HANBAT NATIONAL UNIVERSITY

Density Functional Studies on Compositional Mixing of Metal-Halide Perovskites

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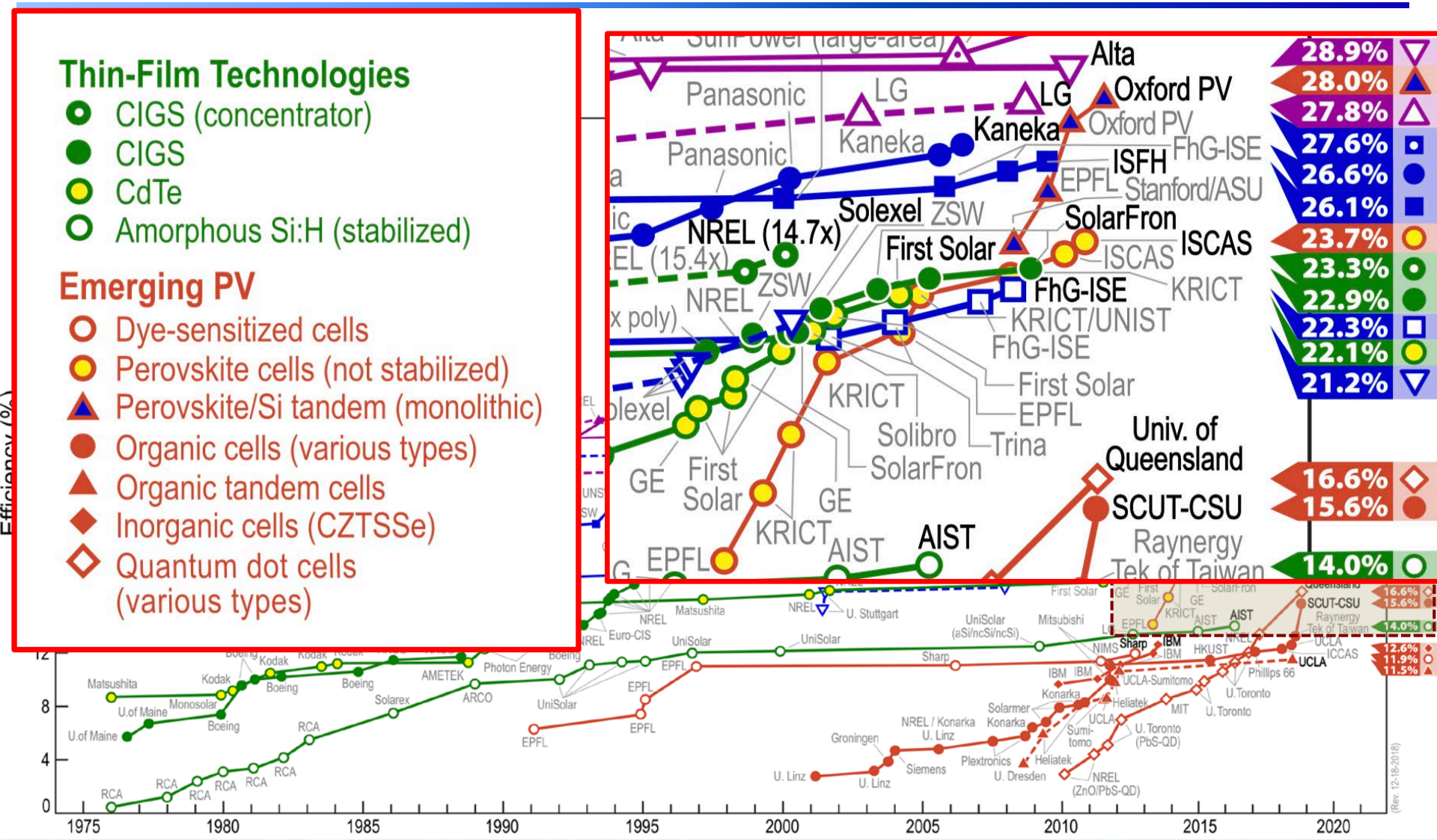
2019.01.16. ICTP

Contents

Efficiency Chart (NREL)



Research Trends

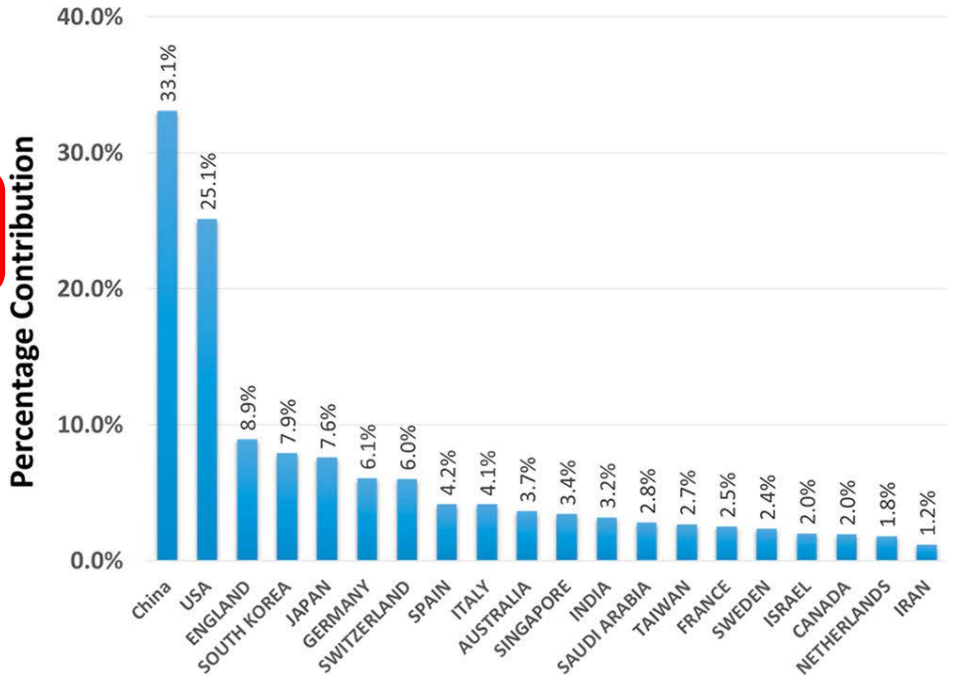
CHEMISTRY OF MATERIALS
Editorial
Cite This: Chem. Mater. 2017, 29, 8915-8917
pubs.acs.org/cm

Virtual Issue on Metal-Halide Perovskite Nanocrystals—A Bright Future for Optoelectronics

Table 1. Top Ten Journals Publishing Metal-Halide Perovskite Papers[a]

Journal	No. of Papers	Percentage
JOURNAL OF PHYSICAL CHEMISTRY LETTERS	251	7.127%
JOURNAL OF MATERIALS CHEMISTRY A	240	6.814%
JOURNAL OF PHYSICAL CHEMISTRY C	175	4.969%
ACS APPLIED MATERIALS INTERFACES	151	4.287%
ADVANCED MATERIALS	103	2.924%
ACS ENERGY LETTERS	97	2.754%
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY	95	2.697%
CHEMISTRY OF MATERIALS	91	2.584%
NANO LETTERS	90	2.555%
PHYSICAL CHEMISTRY CHEMICAL PHYSICS	86	2.442%

[a]Source: Web of Science, Clarivate Analytics, October 12, 2017. Search term: [Perovskite and (lead or tin) and solar]. Data set: 3552 papers.



Spread of metal-halide perovskite publications

$CH_3NH_3PbI_3$

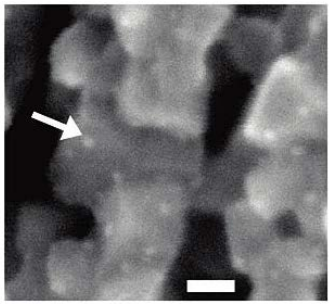
- Miyasaka group firstly adopted as a sensitizer of DSSCs.

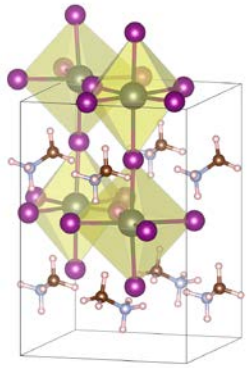
J|A|C|S COMMUNICATIONS

Published on Web 04/14/2009

Organometal Halide Perovskites as Visible-Light Sensitizers for Photov Cells

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





I4/mcm (@ RT)
a=8.8660
b=8.8660
c=12.6524

Table 1. Photovoltaic Characteristics of Perovskite-Based Cells[a]

perovskite sensitizer on TiO_2	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)
$CH_3NH_3PbBr_3$	5.57	0.96	0.59	3.13
$CH_3NH_3PbI_3$	11.0	0.61	0.57	3.81

[a] Measured with an effective incident area of 0.24 cm^2 under 100 mW/cm^2 AM 1.5 simulated sunlight irradiation.

Cost Efficiency

- Crystallization @ RT
- Solution process

Good Properties

- Proper band gap (1.55 eV)
- High absorption coeff. (> 3×10^4 cm^{-1})
- Low exciton binding E (< 50 meV)
- High dielectric constant (ε ~ 30)
- Ambipolar carrier transport
- Immunity to intrinsic defects
- Long carrier lifetime (Rashiba spin-or bit coupling)

Organic-Inorganic Hybrid Perovskites

First $MAPbI_3$ paper

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

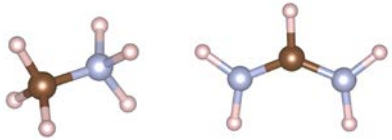
$CH_3NH_3PbX_3$, a Pb(II)-System with Cubic Perovskite Structure

Dieter Weber
Institut für Anorganische Chemie der Universität Stuttgart

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

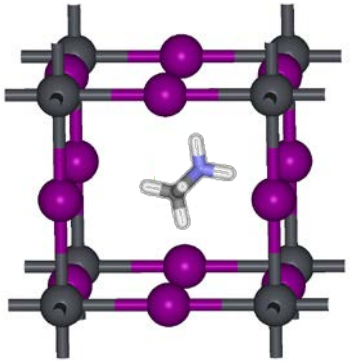
ABX_3 Perovskites

A= MA, FA, Cs
B = Pb, Sn
X = I, Br, Cl

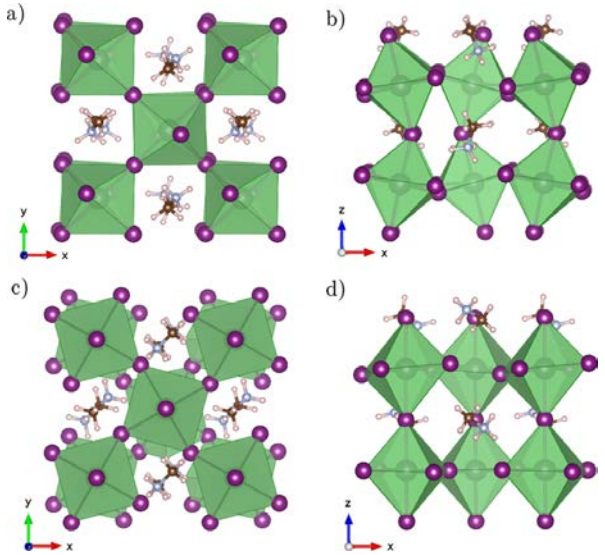


MA FA

Cs



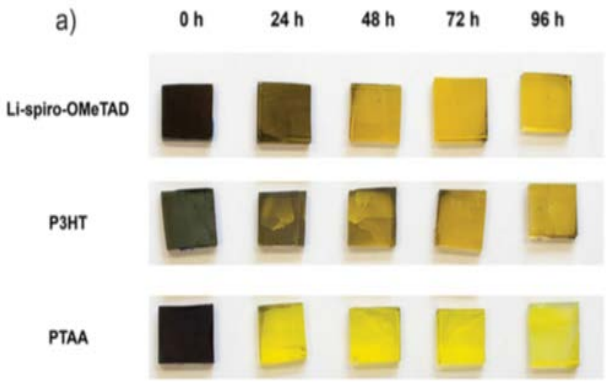
Octahedron Tilting of $MAPbI_3$



C. Motta et al. Sci. Rep. (2015)

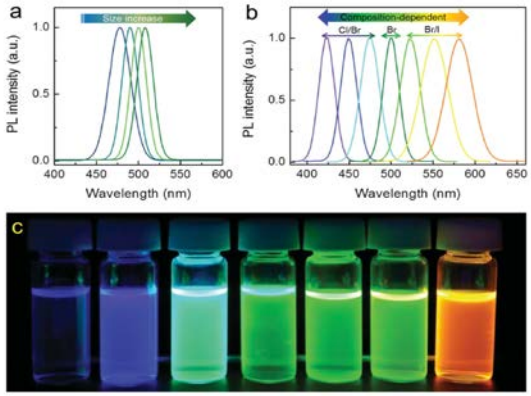
Issues : ABX_3 (X= I, Br, Cl) Perovskites

Stability



Leijtens, T. et al. Adv. Energy Mater. (2015)

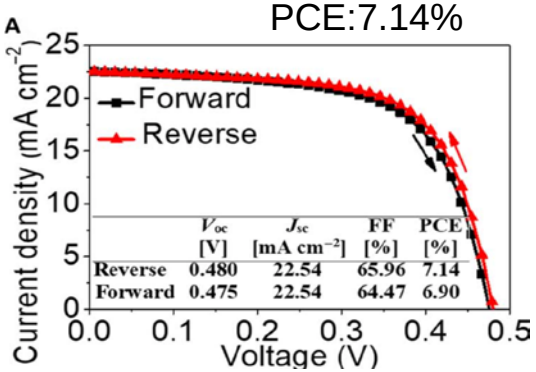
Band Engineering



Song, J. et al. Adv. Energy Mater. (2015)

Pb-free

{en}$FASnI_3$
PCE:7.14%



Kanatzidis group Science Adv. (2017)

$MA_xFA_{1-x}Pb(Br_xI_{1-x})_3$

$MAPb(Br_xI_{1-x})_3$
$MAPb(Br_xCl_{1-x})_3$

Cs_3BiInI_9
Cs_2AgBiI_6

Mixing of A or X sites

Mixing of B sites

Alloying or Mixing

Theoretical Investigation

- Ab initio thermodynamics
  - Density functional theory (DFT) calculation of alloys
  - Including statistical thermodynamics concept.

High Symmetry: $FAPbI_3$ mixing

Single Phase

- **Lattice optimization of single phase**

Mixed Phase by SOD

- **Site Occupancy Disorder (SOD)**

Phase Diag. by GQCA

- **Generalized Quasi-Chemical Approximation (GQCA)**

Low Symmetry: Pb-free double perov.

DFT Calc. Training sets

Cluster Expansion

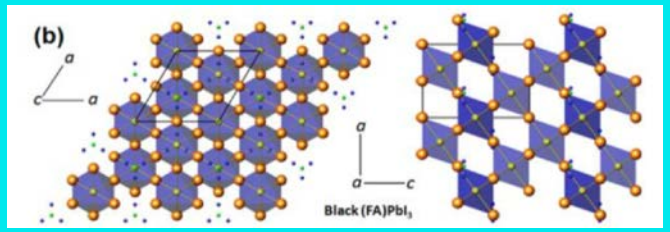
Monte Carlo Simulation

Polymorph Control Issues

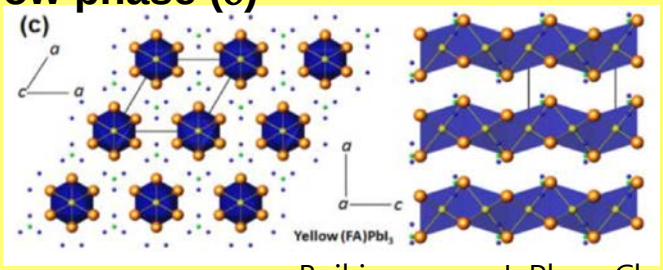
$FAPbI_3$

Lowest band gap Pb halide perovskites

Black phase (α)



Yellow phase (δ)



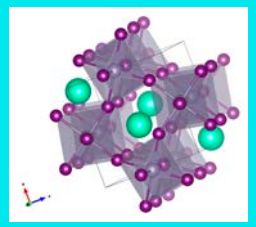
Baikie group, J. Phys. Chem. C 2014

Photovoltaic but unstable mater. @ ambient Temp.

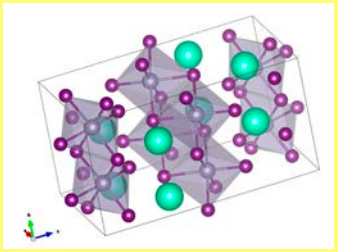
Stable but non-photovoltaic mater @ ambient Temp.

$CsSnI_3$

Black phase (α)



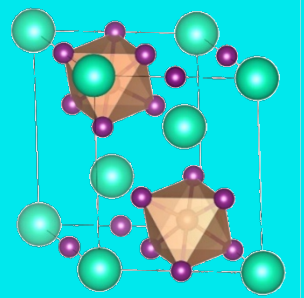
Yellow phase (δ)



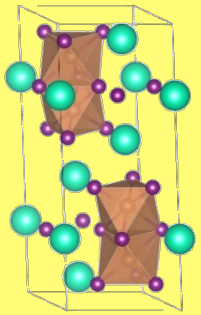
A Pb-free perovskite candidate

$Cs_3Sb_2I_9$

$Cs_3Sb_2I_9$ ($P\bar{3}m1$)



$Cs_3Sb_2I_9$ ($P6_3/mmc$)



Stabilization of Black $FAPbI_3$

A-Site Mixing

Double Cation

- MA-FA
  - Binek, A. et al. (2015) JPC Lett
  - Pellet, N. et al. (2014) Ange. Chem.
- Cs-FA
  - Li, Z. et al. (2016) Chem. Mat.
  - Lee, J.-W. et al. (2015) Adv. Ener. Mat.

Triple Cation

- Cs-MA-FA
  - Saliba, M. et al. (2016) Ener. Env. Sci.

Quadruple Cation

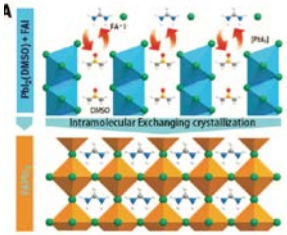
- Rb-Cs-MA-FA
  - Saliba, M. et al. (2016) Science

X-Site Mixing

- Br-I — Rehman, W. et al. (2015) Adv. Mat.
- Cl-I — Mu, C. et al. (2016) Adv. Ener. Mat.

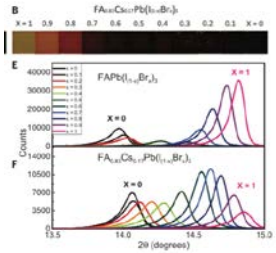
A & X-Site Mixing

Seok group



$(FAPbI_3)_{1-x}(MAPbBr_3)_x$

Snaith group

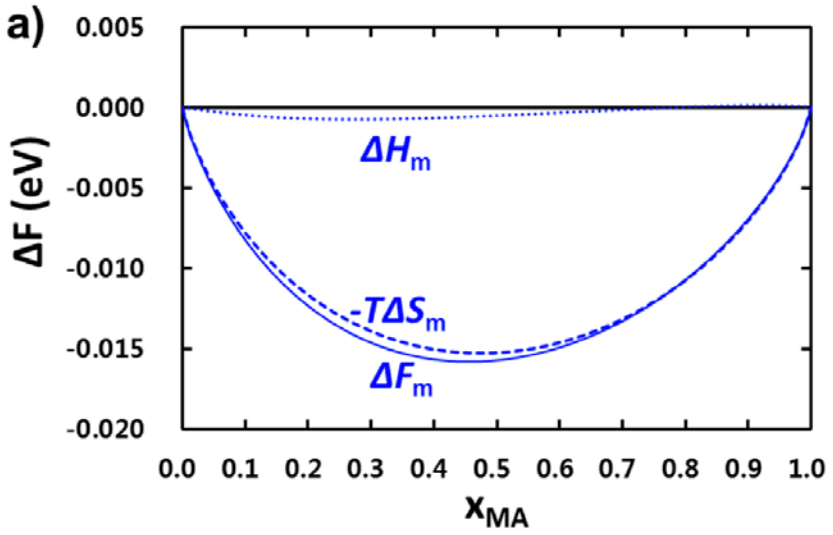


$FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$

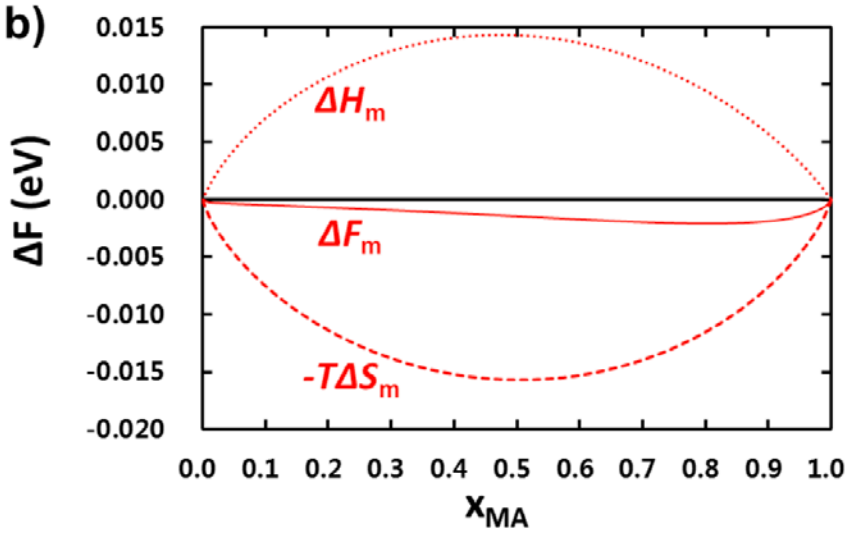
A-Site Mixing (MA into FA)

Solution free energy curves

Trigonal (α)

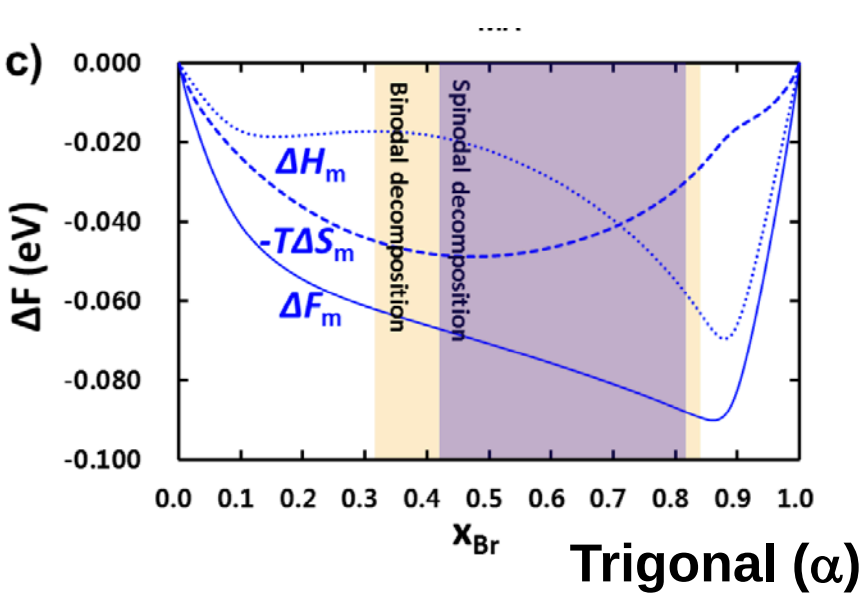


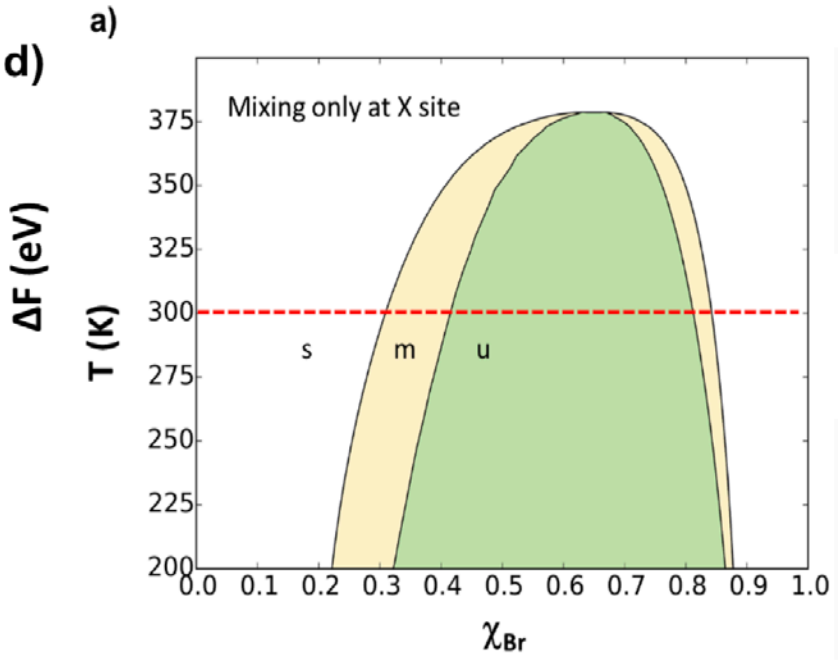
Hexagonal (δ)



- MA mixing is favored to the black(trigonal) phase
- Negligible Enthalpy of mixing (H or U)
- Entropy driven solid solution

X-site Mixing: $FAPb(Br_xI_{1-x})_3$



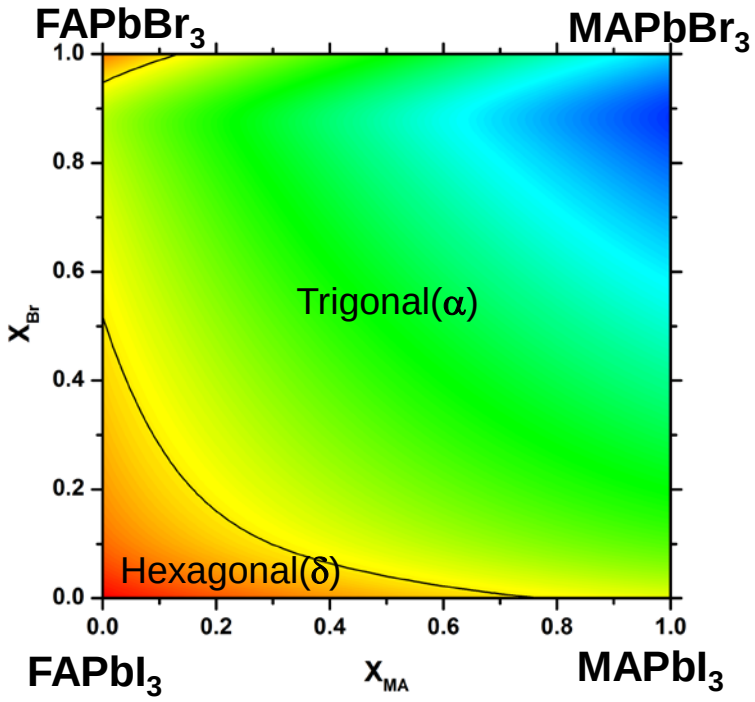


- Br mixing is favored for the trigonal phase
- Phase separation in the trigonal phase mid-level Br mixing cannot be achieved

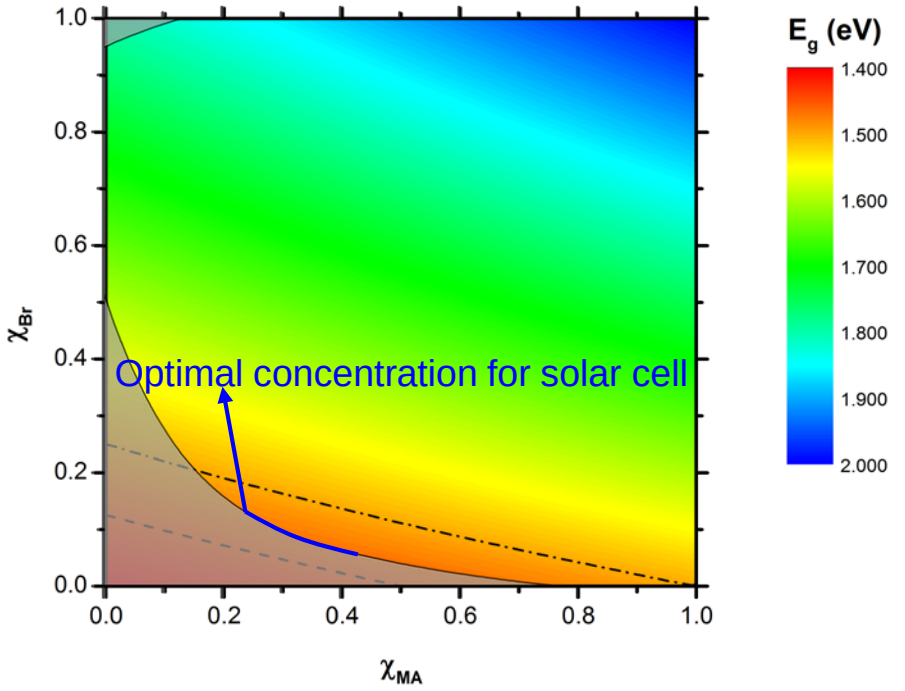
Joen. J. et al. JPCc. (2017)

Phase Map of $(FAPbI_3)_{1-x}(MAPbBr_3)_x$

Energy diff. bet. Tri. and Hex.



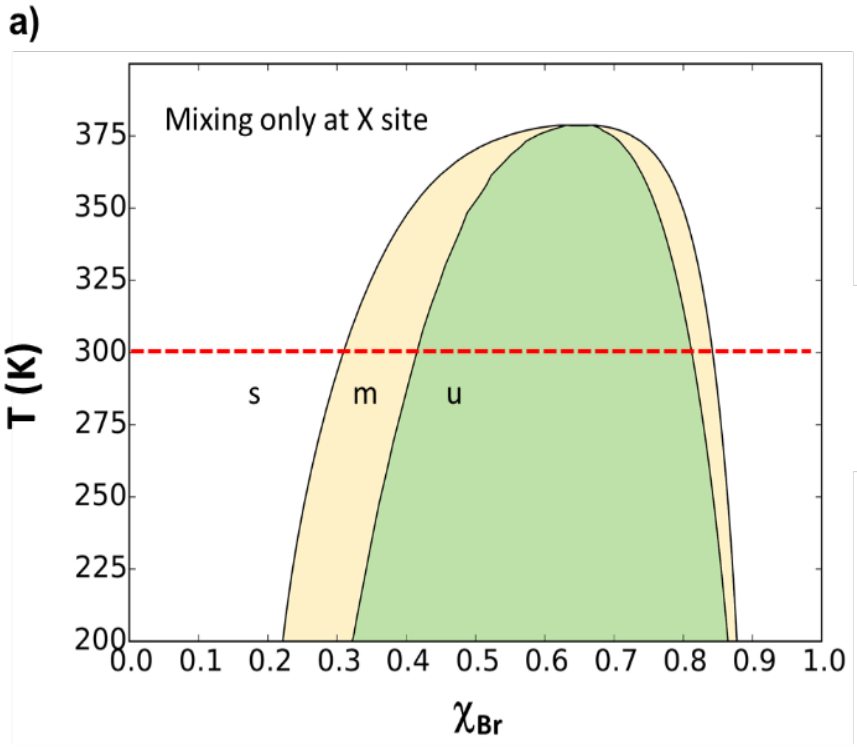
Calculated band gap (Vegard's Law)

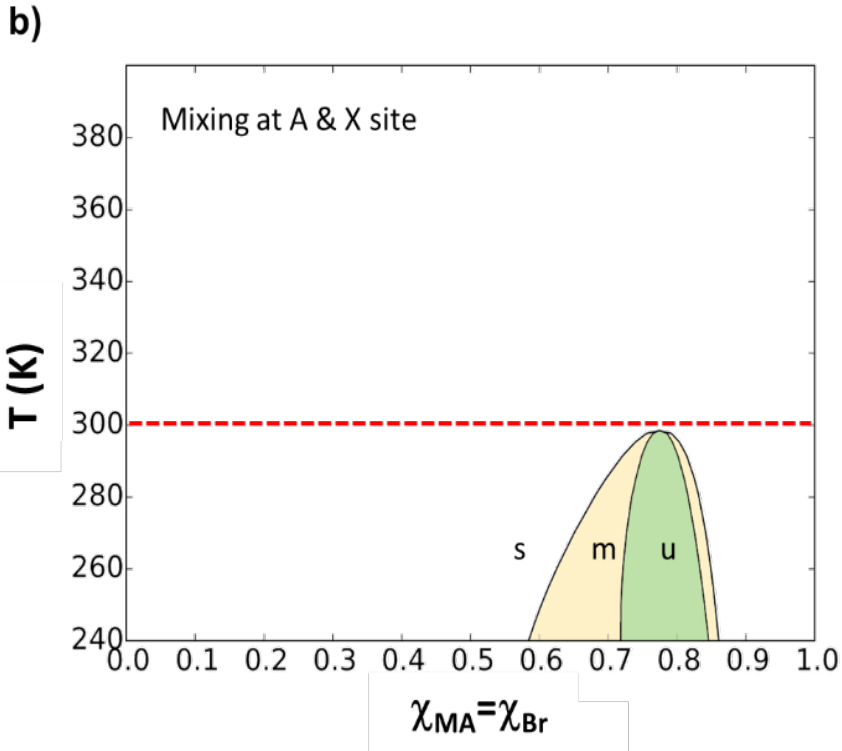


- Dual-site alloying (@ A-X sites) can reduce the amount of alloying elements that stabilize trigonal phase
- Optimal conditions approaching SQ-limit are obtained by dual-site alloying

Joen. J. et al. JPCc. (2017)

Effects on Phase Separation



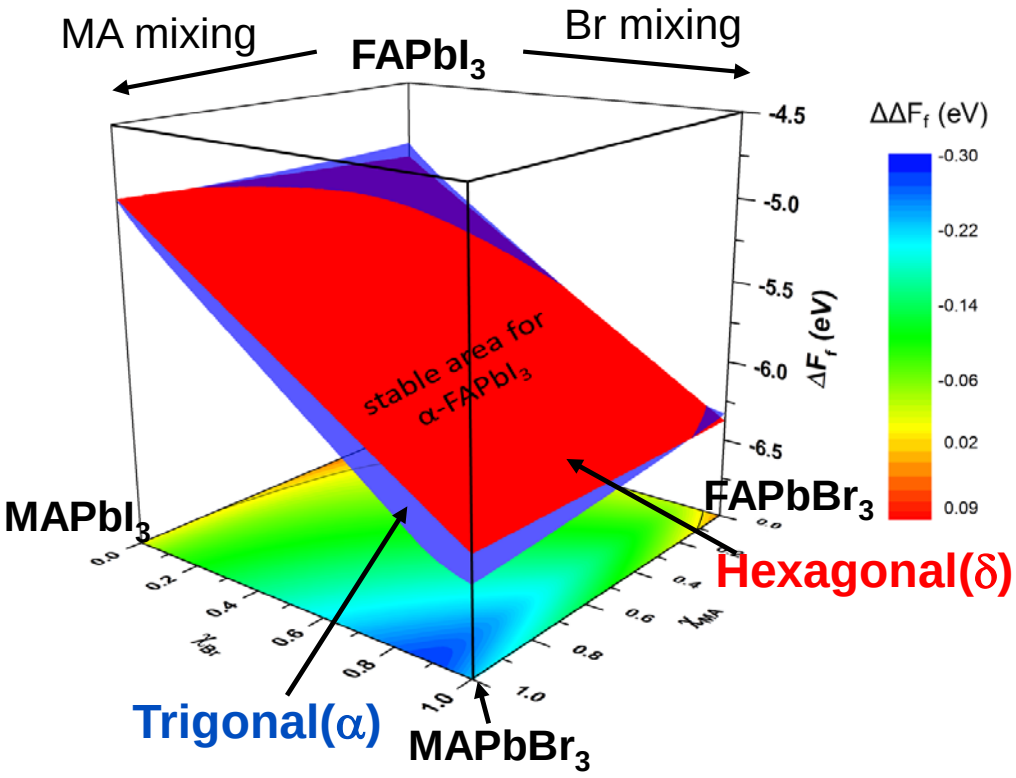


Mixing only a X-site

Mixing both A & X sites

- Phase separation can be avoided by dual-site alloying
- A site mixing improves solubility and can alleviate immiscibility

Mechanism of Polymorph Control



$$\Delta E = E_f(\alpha) - E_f(\delta)$$

	$E_f(\alpha)$/FU	$E_f(\delta)$/FU	ΔE [eV]
$FAPbI_3$	-4.908	-5.000	0.092
$FAPbBr_3$	-6.330	-6.375	0.045
$MAPbI_3$	-4.928	-4.914	-0.014
$MAPbBr_3$	-6.492	-6.331	-0.161

- Importance of the **energy difference between tri. and hex. phases**

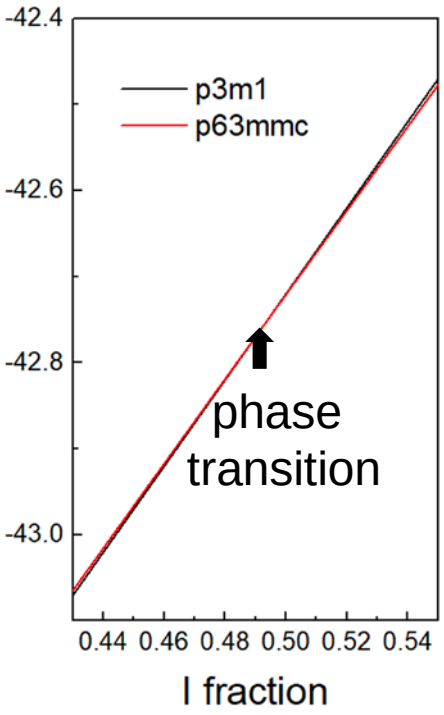
Anti-stabilizer of δ-phase:
$MAPbBr_3$

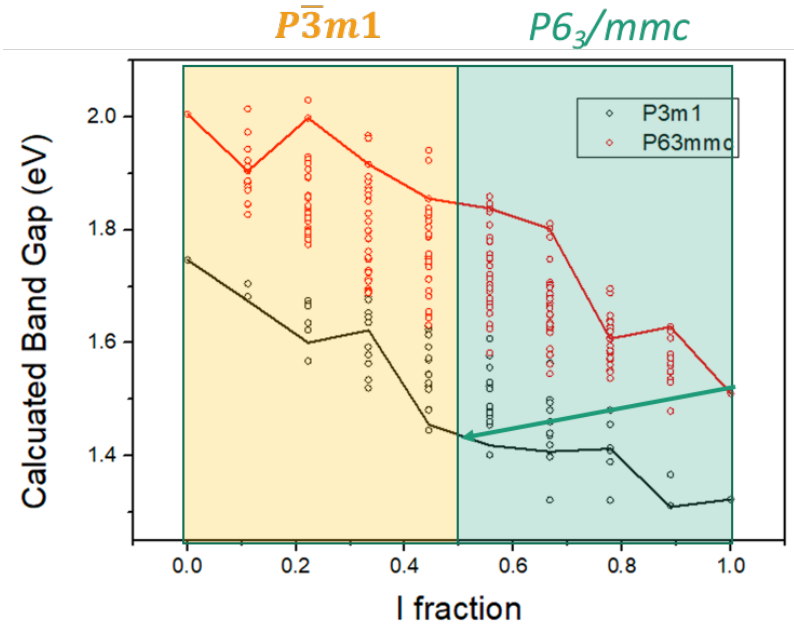
Joen. J. et al. JPCc. (2017)

Stabilization of $P\bar{3}m1$ $Cs_3Sb_2Br_{9-x}I_x$

Species	Symmetry
$Cs_3Sb_2I_9$	*P6₃/mmc*
$Cs_3Bi_2I_9$	*P6₃/mmc*
$Cs_3Sb_2Br_9$	$P\bar{3}m1$
$Cs_3Bi_2Br_9$	$P\bar{3}m1$

Br addition can destabilize the *P6₃/mmc* structures



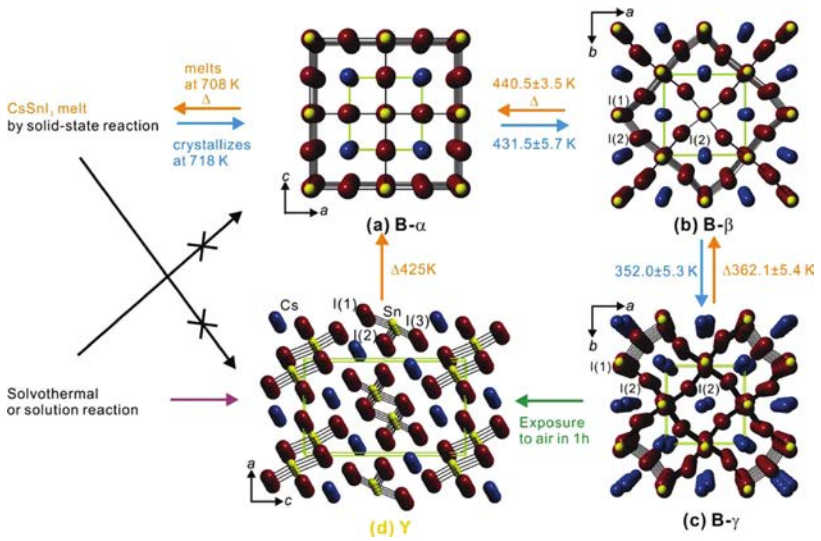


The band gap of energy minimum s tates are represented in solid lines

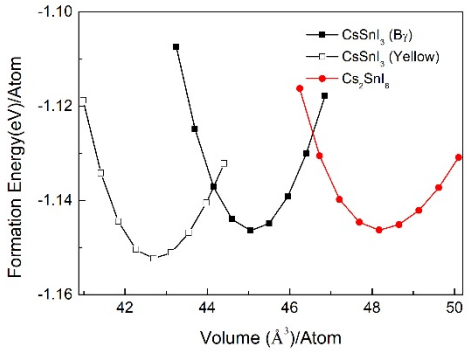
Phase transition
& band gap narrowing

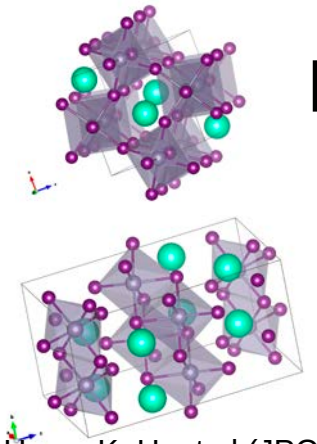
Hong, K. H. (preparing)

Anti-Stabilizing Y-$CsSnI_3$



Chung, I. et al. JACS (2012)



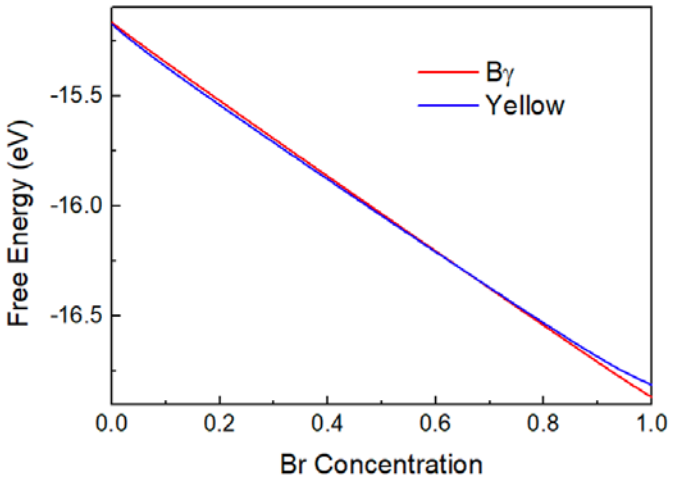


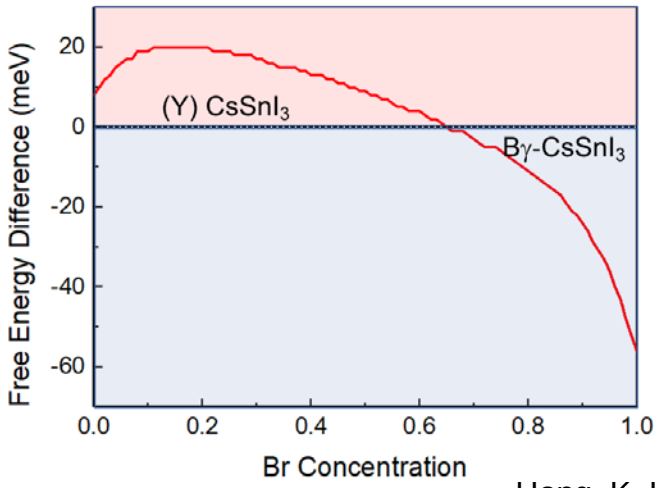
Bγ

Y

Hong, K. H. et al.(JPC Lett. 2018)

Yellow phase is stable
@ ambient condition





Hong, K. H. (preparing)

Computational Issues

- Convergence or quantitative evaluation
- Polymorph changes between 0K and RT
- Computational approaches for excited states
- Defect and Surface Structures
- Development of Pb-free perovskites

Different Activation E of V_I

- I vacancy diffusion barrier

A. Walsh group.
Nat. Comm. (2015)

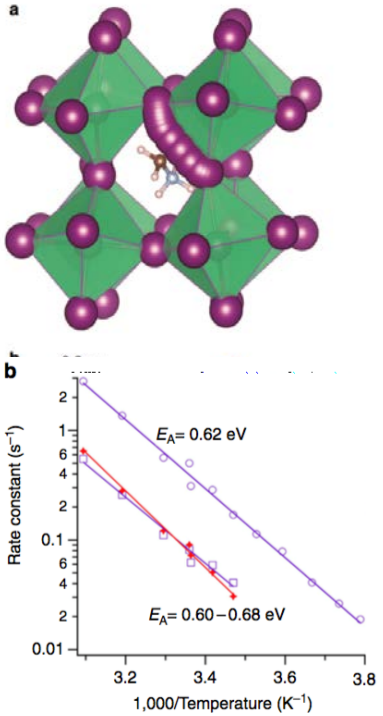
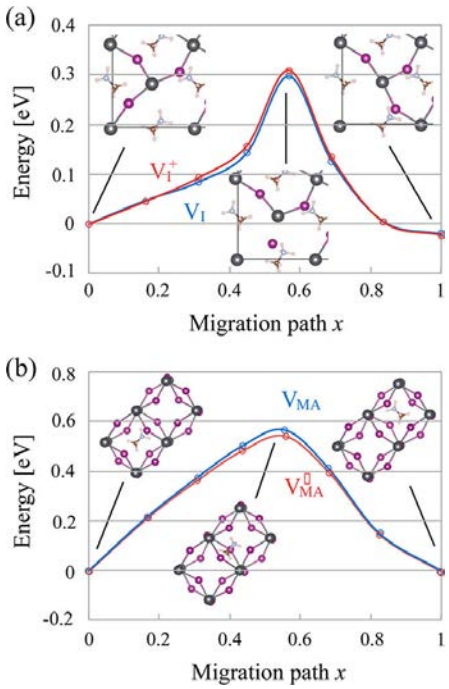


Figure 4 | Chronophotoamperometry measurements of a perovskite-based cell. (**a**) The measurement sequence in a d-TiO_2/$CH_3NH_3PbI_3$/

0.62 eV

Y. Tateyama group.
JACS (2015)



0.3 eV

F. Angelis group.
Energy Env. Sci. (2015)

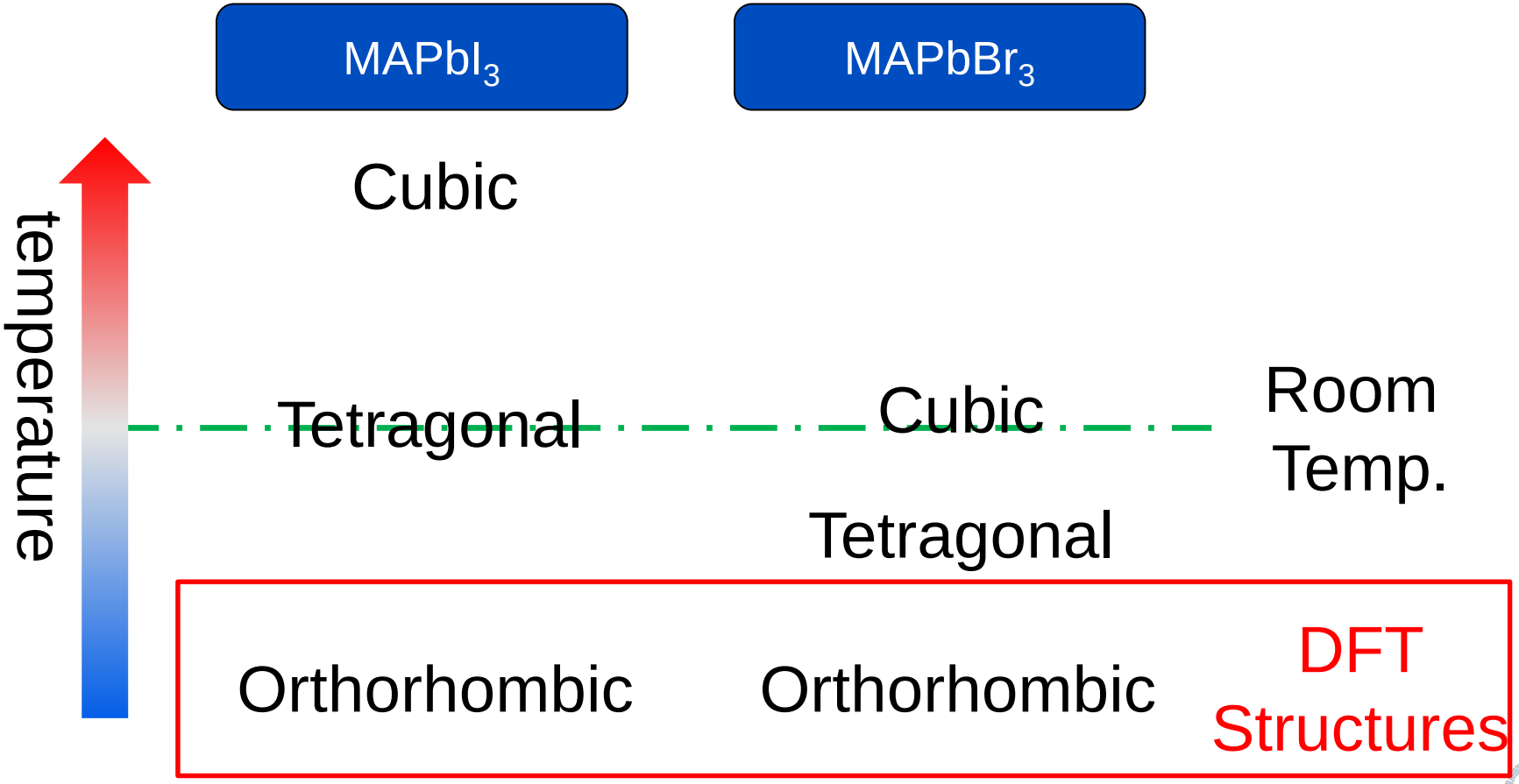
Table 1 Activation energies (E_a, in eV) and rate constants (k, in s^{-1}), calculated according to eqn (1), for the migration of the different investigated point defects in $MAPbI_3$ and $MAPbBr_3$. Values in parentheses for $MAPbI_3$ refer to the energetics and rates of two consecutive hops

	$MAPbI_3$		$MAPbBr_3$	
Defect	E_a (eV)	k (s^{-1})	E_a (eV)	k (s^{-1})
$V_{I/Br}$	0.08 (0.16)	1.7×10^{12} (7.7×10^{10})	0.09	1.2×10^{12}
V_{MA}	0.46	6.5×10^{5}	0.56	1.3×10^{4}
V_{Pb}	0.80	1.2×10^{0}	—	—
I_i	0.08 (0.16)	1.7×10^{12} (7.7×10^{10})	—	—

0.08 eV

Numerically Unstable Crystal Structures

- Minimum energy structures used in DFT calculation are different from the crystal structures @ room temp.



Computational Approaches for Excited States

Phase Separation

Photostriction

NANO LETTERS
Letter
pubs.acs.org/NanoLett

Origin of Reversible Photoinduced Phase Separation in Hybrid Perovskites

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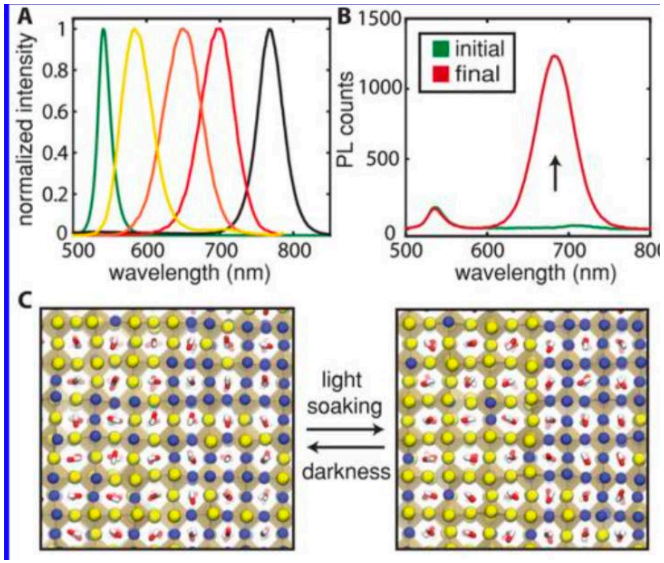
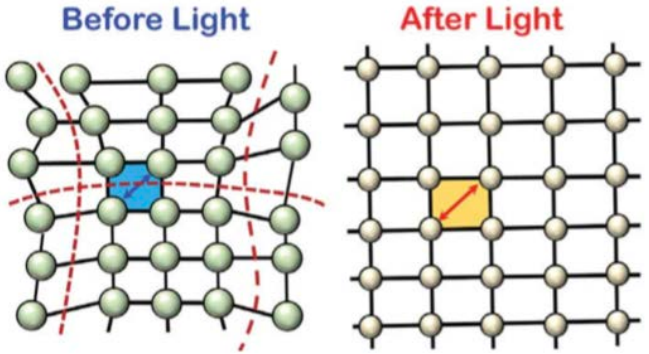


Irradiation induced halide phase separation

RESEARCH
SOLAR CELLS

Light-induced lattice expansion leads to high-efficiency perovskite solar cells

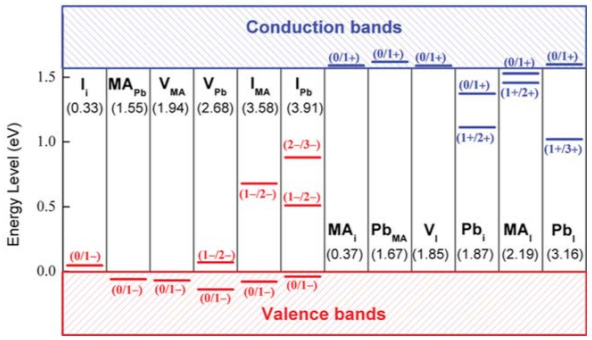
Hsinhan Tsai,[1,2] Reza Asadpour,[3] Jean-Christophe Blancon,[1] Constantinos C. Stoumpos,[4] Olivier Durand,[5] Joseph W. Strzalka,[6] Bo Chen,[7] Rafael Verduzco,[2,8] Pulickel M. Ajayan,[2] Sergei Tretiak,[9] Jacky Even,[5] Muhammad Ashraf Alam,[3] Mercouri G. Kanatzidis,[4] Wanyi Nie,[1]* Aditya D. Mohite[1,8]*



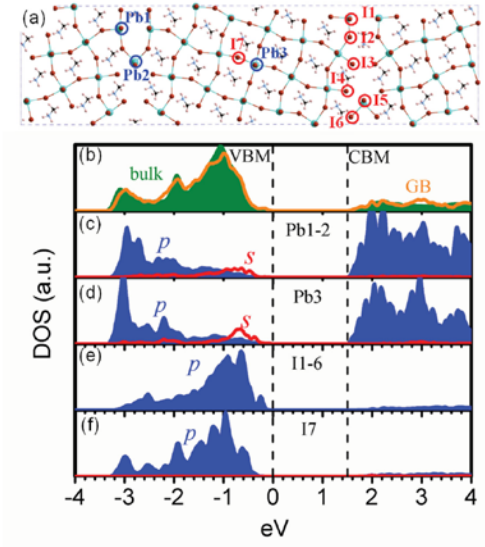
Light induced lattice strain (~1%)

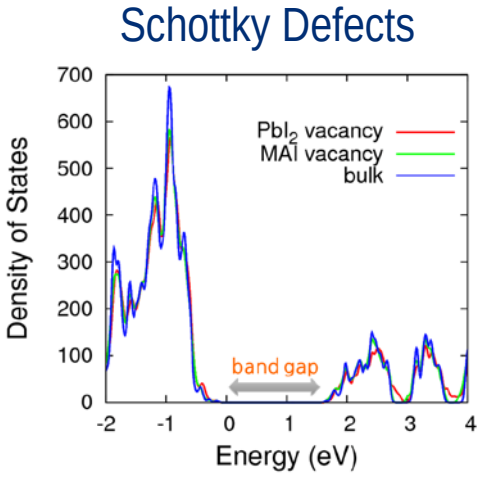
Analysis of Defects

- Dominant point defects generate shallow-level defects
- Even grain boundaries and surfaces exhibit shallow-level defects
- But there are deep-level defects in experimental data



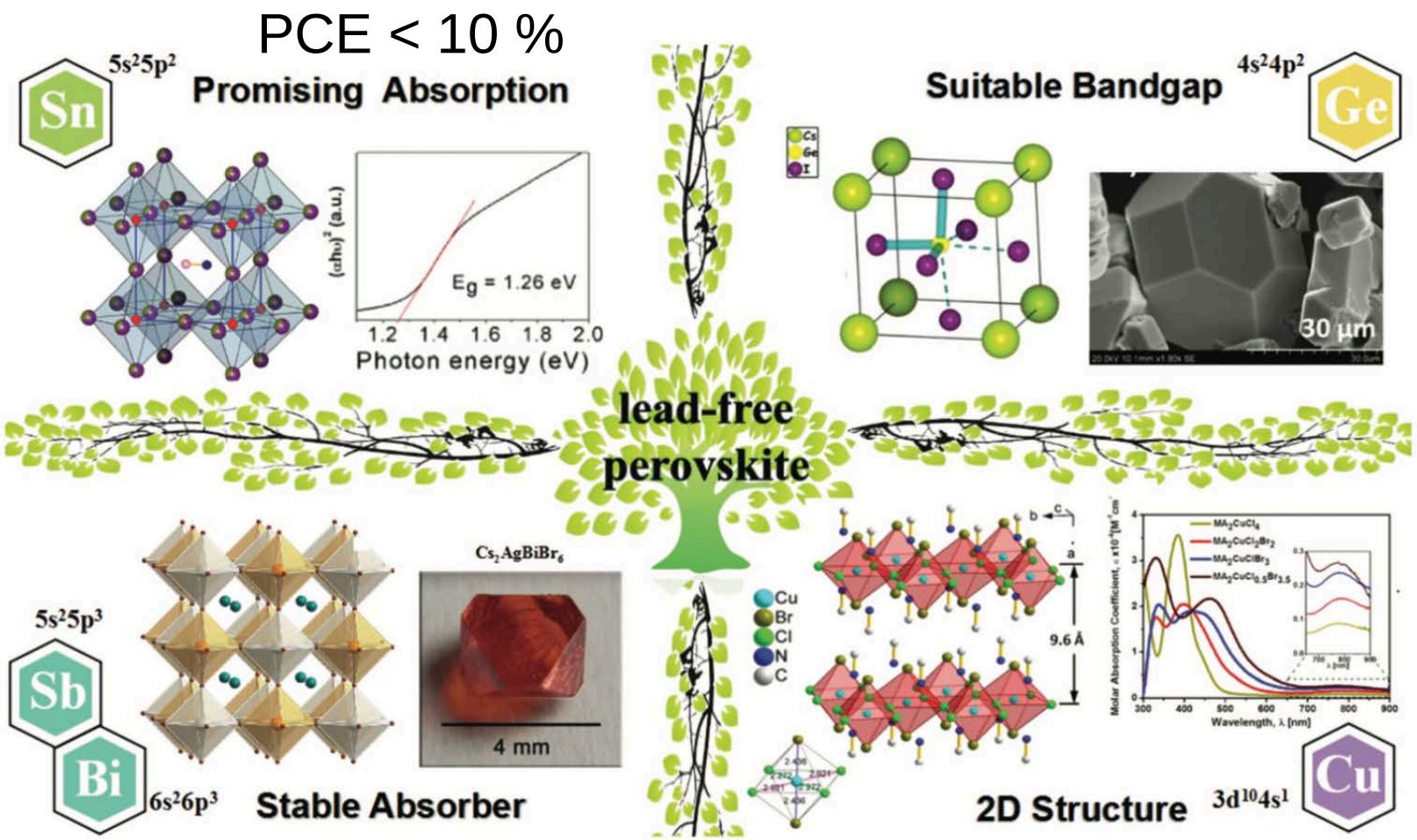
W.-J. Yin et al. *Adv. Mat.* (2014)





J. Kim et al. JPC Lett. (2014)

Categories of Pb-free Perovskites



Shi, Z. et al. (2017). Adv. Mat., 29(16)

Computational Screening

CHEMISTRY OF MATERIALS
Article
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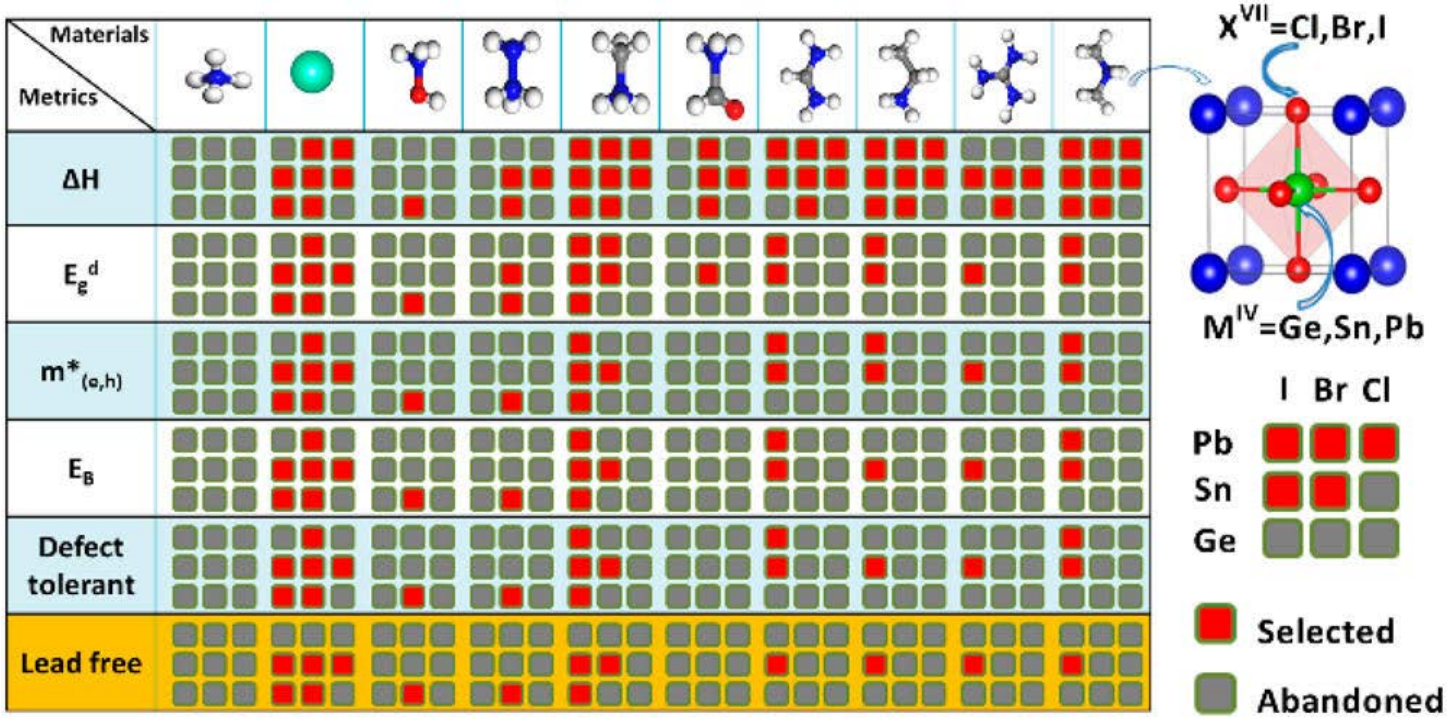
Functionality-Directed Screening of Pb-Free Hybrid Organic–Inorganic Perovskites with Desired Intrinsic Photovoltaic Functionalities

Dongwen Yang,[†,‡] Jian Lv,[†,‡] Xingang Zhao,[†] Qiaoling Xu,[†] Yuhao Fu,[†] Yiqiang Zhan,[§] Alex Zunger,[*,⊥] and Lijun Zhang[*,†,∥]



Extension to Machine Learning

CHEMISTRY OF MATERIALS
Article
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Predicting the Thermodynamic Stability of Solids Combining Density Functional Theory and Machine Learning

Jonathan Schmidt,[†] Jingming Shi,[‡] Pedro Borlido,[§] Liming Chen,[∥] Silvana Botti,[§] and Miguel A. L. Marques*[,†]

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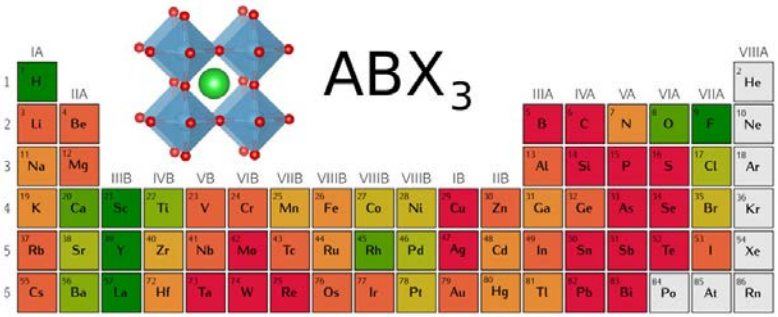
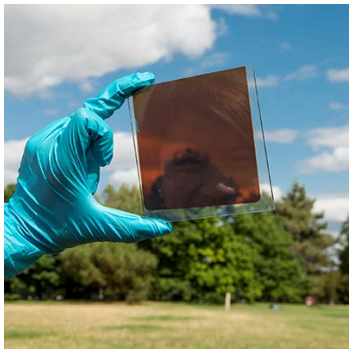
[‡]Université de Lyon, Institut Lumière Matière, UMR5306, Université Lyon 1-CNRS, 69622 Villeurbanne Ced
[§]Institut für Festkörpertheorie und -optik, Friedrich-Schiller-Universität Jena and European Theoretical Spectr Max-Wien-Platz 1, 07743 Jena, Germany
[∥]Liris laboratory UMR CNRS 5205, Ecole Centrale de Lyon, University of Lyon, 69134 Écully, France



"We start by constructing a data set that comprises density functional theory calculations of around 250000 cubic perovskite systems.
This includes all possible perovskite and antiperovskite crystals that can be generated
with elements from hydrogen to bismuth, excluding rare gases and lanthanides. Incidentally, these calculations already reveal a large number of systems (around 500) that are thermodynamically stable but that are not present in crystal structure databases."

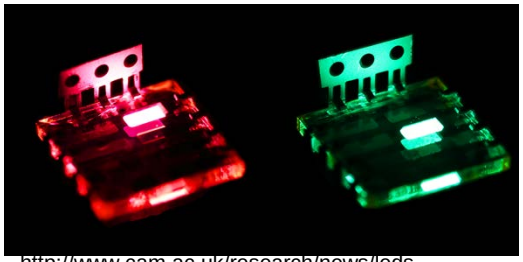
Various Applications of Halide PVKs

Solar Cell



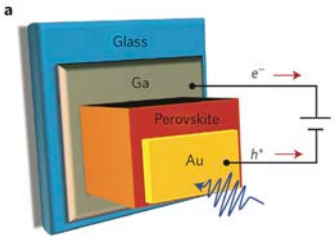
https://www-thz.physics.ox.ac.uk/perovskites.html

LED



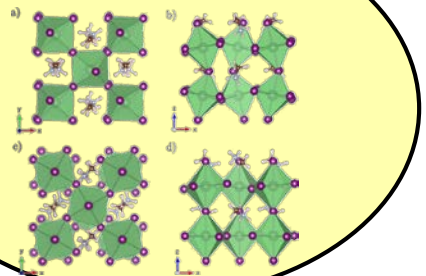
http://www.cam.ac.uk/research/news/leds-made-from-wonder-material-perovskite

Photodetector

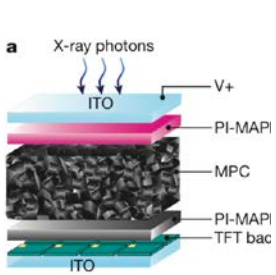


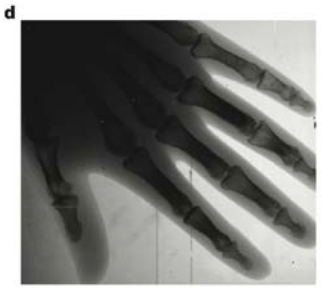
J. S. Huang group. Nat. Photon. (2015)

Halide PVKs



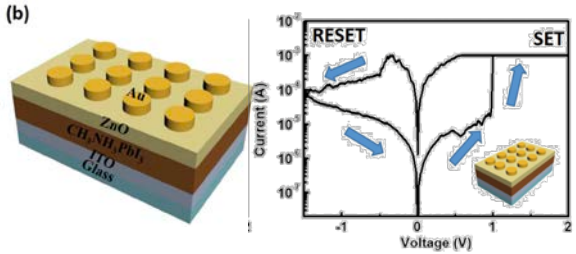
X-ray Imaging





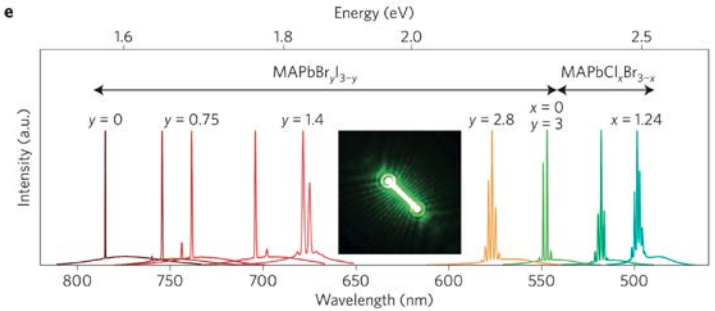
Samsung Elec & N.G. Park Nature. (2017)

Memory



J. S. Lee group. Sci. Rep. (2017)

Laser



Zhu et. al. Nat. Mat. (2014)

Summary

- Compositional mixing for the phase stabilization.
  - Concept of anti-stabilizer
  - $MAPbBr_3$ to $FAPbI_3$
  - Br into $Cs_3Bi_2I_9$ & $CsSnI_3$
- More sophisticated structural model
  - Surface, interface, nanostructures, and defects
- Quick and accurate materials screening methods
  - Machine learning and big data
  - Pb-free perovskites can be a strong candidates for next-generation solar cells and light emitting diodes