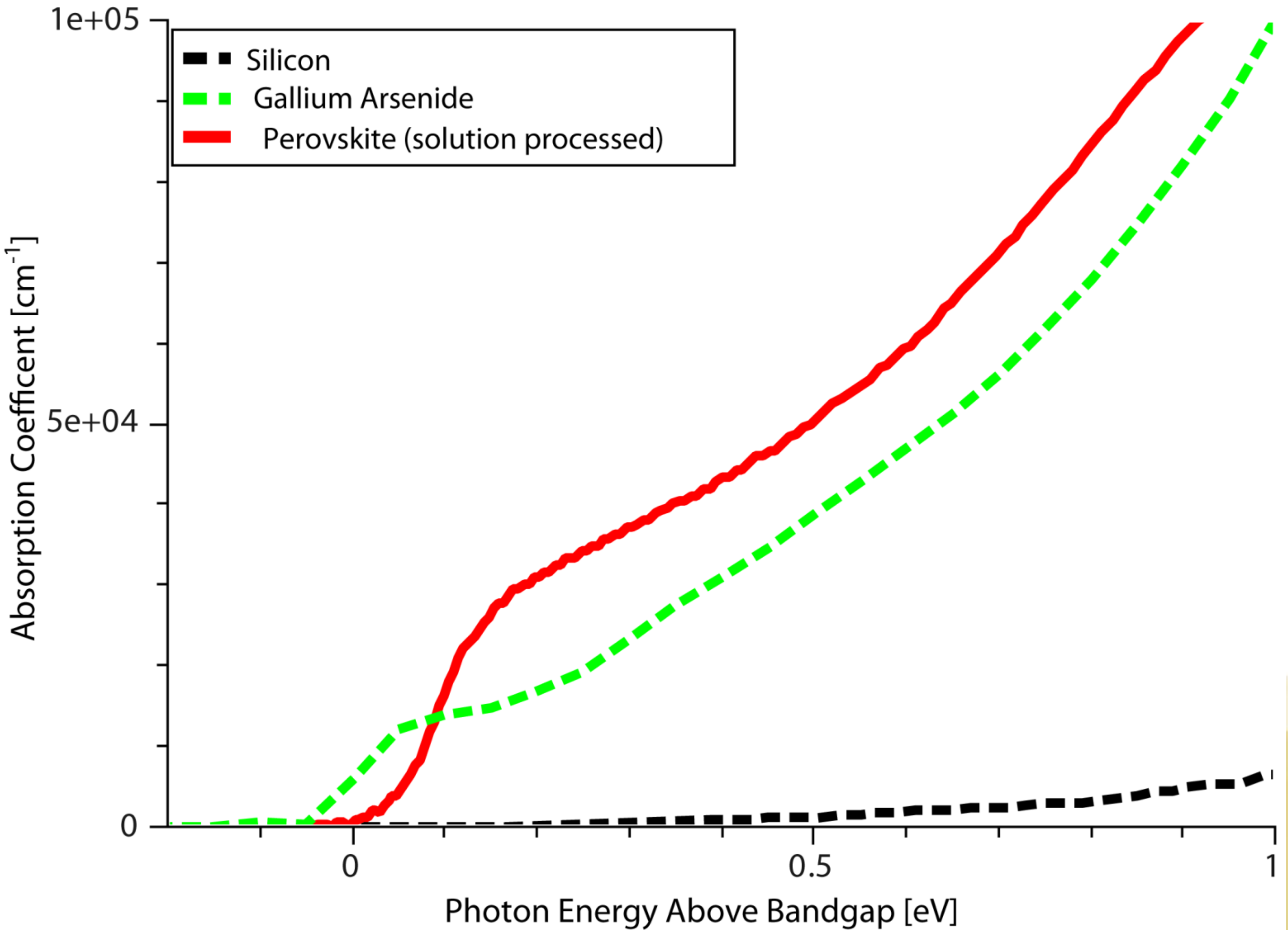


Low Bandgap – $q \cdot V_{oc}$ Loss in Perovskite Solar Cells

Material	Bandgap (eV)	q·Voc (eV)	Energy loss (eV)
GaAs	1.43	1.12	0.31
Silicon	1.12	0.75	0.37
CIGS	~1.15	0.74	0.41
Perovskite ($CH_3NH_3PbI_3$)	**1.55**	**1.07**	**0.48**
CdTe	1.49	0.90	0.59
a-Silicon	1.55	0.89	0.66

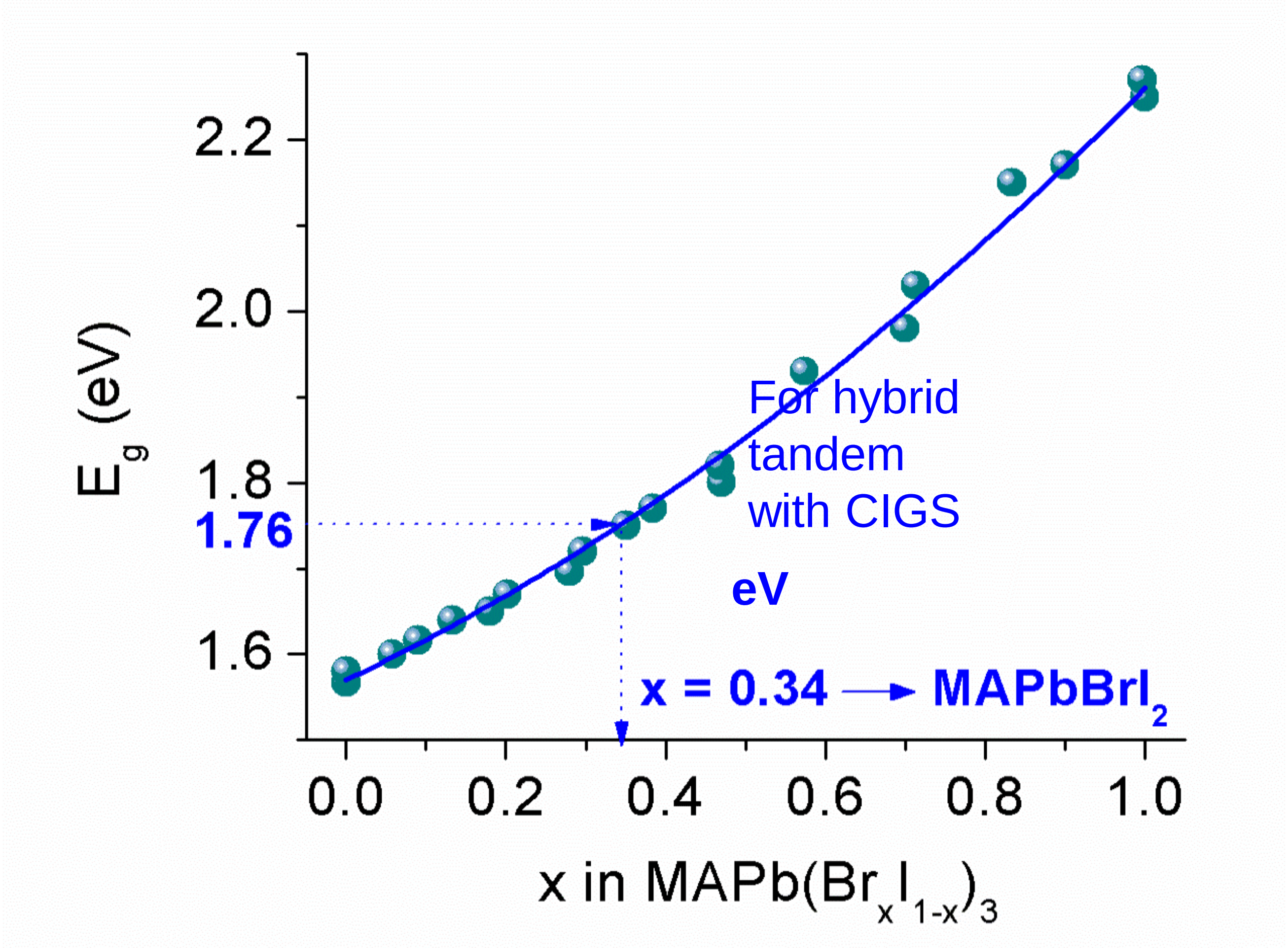
M. Green et al. Solar cell efficiency tables (version 42) July 2013

The hybride Perovskite is a Strongly-Absorbing Direct Band Gap Semiconductor



The Perovskite Bandgap can be tuned by Chemical Substitution

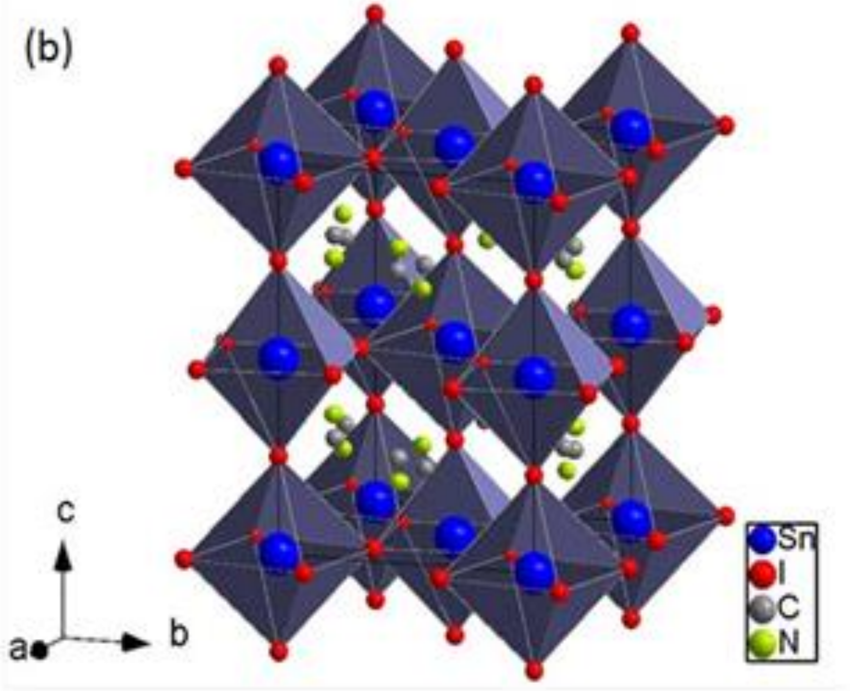
The band gap can be tuned from 1.57 eV to 2.23 eV by substituting bromine for iodine in $CH_3NH_3Pb(Br_xI_{1-x})_3$



But the morphology is not stable!

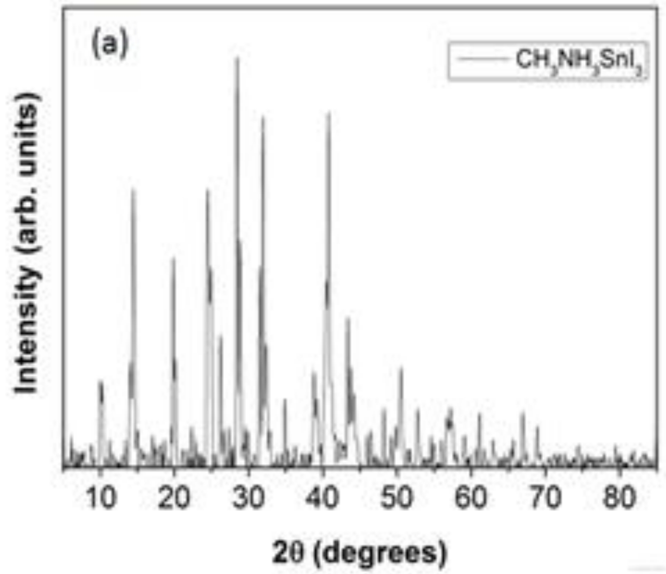
Noh et al., *Nano Lett.* 2013

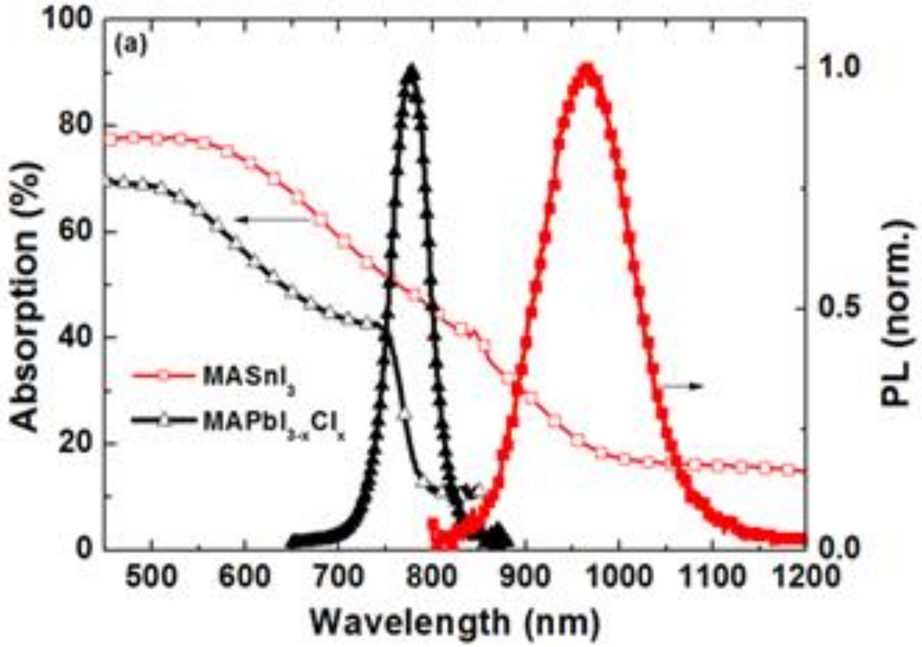
Lead-free: $CH_3NH_3SnI_3$ Perovskite



a=b= 8.7912 Å and c = 4.4770 Å

ee: Hayase and co workers 2014; Kanitzidis and co workers Nat Photo 2014, K-Y Jen and coworkers 2014



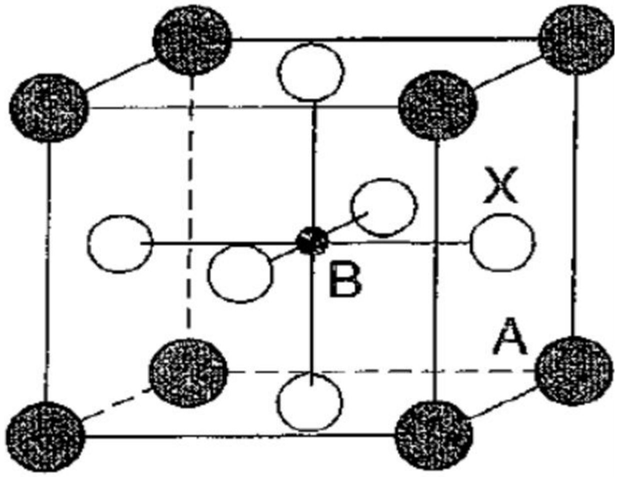


Tuning the structure of perovskites from 3D to 2D

- When will a 3D perovskite form?
- When the A, B and X components fit together neatly in the crystal lattice.
- Assuming ionic radii of R_A etc, For a close packed cubic perovskite the structure is possible, provided:

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

Where t is a non defined tolerance factor, typically $0.8 < t < 1$, which relates to how much strain the lattice can tolerate before it will no longer form.



ABX_3

Low dimensional perovskite with more possibilities

Conducting Layered Organic-inorganic Halides Containing <110>-Oriented Perovskite Sheets

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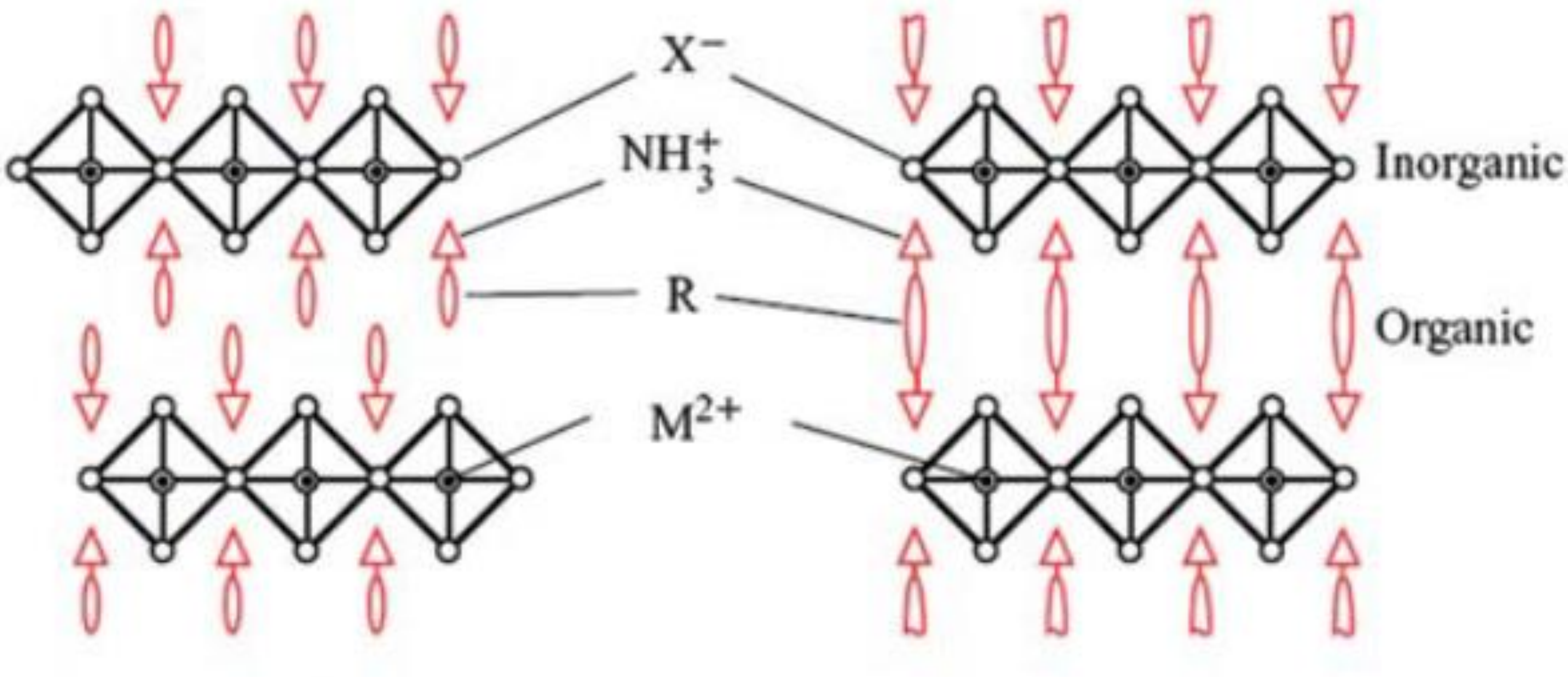
***Science* 10 March 1995**:
Vol. 267 no. 5203 pp. 1473-1476
DOI: 10.1126/science.267.5203.1473

Abstract

Single crystals of the layered organic-inorganic perovskites, $[NH_2C(I=NH_2]_2(CH_3NH_3)_m Sn_mI_{3m+2}$, were prepared by an aqueous solution growth technique. In contrast to the recently discovered family, $(C_4H_9NH_3)_2(CH_3NH_3)_{n-1}Sn_nI_{3n+1}$, which consists of (100)-terminated perovskite layers, structure determination reveals an unusual structural class with sets of *m* <110>-oriented $CH_3NH_3SnI_3$ perovskite sheets separated by iodoformamidinium cations. Whereas the $m = 2$ compound is semiconducting with a band gap of 0.33 ± 0.05 electron volt, increasing *m* leads to more metallic character. The ability to control perovskite sheet orientation through the choice of organic cation demonstrates the flexibility provided by organic-inorganic perovskites and adds an important handle for tailoring and understanding lower dimensional transport in layered perovskites.

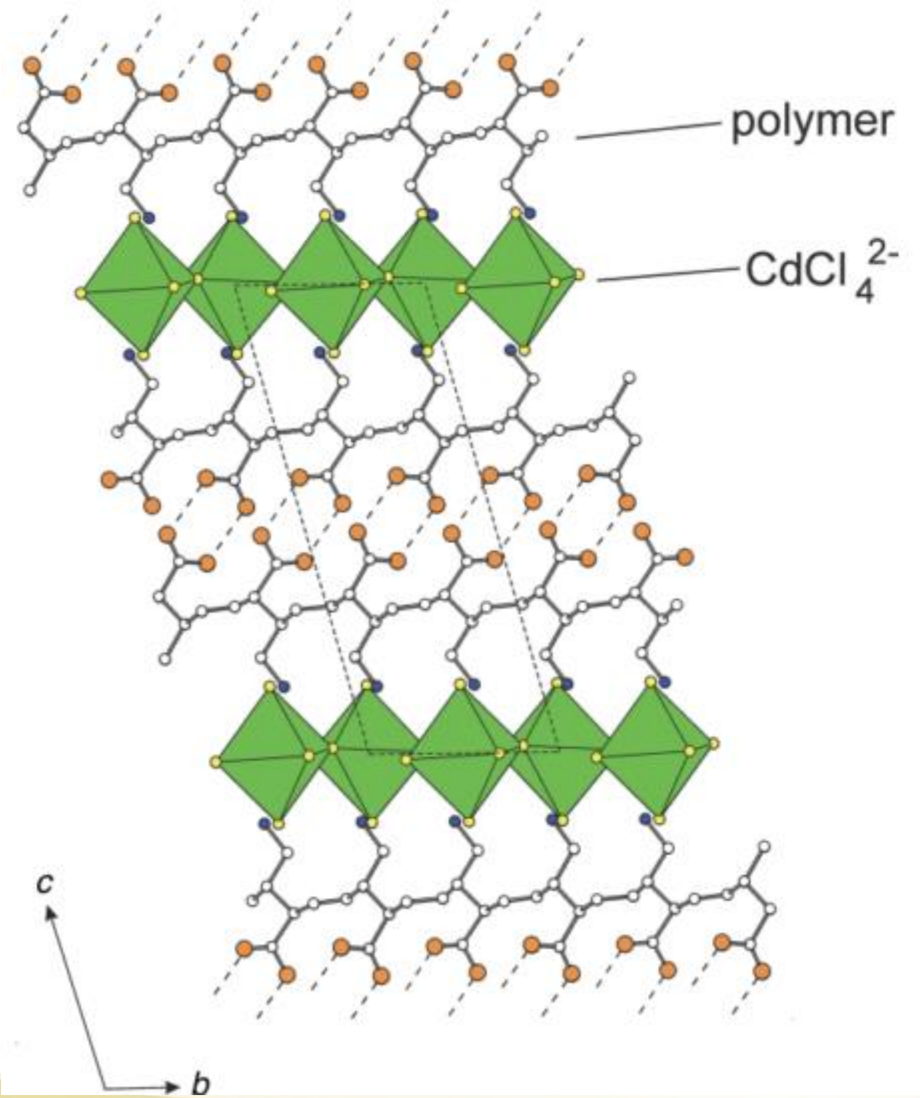
The basic structures of 2D organic–inorganic perovskite with bilayer and single layer intercalated organic molecules



$(R\text{-}NH_3)_2MX_4$
(a)

$(NH_3\text{-}R\text{-}NH_3)MX_4$
(b)

Polymerization within the organic layer of perovskite structures

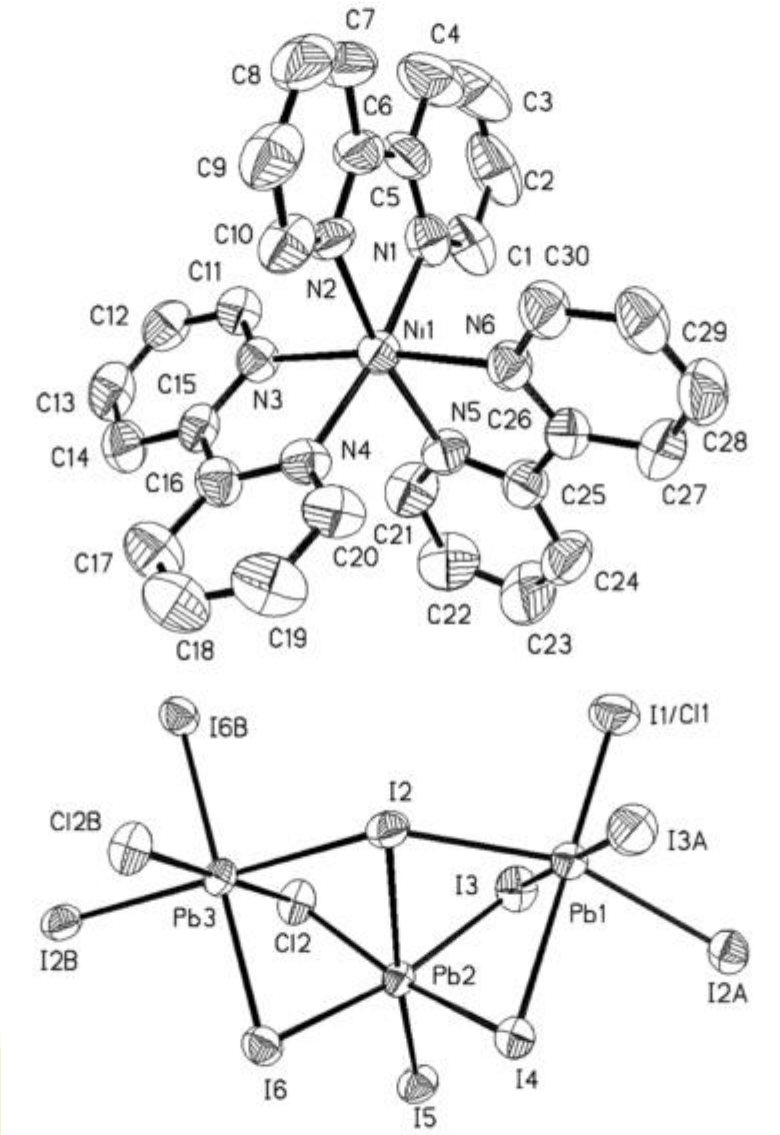


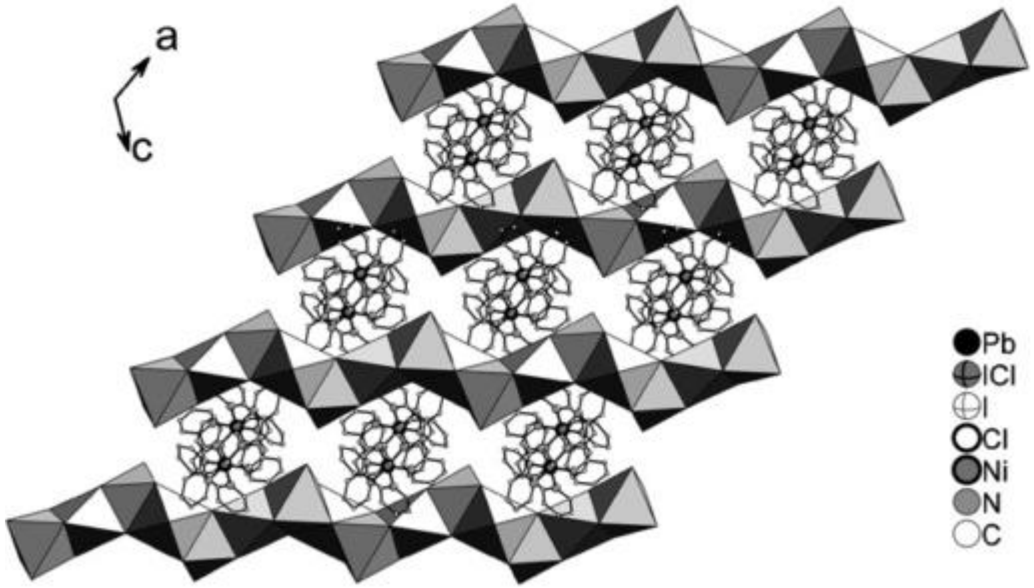
6-amino-2,4-trans,trans-hexadienoic acid, within a cadmium (II) chloride perovskite framework, polymerizes under ultraviolet (UV) irradiation.

More rigid and stable perovskite structure!

B. Tieke and G. Chapuis, Mol. Cryst. Liq. Cryst., 1986, 137, 101

Ni(bipy)$_3$ as cations for 2D perovskite as hybrid magnetic semiconductor





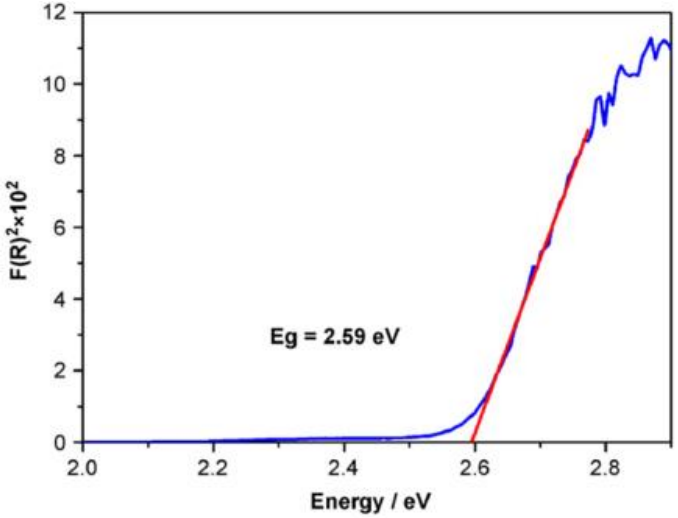


Fig. 4. Plot of $F(R)^2$ vs. photon energy for **1**.

10.1016/j.jssc.2007.10.010

Take home message

- Being toxic and instable, Lead-Halide perovskite is an excellent 'MODLE' material for electronic application.

- 3D type , Lead-Halide perovskite has found prevailing application in PV field.

- 3D type , Lead-Halide perovskite can be strong competitor to silicon PV

- 2D or 1D type perovskite provide more possibility for more broad applications.

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