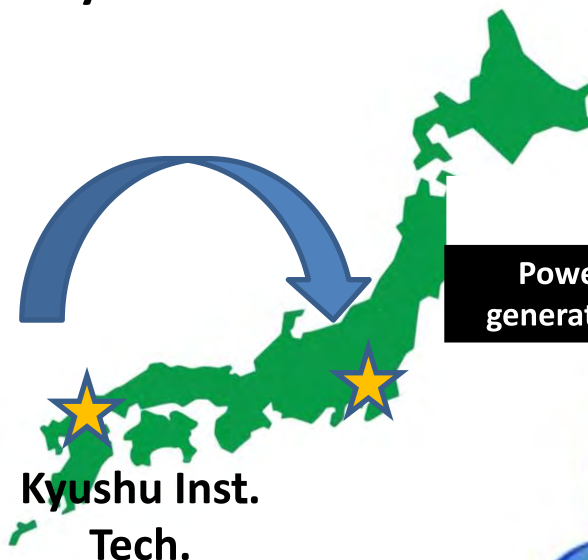
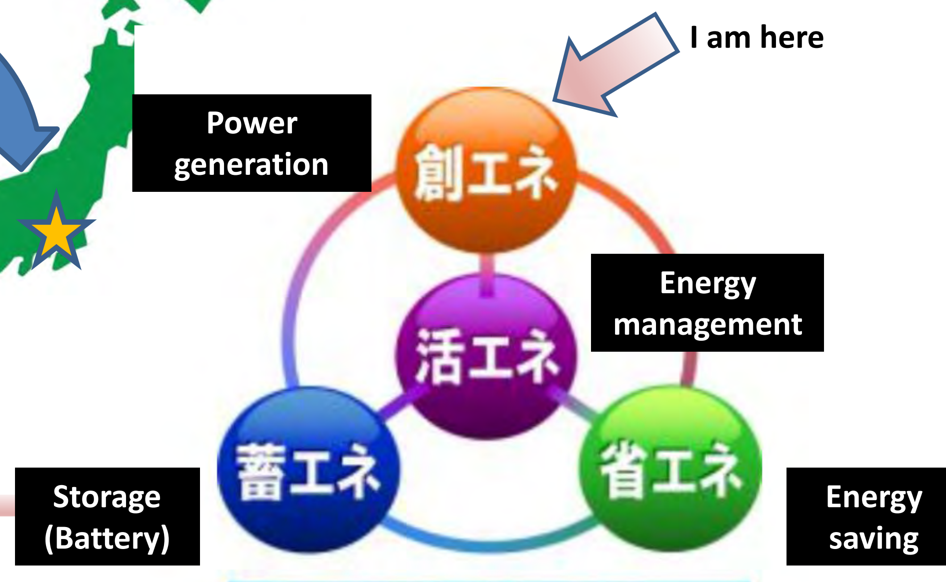
Narrow band gap perovskite solar cells consisting of thin perovskites and application to perovskite tandem solar cells

Shuzi Hayase

i-Powered Energy System Research Center
The University of Electro-Communications





Summer School on Future prospects of perovskite based solar cells: Low carbon energy conversion through advanced functional materials, Day 5, May 18、9:30-10:30

Acknowledgment

- **The University of Electro-Communication**
  Hayase Lab. Students and post doctoral researchares
  Huan Bi, Yasuhiro Fujiwara,, Gaurav Kapil, Zheng Zhang, Liang Wang, Chao Ding, Shahrir Razey Sahamir, Ajay Kumar Baranwal, Yoshitaka Sanehira, Kitamura Takeshi, Guozheng Shi, Mengmeng Chen

- **The University of Electro-Communications**
  Shen Qing

- **Kaunas University of Technology**
  Daiva Tavgeniene
  Saulius Grigalevicius

- **The University of Tokyo**
  Takeru Bessho
  Hiroshi Segawa

- **Fudan University**
  Shuzhang Yang

- **Chinese Academy of Sciences**
  Qingqing Miao

- **High Energy Accelerator Research Organization**
  Kenichi Ozawa

- **Kyushu Institute of Technology**
  Tingli Ma

- **University of Tsukuba**
  Namiki Uezono, Takeaki Sakurai

- **Funding**

NEDO New Energy and Industrial Technology Development Organization

JST 国立研究開発法人 科学技術振興機構 Japan Science and Technology Agency

Content

1. Introduction: Comparison of Tin Perovskite solar cells and Lead perovskite solar cells

2. Halide Tin perovskite solar cells

3. Halide Tin Lead alloyed perovskite solar cells

4. Perovskite tandem solar cells

5. Conclusion

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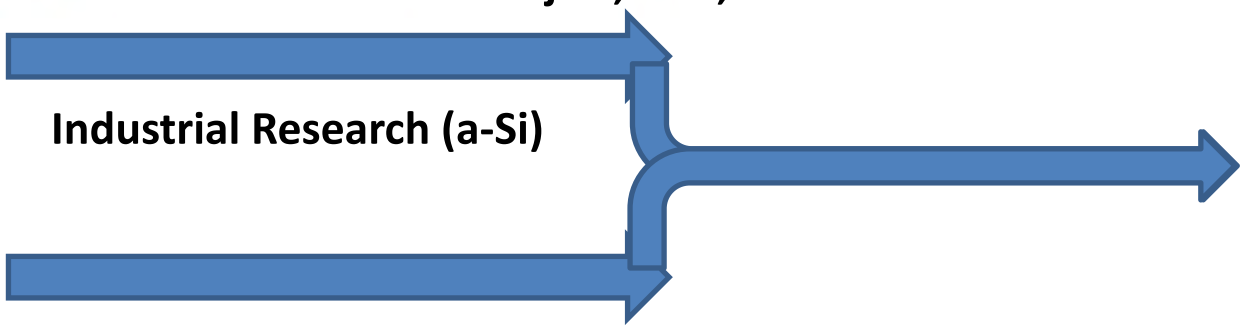
Introduction of our research

a-Si

Collaboration with Fujico, CKD, Ushio



Industrial Research (a-Si)

Fundamental Research

Flexible solar cell

- **Dye-sensitized solar cells**
- **Perovskite solar cells**

Semi-flexible cylindrical solar cells with flexible a-Si sheet (Demonstration Experiment)

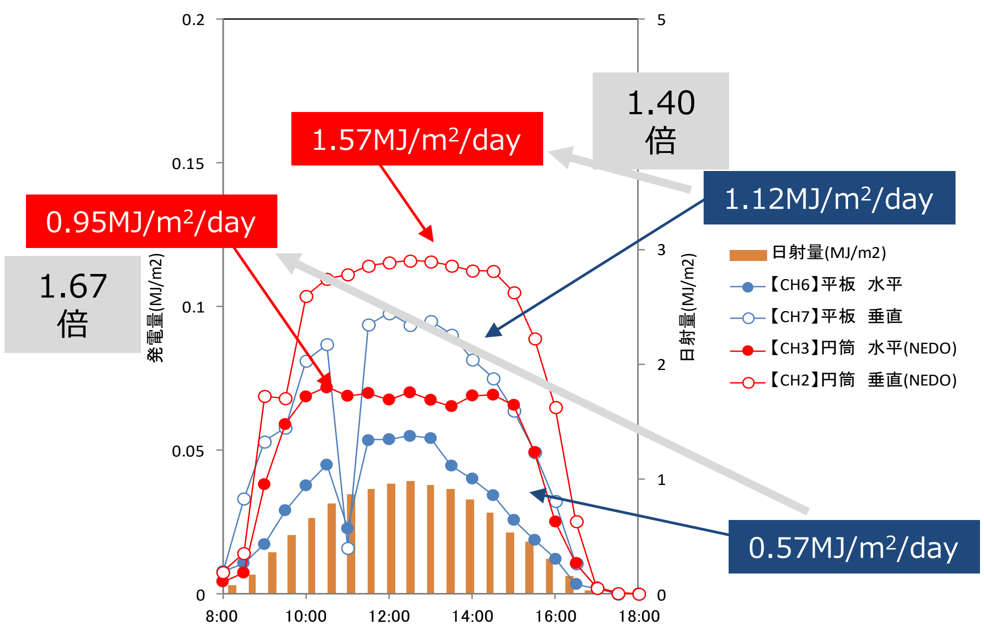
Agri photovoltaics

Started from 2005
Cylindrical Dye-sensitized solar cells→
Cylindrical a-Si soalr cells →
Cylindrical perovskite solar cells

<u>Fundamental research: DSSC(1995), Perovskite: (2015)</u>

Collaboration: Fujico Co. Ltd, CKD Co., Ushio Inc

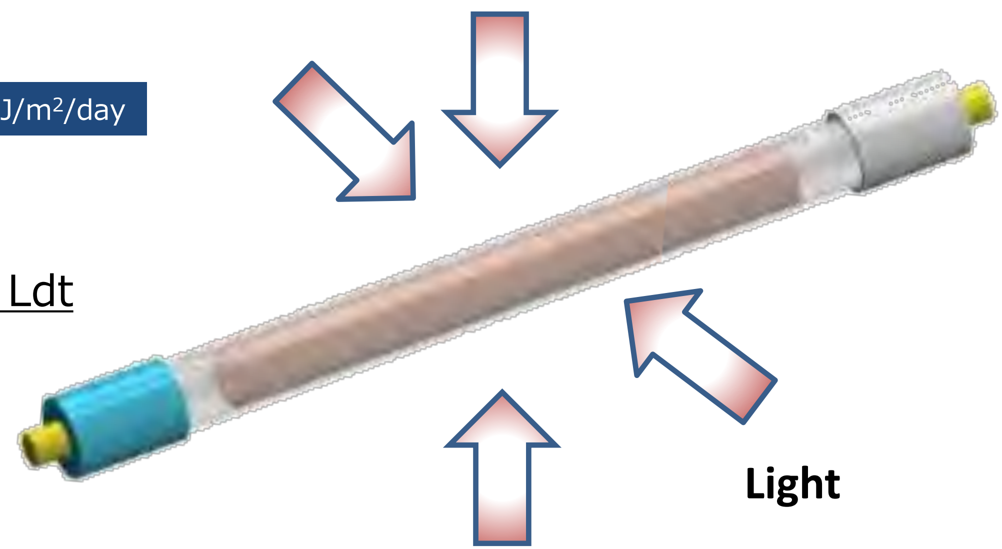
Advantage of cylindrical solar cells with plastic photoconcersion layer



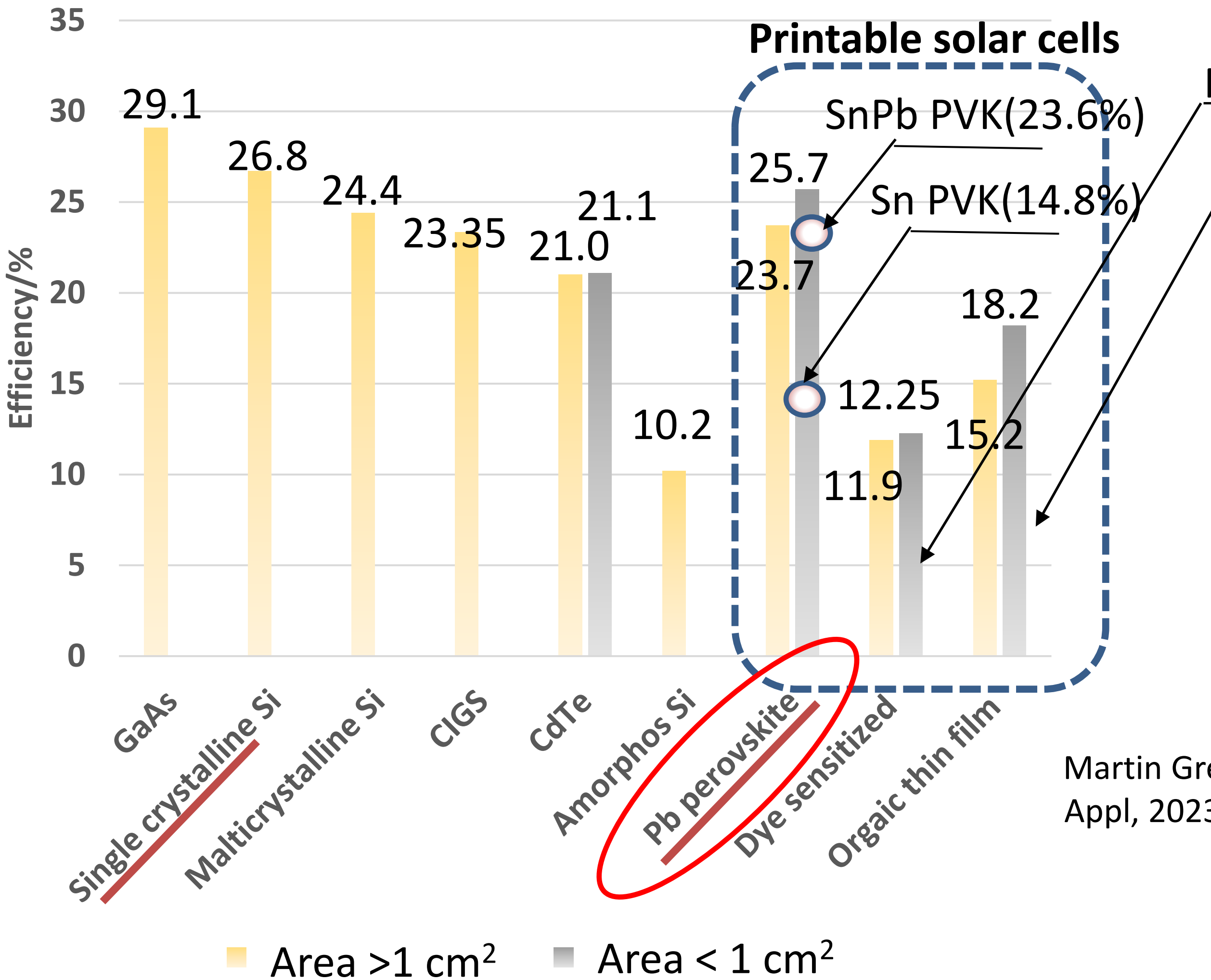
- Light weight
- Perfect glass sealing (High stability)
- Large total power generation in a day

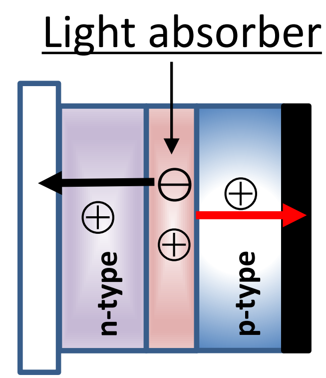
<u>2021/1/42021年　by Fijico co. Ldt</u>

全天日射量：11.09MJ/m²/day



Certified efficiency for various solar cells

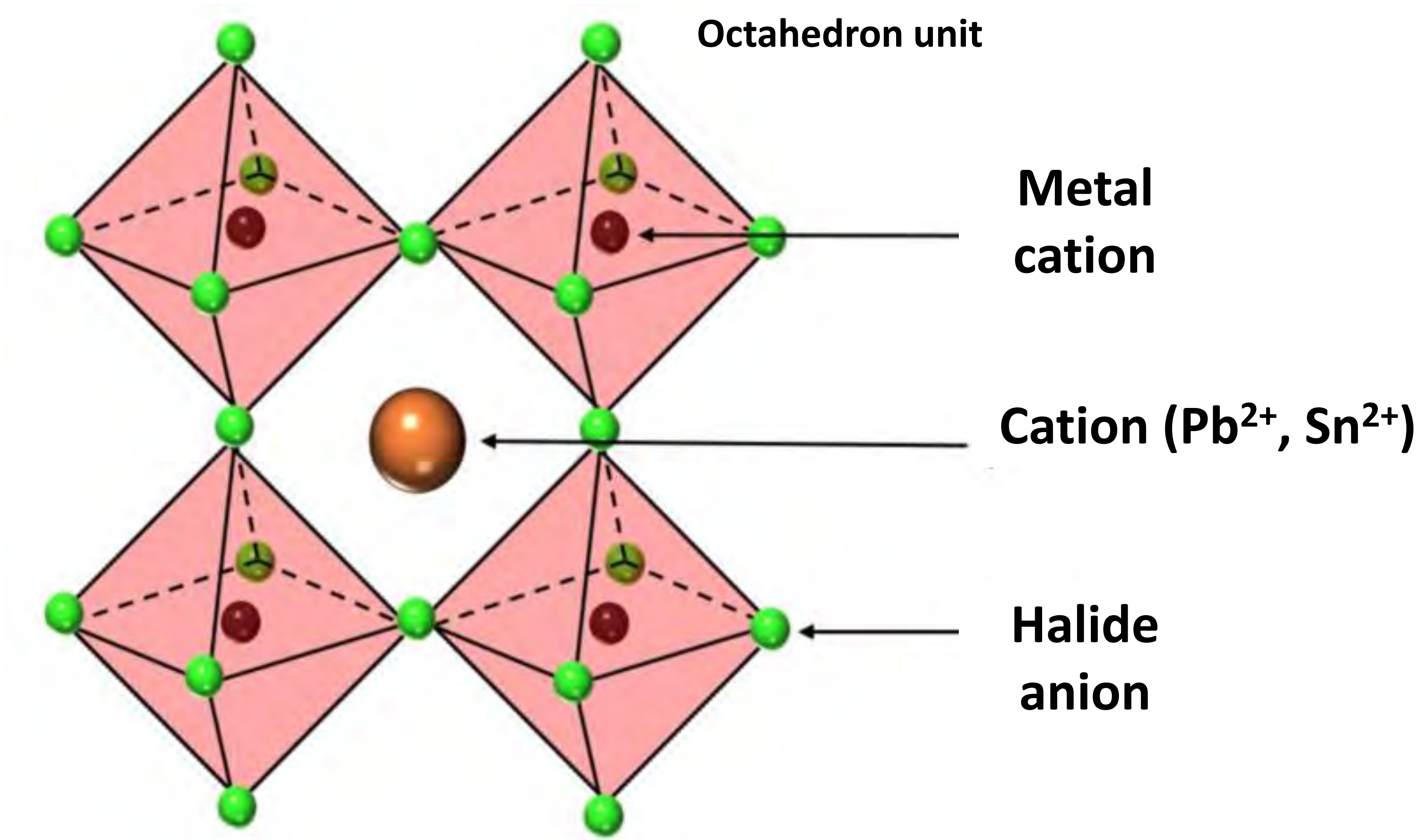




Martin Green, et al., Prog Photovolt Res Appl, 2023, 31, 3-16, Efficiency Table 61

The efficiency of PVK is close to that of the Si solar cell even though the cell is prepared at 100 ℃ process.

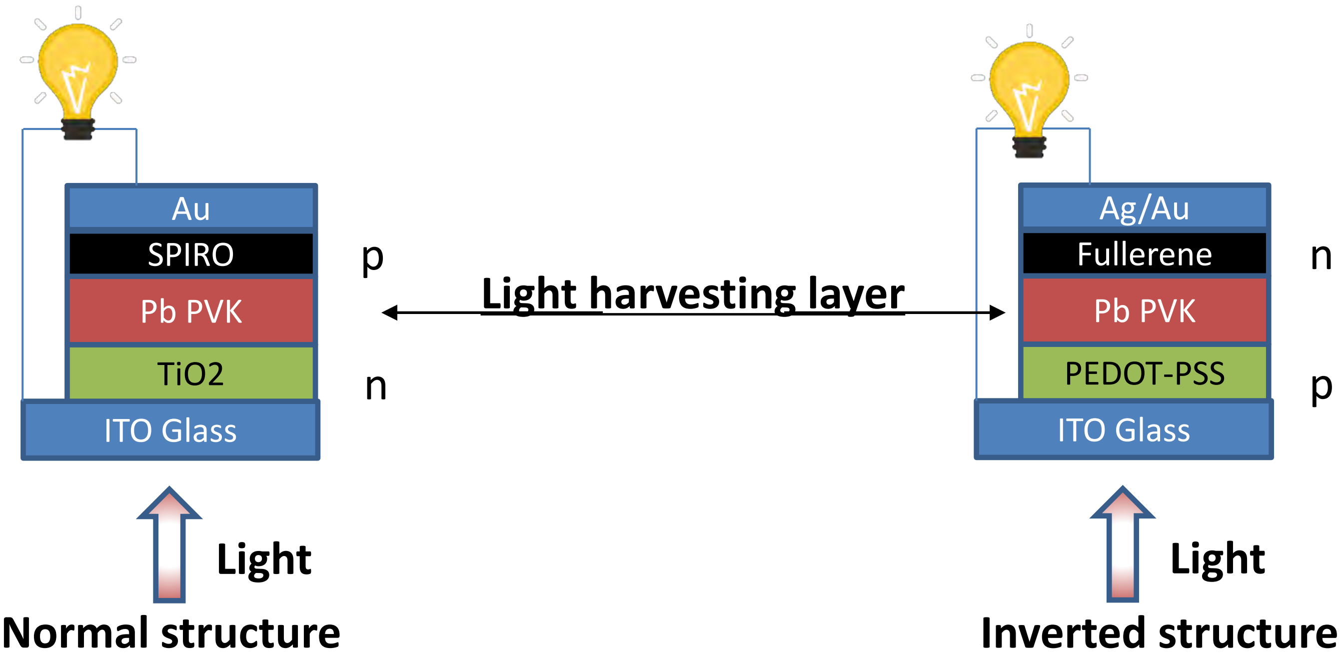
Halide perovskite

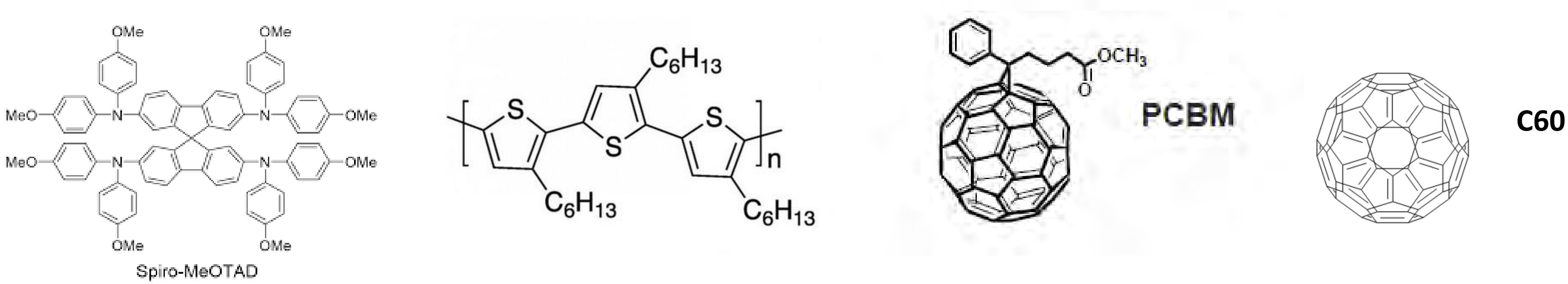


ABX_3: A (Cation, Cs^+, MA^+, etc), B (Pb^{2+} Sn^{2+}); X (I^-, Br^-)

Tin PVK has structure similar to Lead PVK

Two types of perovskite solar cell structures





Pb-PVK PV: Normal (25.7%)> Inverted(25%)

Sn-PVK-PV: Normal(5%) <<<<Inverted(14.8%)

Titania surface passivation (less trap density)

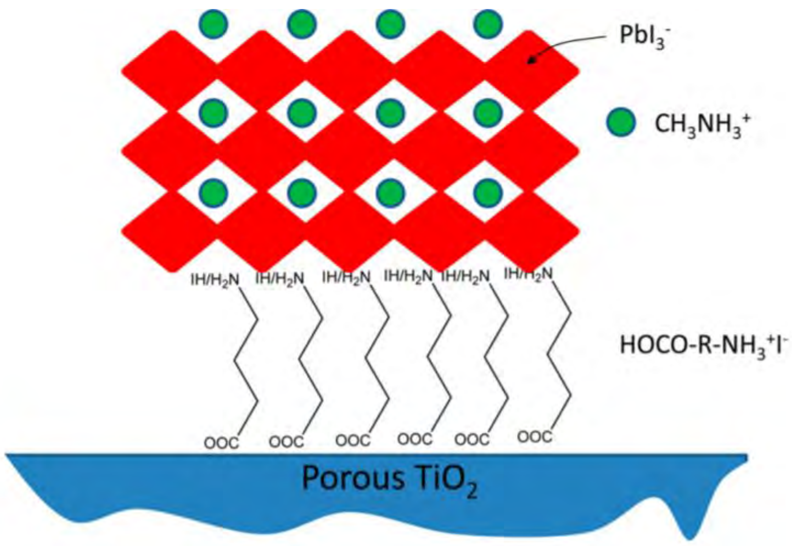
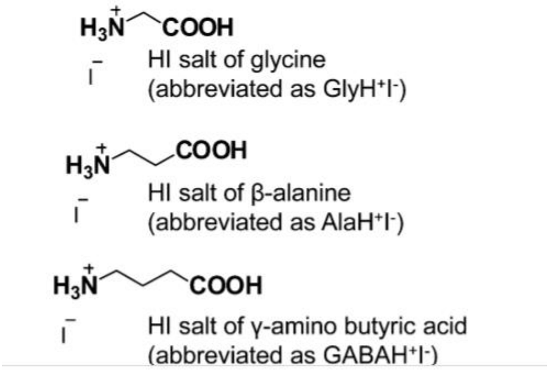
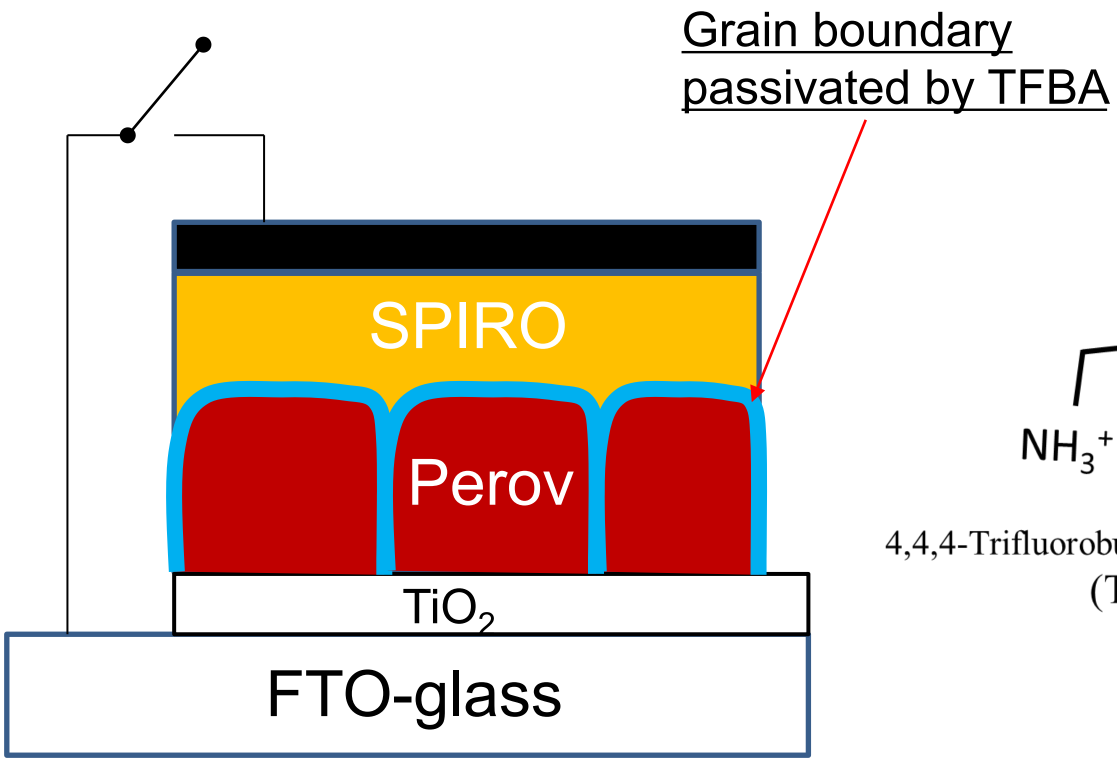


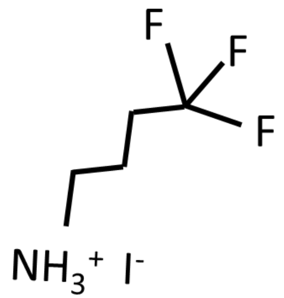
Figure 1. Structure of titania anode where $HOCO\text{-}R\text{-}NH_3^+$ was inserted between perovskite and porous titania.



Ogomi, Y., Morita, A., Tsukamoto, S., Saitho, T., Shen, Q., Toyoda, T., Yoshino, K., Pandey, S.S., Ma, T., Hayase, S., All-solid perovskite solar cells with HOCO-R-NH3+I-anchor-group inserted between porous titania and perovskite, Journal of Physical Chemistry C, 118, p.16651-16659, 2014.

Grain boundary passivation



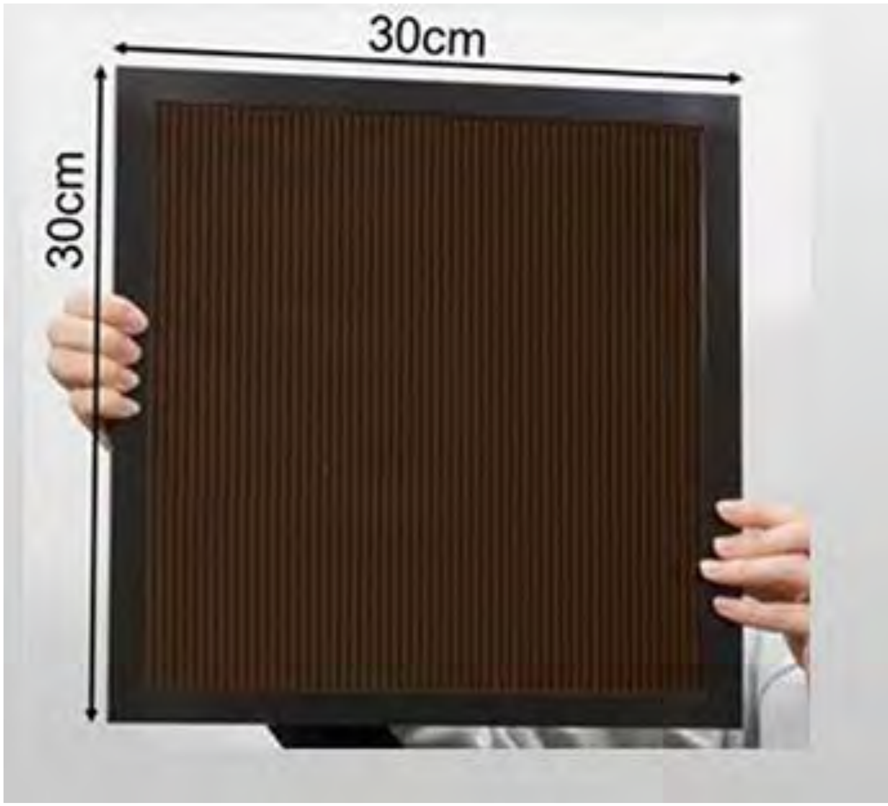


4,4,4-Trifluorobutylamine hydroiodide
(TFBA)

ChemSusChem, 9, p.2634-2639, 2016.

Grain boundary may be passivated by TFBA

Fabrication of Pb perovskite solar cells with large area

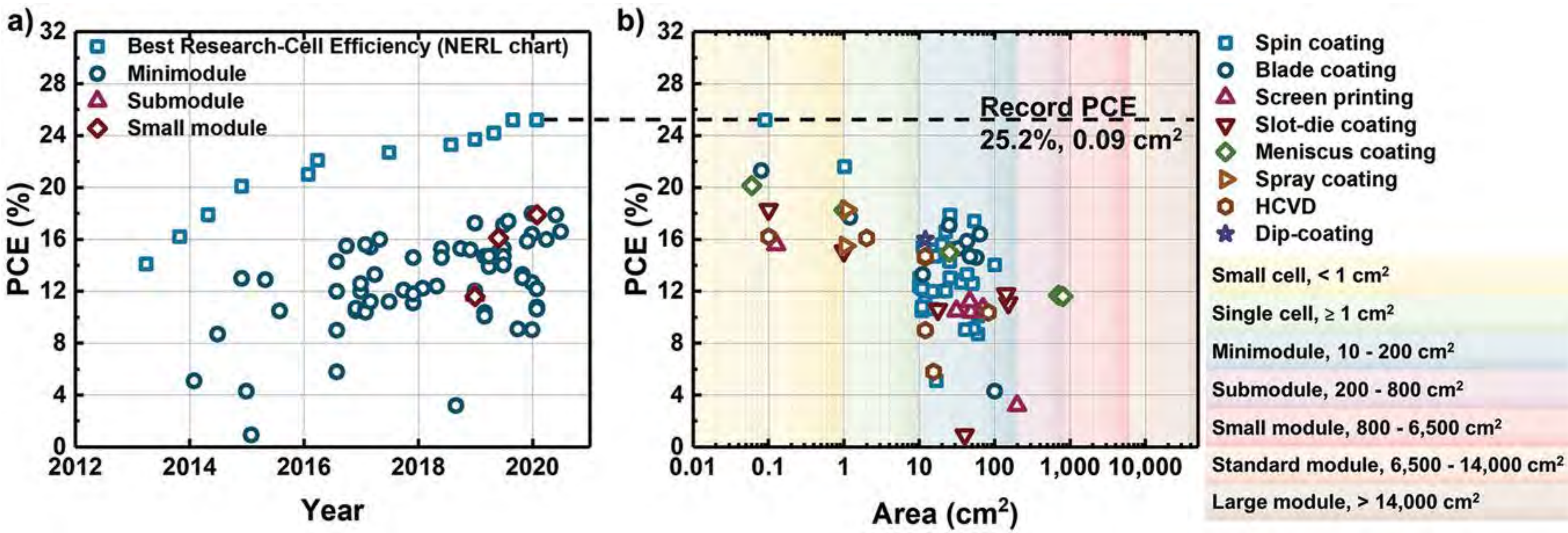


https://www.panasonic.com/jp/corporate/sustainability/eco/communication/ecopro2020/perovskite.html

Panasonic corporation: Prepared by ink-jet printing technology （Aperture size 802 cm^2：30 cm × 30 cm × 2 mm）, Certified efficiency 16.09**%**.

⇒Improved to 17.9% with 804 cm2 (55cells) (Highest certified efficiency)
Martin Green, et al., Prog Photovolt. Res. Appl., 2022;30:687–701.Efficiency Table 60.

Relationship between efficiency and cell area



Sang-Won Lee, et al., Adv. Mater. 2020, 32, 2002202

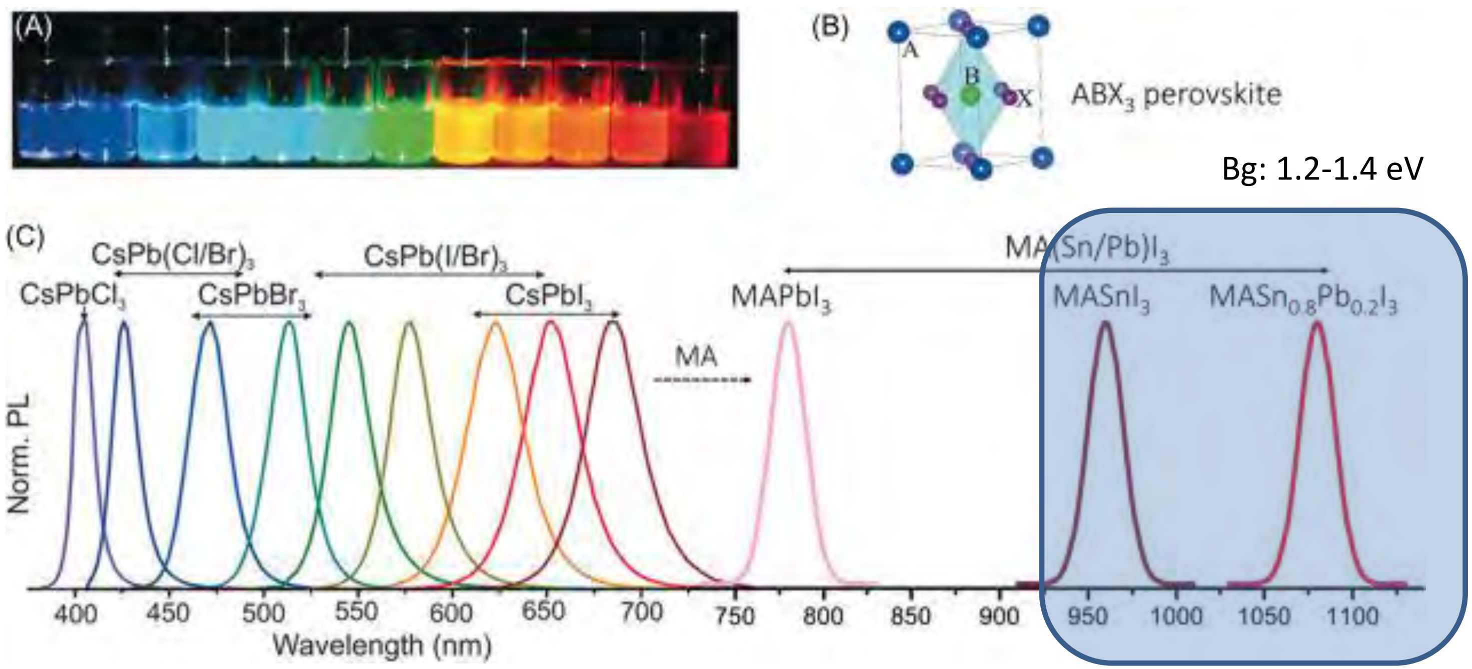
Comparison of Pb perovskite solar cell with conventional Si solar cell

Solar cell	Light harvesting layer	Certified efficiency	Starting material	Crystallization	Substrate
Pb perovskite PV	Perovskite (0.5-1.0μm)	25.7%	Perovskite ink	100℃ （Coating）	Plastic substrate （Light and flexible） （1-4kg/m^2）
Single crystalline Si PV	Si (100-200μm)	26.7%	Si	1500℃ （Crystallization）	With glass (12-15kg/m^2)

The efficiency of the perovskite solar cells crystallized at low temperature-coating process is catching up that of Silicon solar cells crystalized and purified at high temperature.

Band gap control

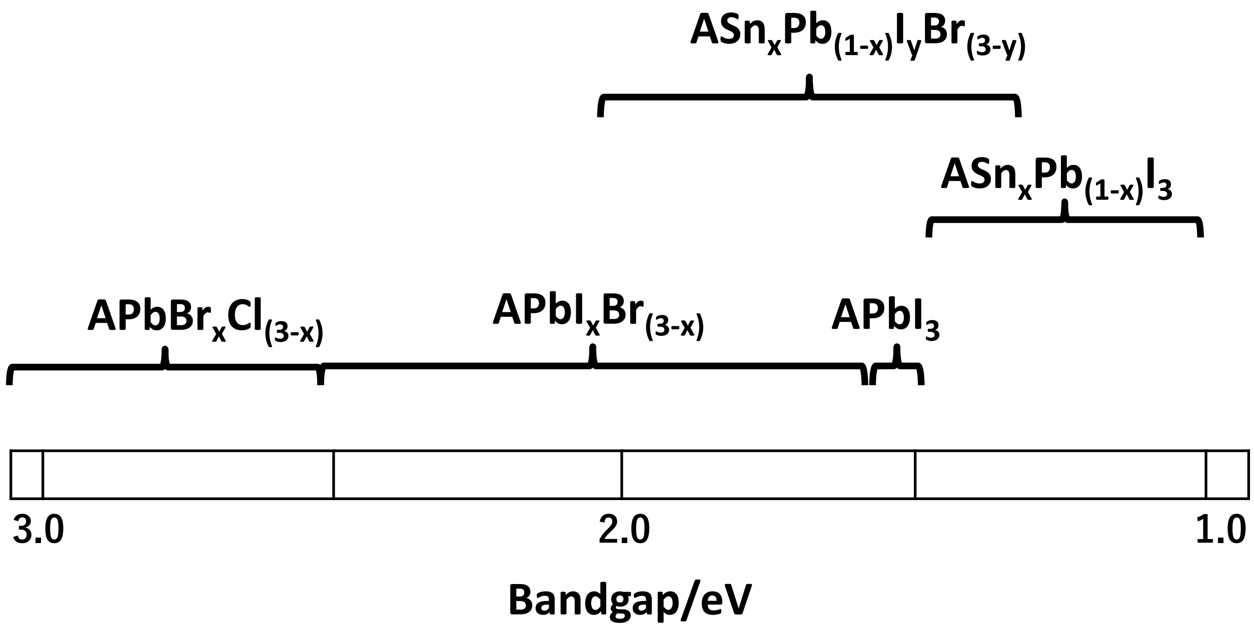
Characterization Techniques for Perovskite Solar Cell Materials, Micro and Nano Technologies, 2020, Pages 1-22
Somayeh Gholipour, Michae lSaliba, https://doi.org/10.1016/B978-0-12-814727-6.00001-3



Top cell Bottom cell

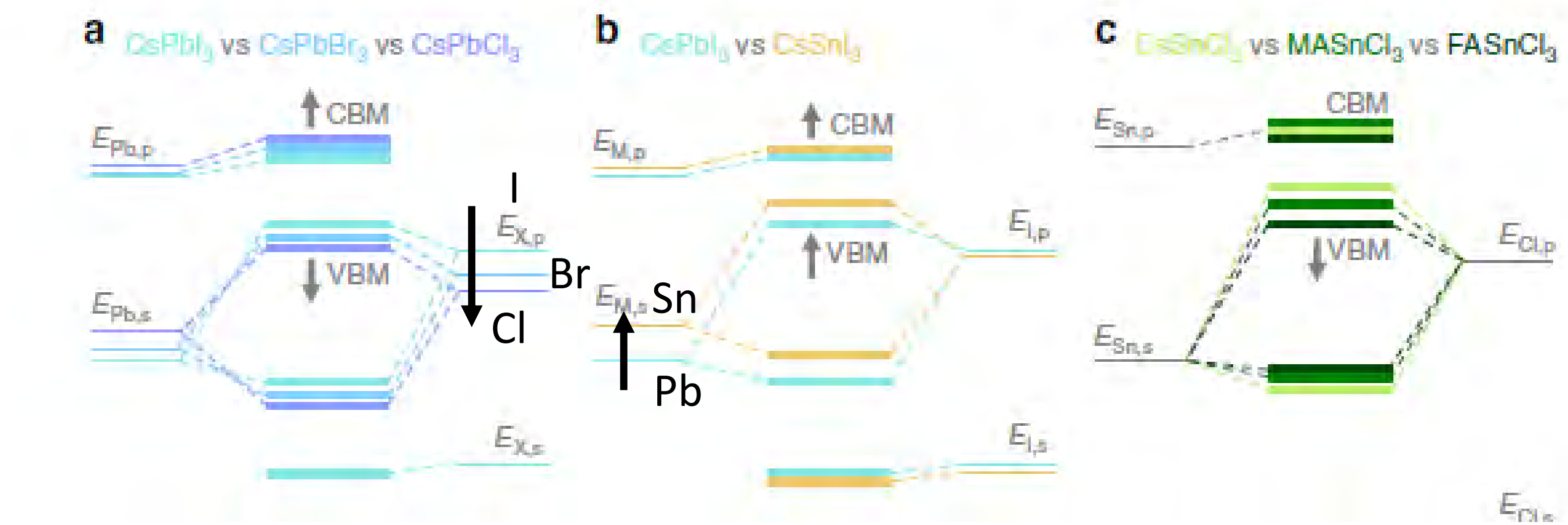
- **Pb perovskite: APbX3: A site:Large size ⇒Narrow band gap**
  X site: Br substitution⇒wide band gap
- **Sn perovskite: ASnX3: A site: Large size ⇒Wide band gap**
  X site: Br substitution⇒wide band gap

Band gap control



Band gap control

$CsPbI_3 \rightarrow CsPbBr_3 \rightarrow CsPbCl_3$ $CsPbI_3 \rightarrow CsSnCl_3$ $CsSnCl_3 \rightarrow MASnCl_3 \rightarrow FAPbCl_3$

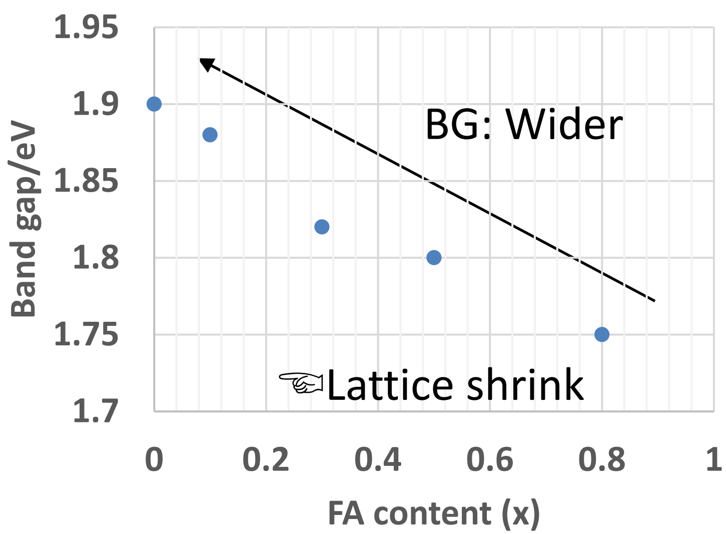


Absolute energy level positions in tin and lead-based halide perovskites
Shuxia Tao, Ines Schmidt, Geert Brocks, Junke Jiang, Ionut Tranca, Klaus Meerholz & Selina Olthof, Nature Communication, 2019, 10, 2560.

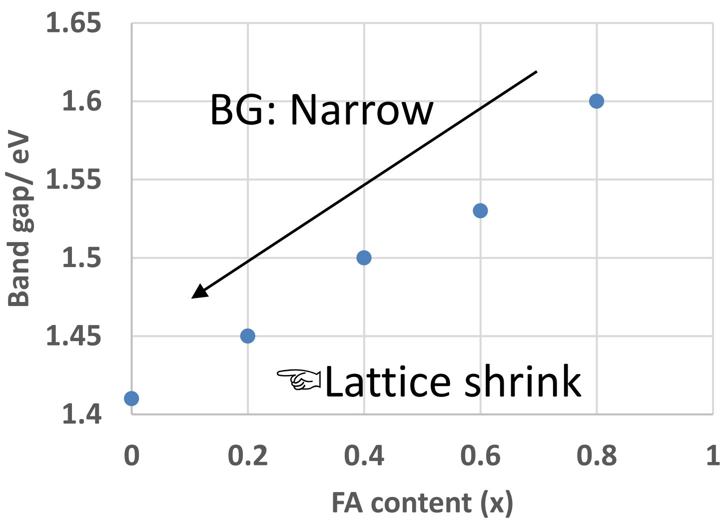
X dependence on band gap: $FA_xCs_{(1-x)}MI_2Br$

211010EXL

$FA_xCs_{(1-x)}$PbI$_2$Br



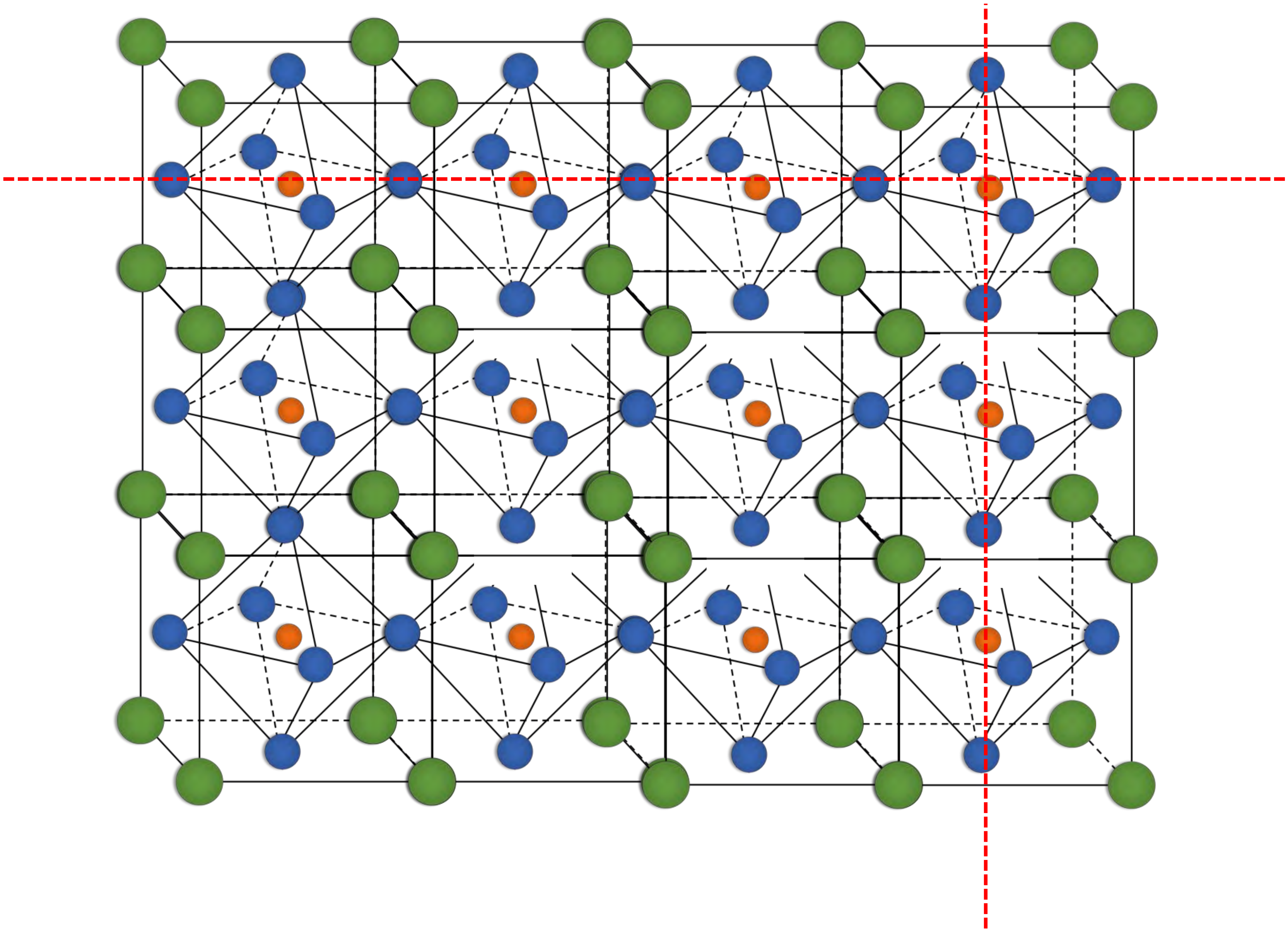
$FA_xCs_{(1-x)}$SnI$_2$Br



Pb perovskite: APbX3:
Small size A site⇒Wide band gap

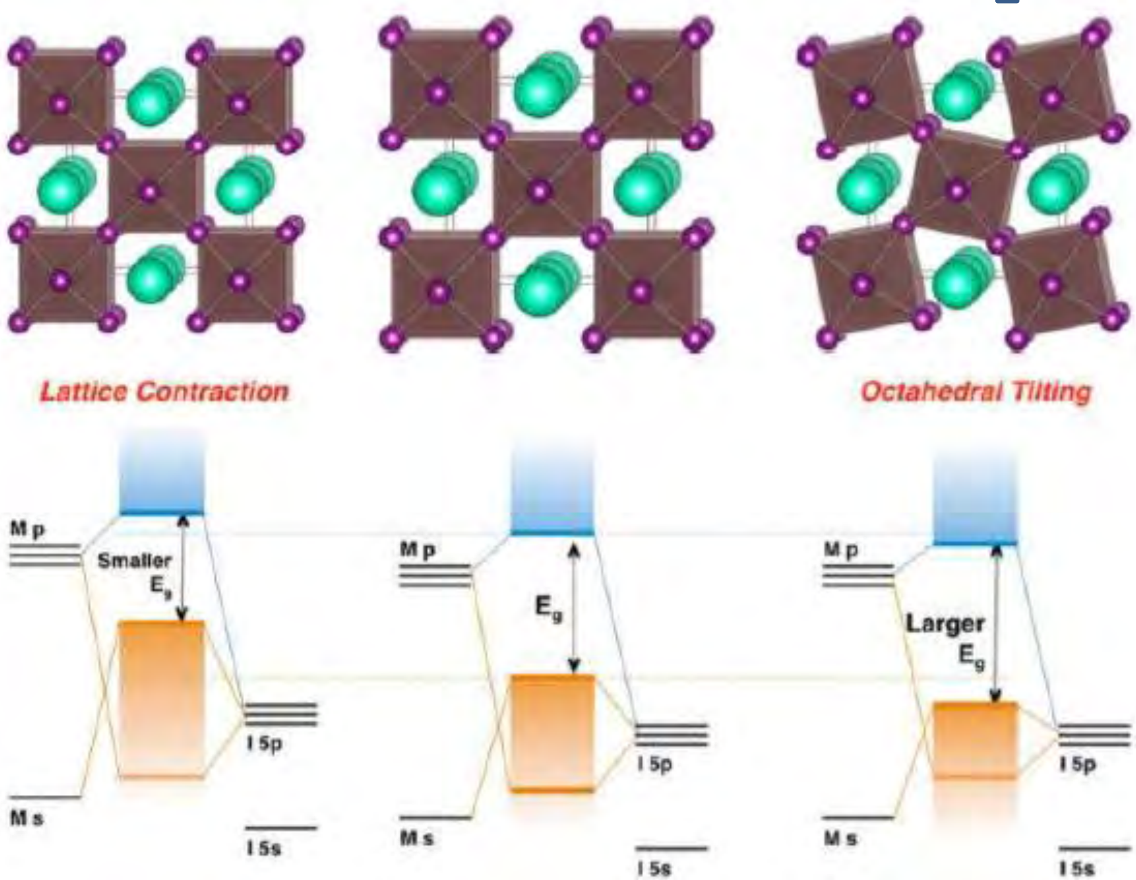
Sn perovskite: ASnX3:
Small A site⇒Narrow band gap

Perovskite ($MAPbI_3$) structure (-Pb-I-Pb-I- arrangement)



Relationship between tilting and contraction of lattice

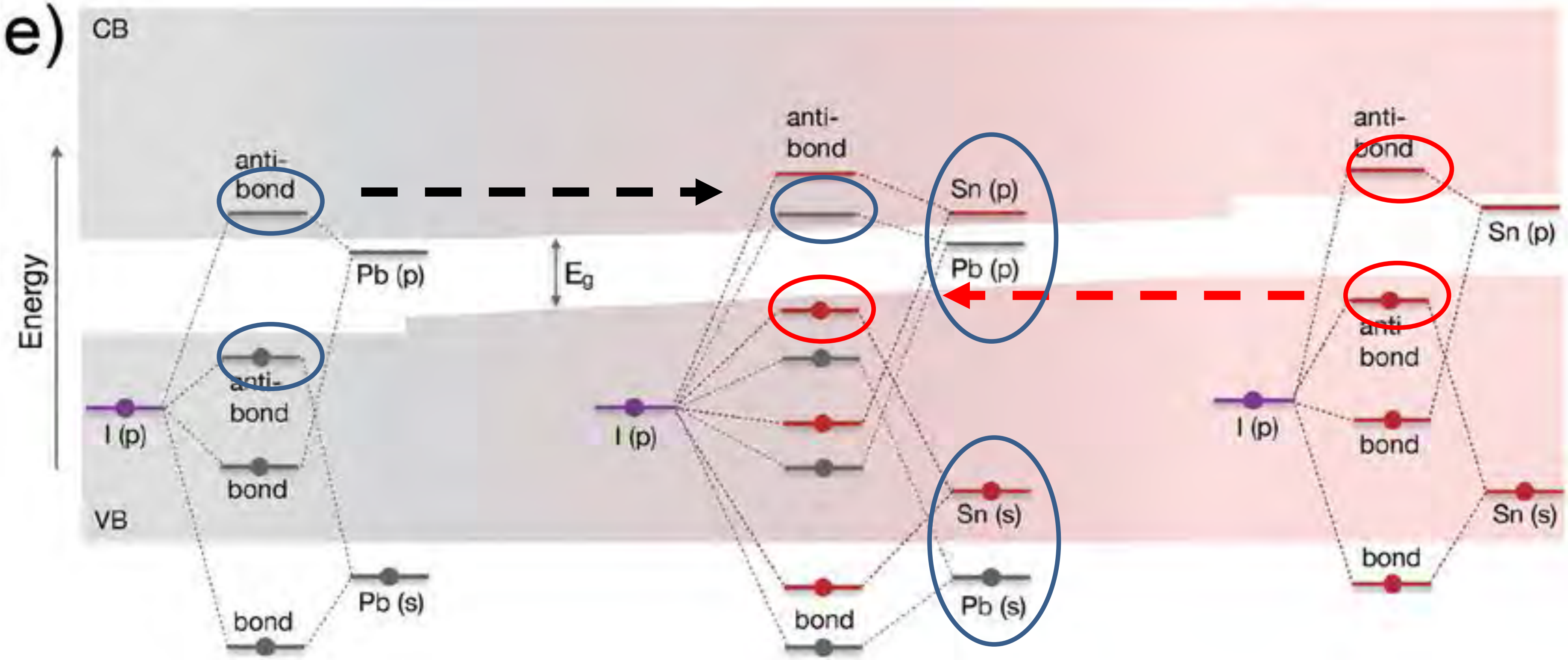
Sn PVK:
Introduction of
small size ions
⇓
Contraction of lattice size
⇓
Strong interaction of I-Pb orbital
⇓
leading to Shallow band energy and narrow bandgap.



Pb PVK:
Introduction of small size ions
⇓
Lattice tilting
⇓
weak interaction of I-Pb orbital
⇓
leading to deep band energy and wide bandgap.

Rohit Prasanna, Aryeh Gold-Parker, Tomas Leijtens, Bert Conings, Aslihan Babayigit, Hans-Gerd Boyen, Michael F. Toney, and Michael D. McGehee, . Am. Chem. Soc. 2017, 139, 11117—11124

Why is the bandgap of SnPb PVK narrower than Sn PVK?



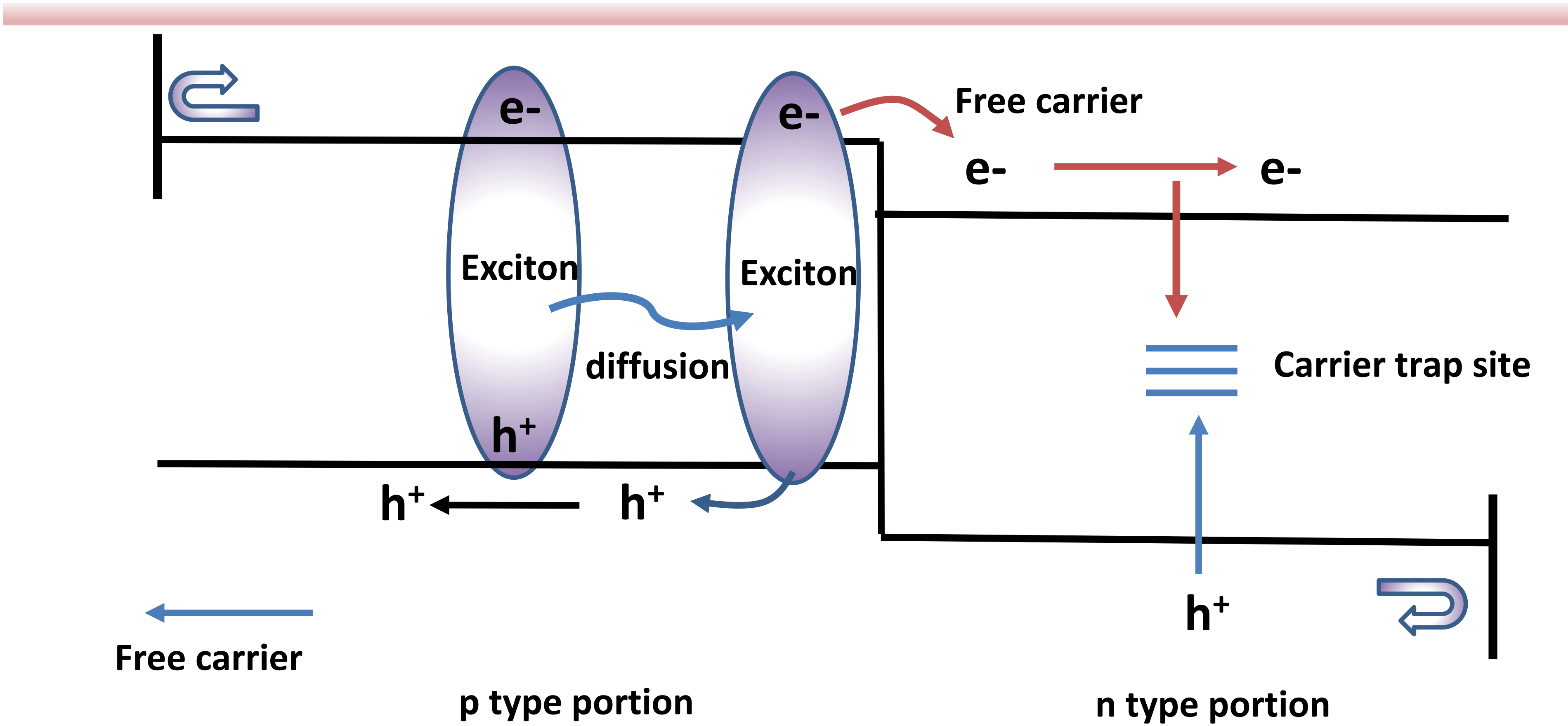
CVM: Antibonding from Pb PVK
VBM: :Antibonding from Pb PVK

CVM: Antibonding from Pb PVK
VBM: :Antibonding from Sn PVK

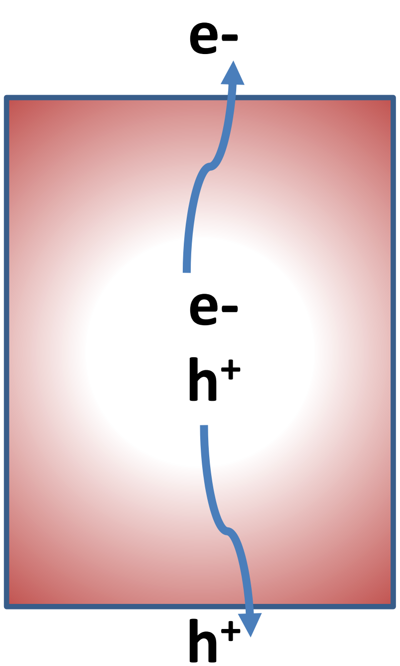
CVM: Antibonding from Sn PVK
VBM: :Antibonding from Sn PVK

Origin of Pronounced Nonlinear Band Gap Behavior in Lead−TinHybrid Perovskite Alloys
Anuj Goyal, Scott McKechnie, Dimitar Pashov, William Tumas, Mark van Schilfgaarde, and Vladan Stevanović, Chem. Mater. 2018, 30, 3920−3928

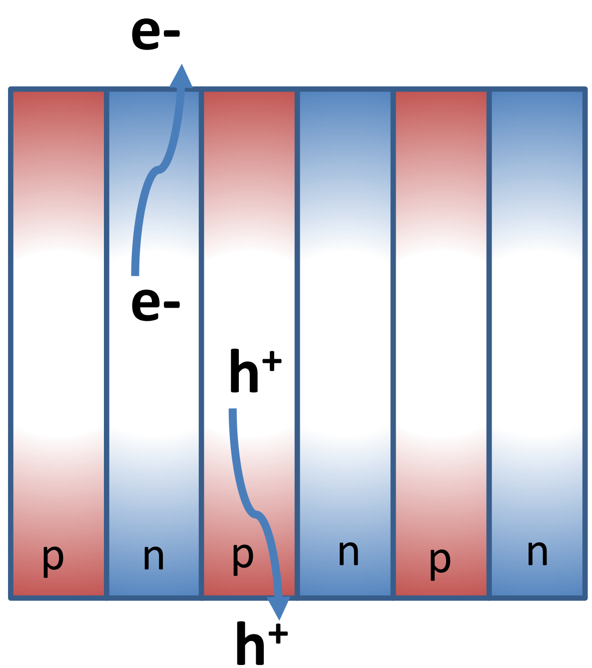
Carrier genaration and collection



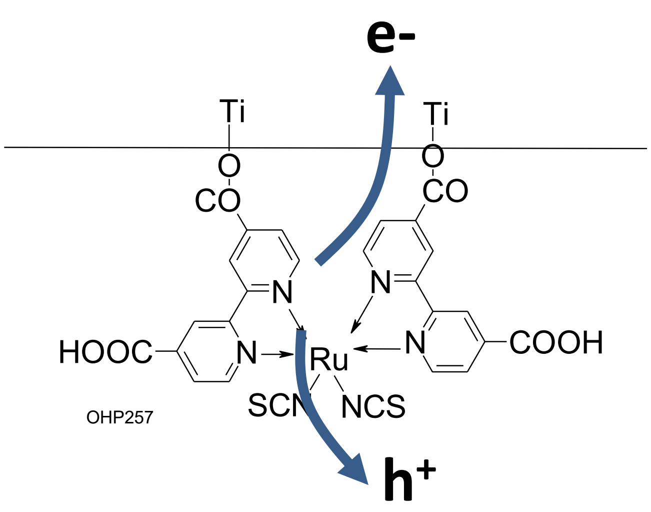
Carrier genaration and collection



a) Perovskite LHL in perovskite solar cells

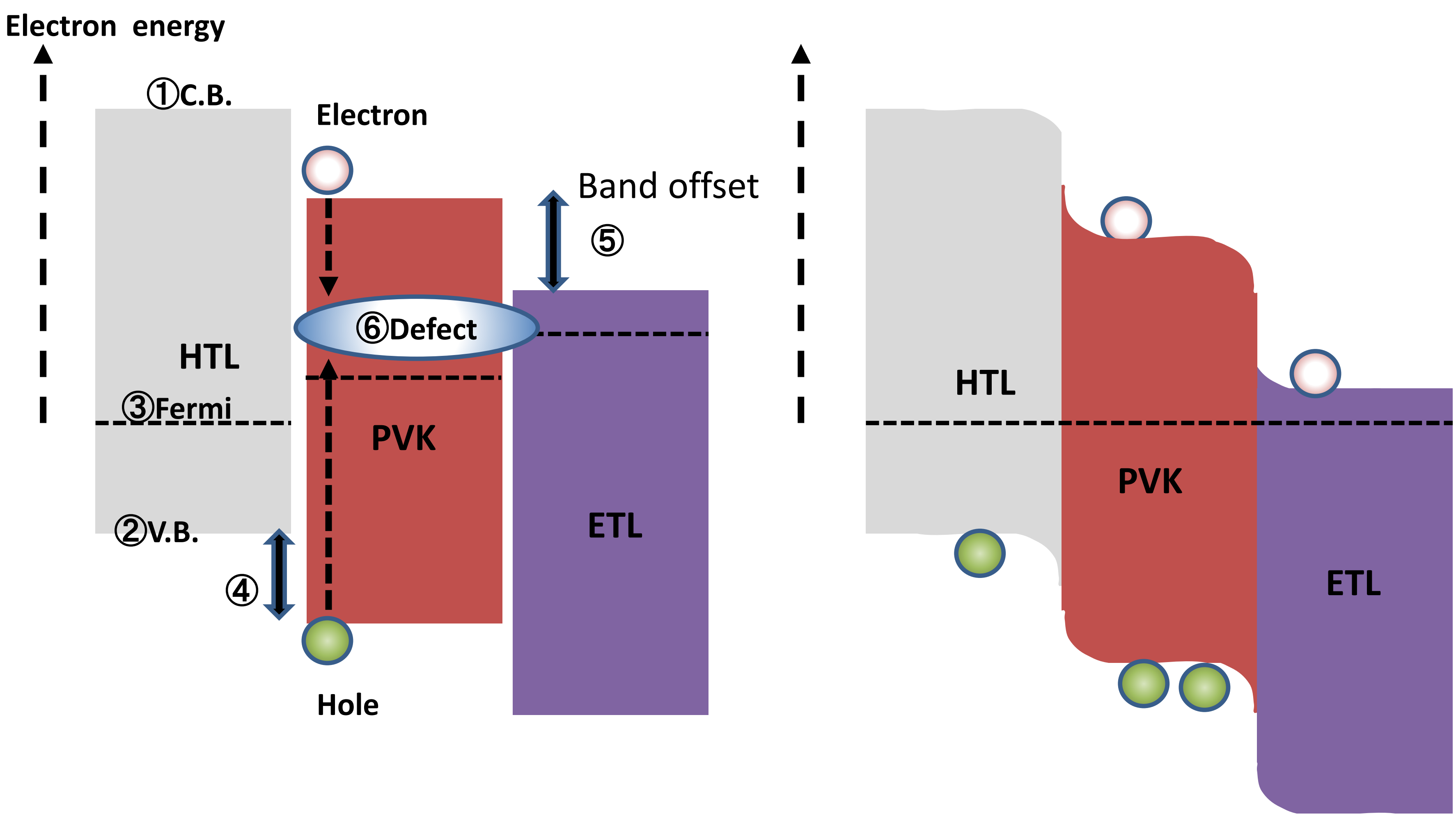


b) Bulk hetero LHL in organic thin film solar cells

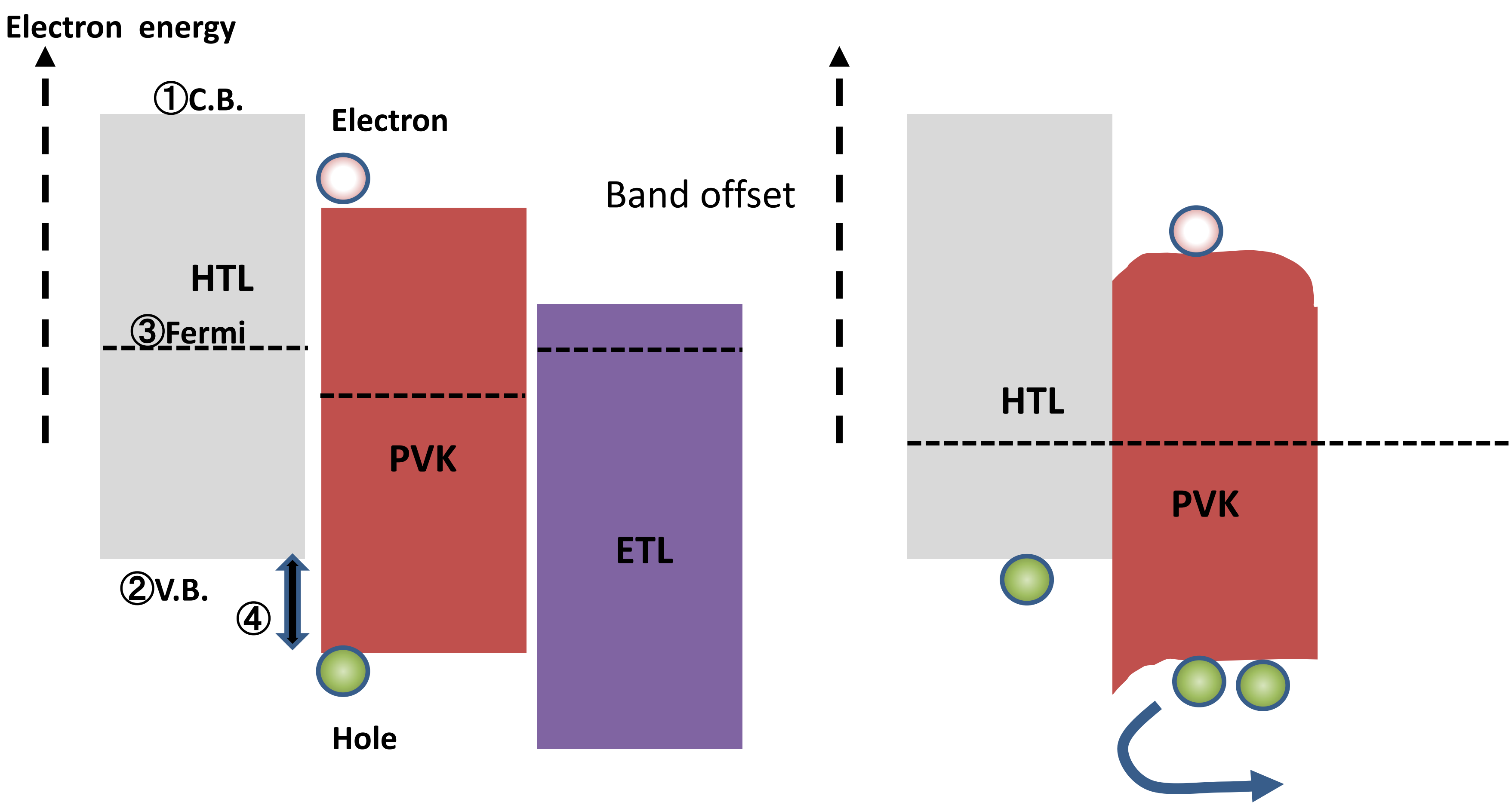


c) Dye LHL in DSSC

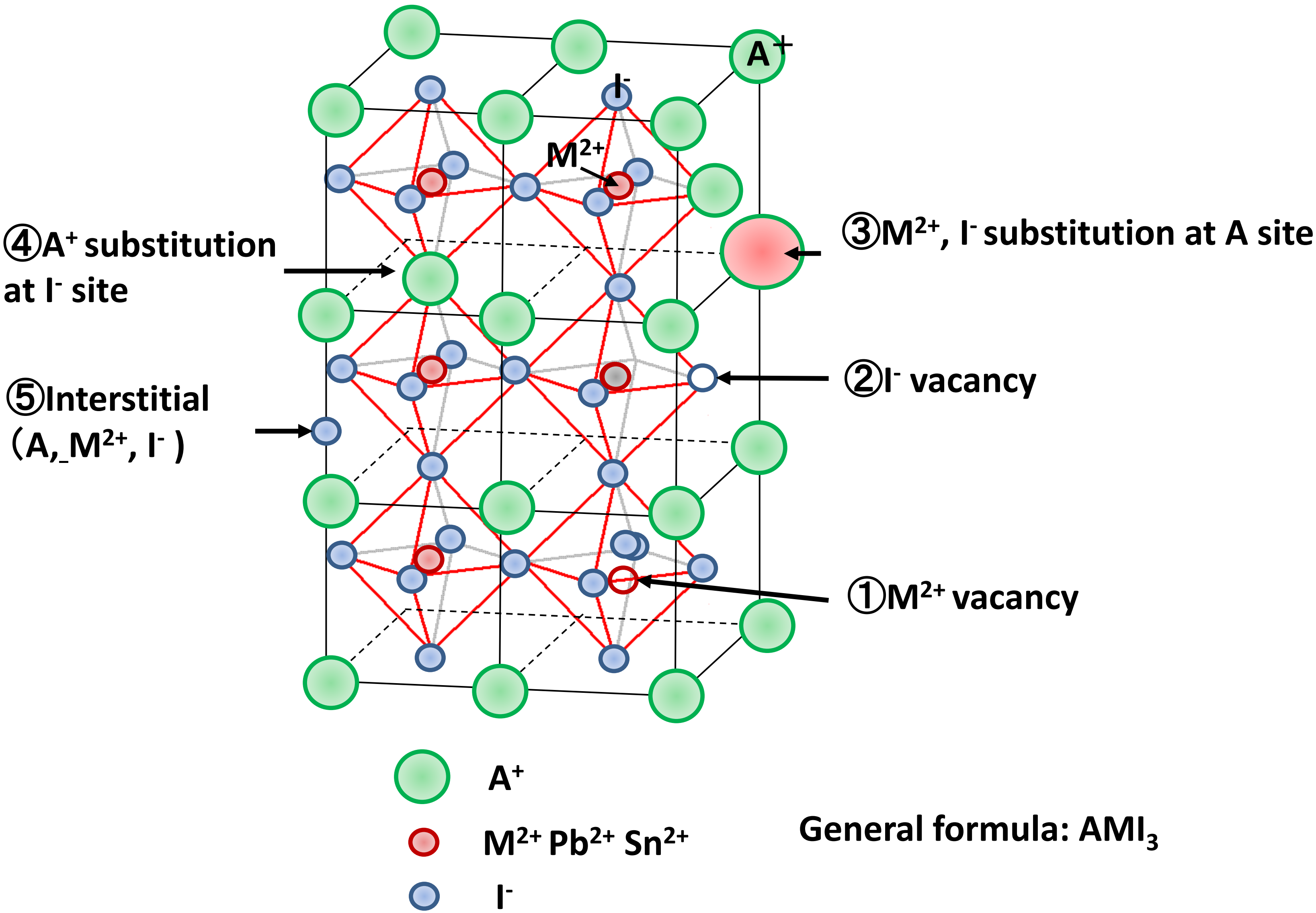
Gereral items for enhancing solar cell efficiency



Gereral items for enhancing solar cell efficiency



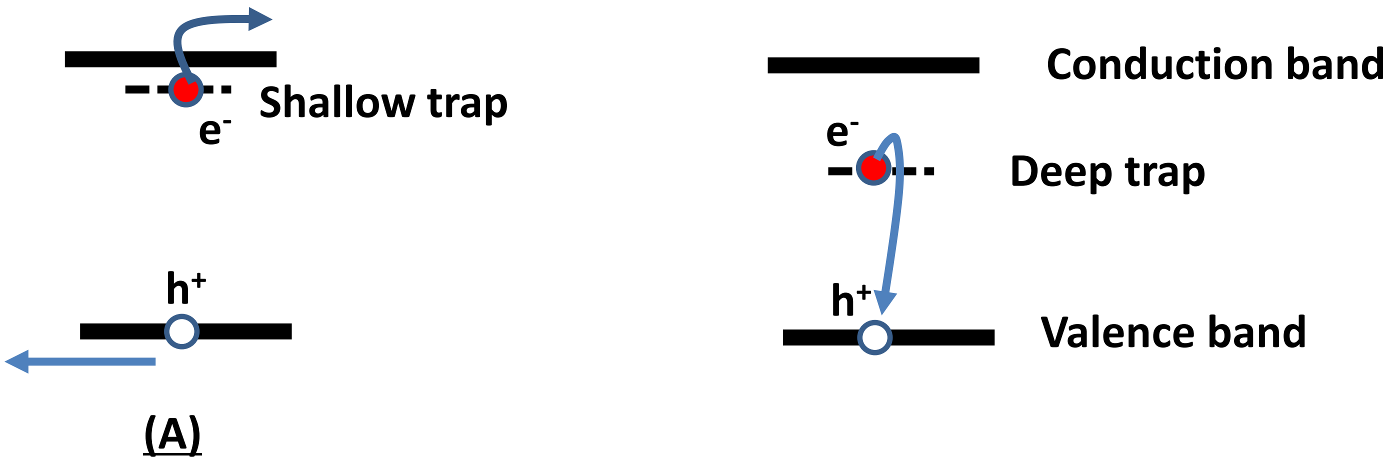
Defects in metal perovskite



General formula: AMI_3

Carrier trap depth and defect formation energy

Low defect formation energy and deep trap causes serious efficiency decrease



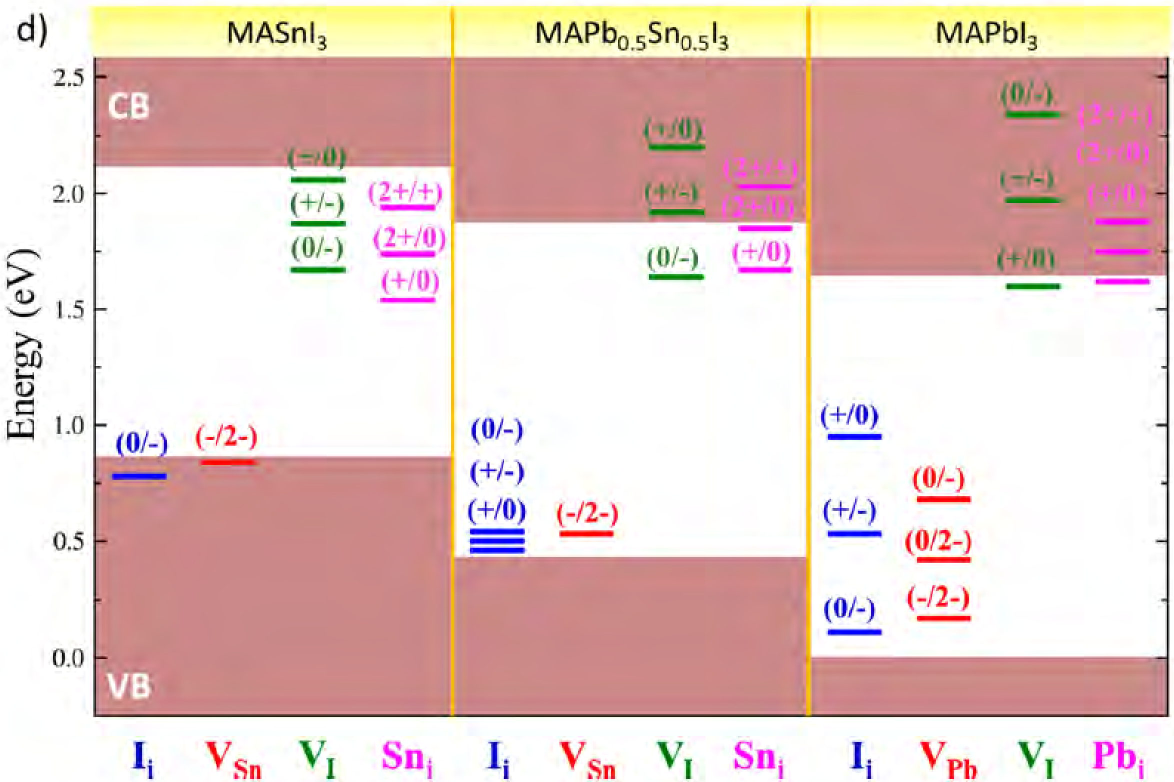
Trapped charge can be escaped

Carrier recombination occurs

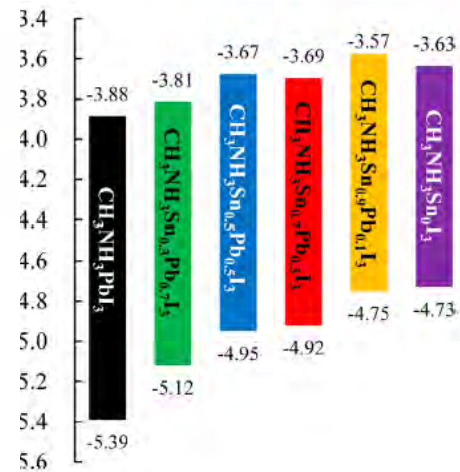
Defect energy level for $MAPbI_3$ MASnPb and $MASnI_3$

(Heat of formation and trap depth)

ABX3



Experimental results



Y. Ogomi, S. Hayase, et al.
I. Phys. Chem. Lett. 2014, 5, 1004-1011

Thermodynamically unstable (large formation energy)

Daniele Meggiolaro, Damiano Ricciarelli, Ahmed A. Alasmari, Fatmah A. S. Alasmary, and Filippo De Angelis, Journal of Physical Chemistry Letter, 2020, 11, 3546-3556

☐ Lead-free perovskite (without Sn based perovskite)

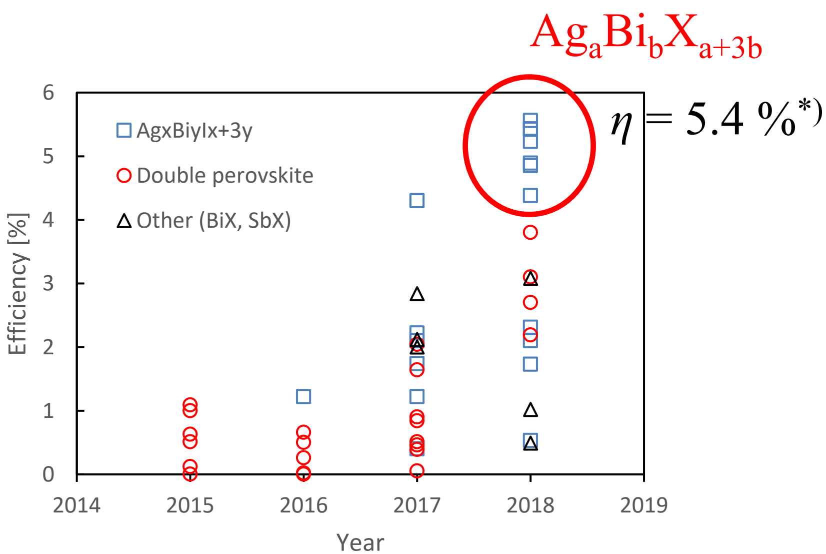
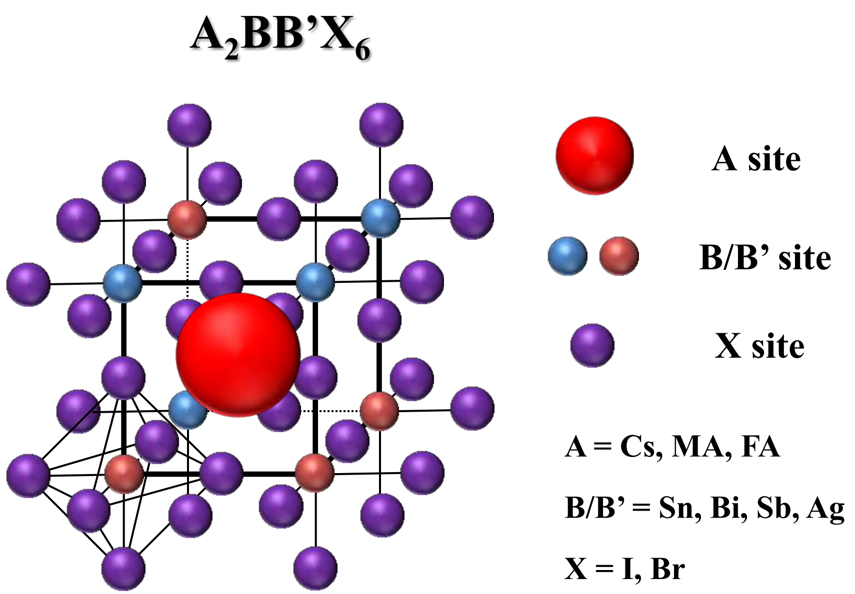


Fig. Changes of efficiency of lead-free double perovskite and silver bismuth solar cells by year.



*) Pai, N., Lu, J., Gengenbach, T. R., Seeber, A., Chesman, A. S. R., Jiang, L., … Simonov, A. N. (2018). Silver Bismuth Sulfoiodide Solar Cells: Tuning Optoelectronic Properties by Sulfide Modification for Enhanced Photovoltaic Performance. Advanced Energy Materials, 1803396. doi:10.1002/aenm.201803396

Summary

Tin perovskite vs. Lead perovskite

- Lead PVK PV：25.7%
- Tin PVK PV:14.8%
- Tin Lead alloyed PVK PV:23.8%

- Band gap of PVK covers 3 eV-1.2 eV

- Lead PVK PV is defect torelance properties

- To enhancement of Tin PVK PV efficiency, defects must be decreased.

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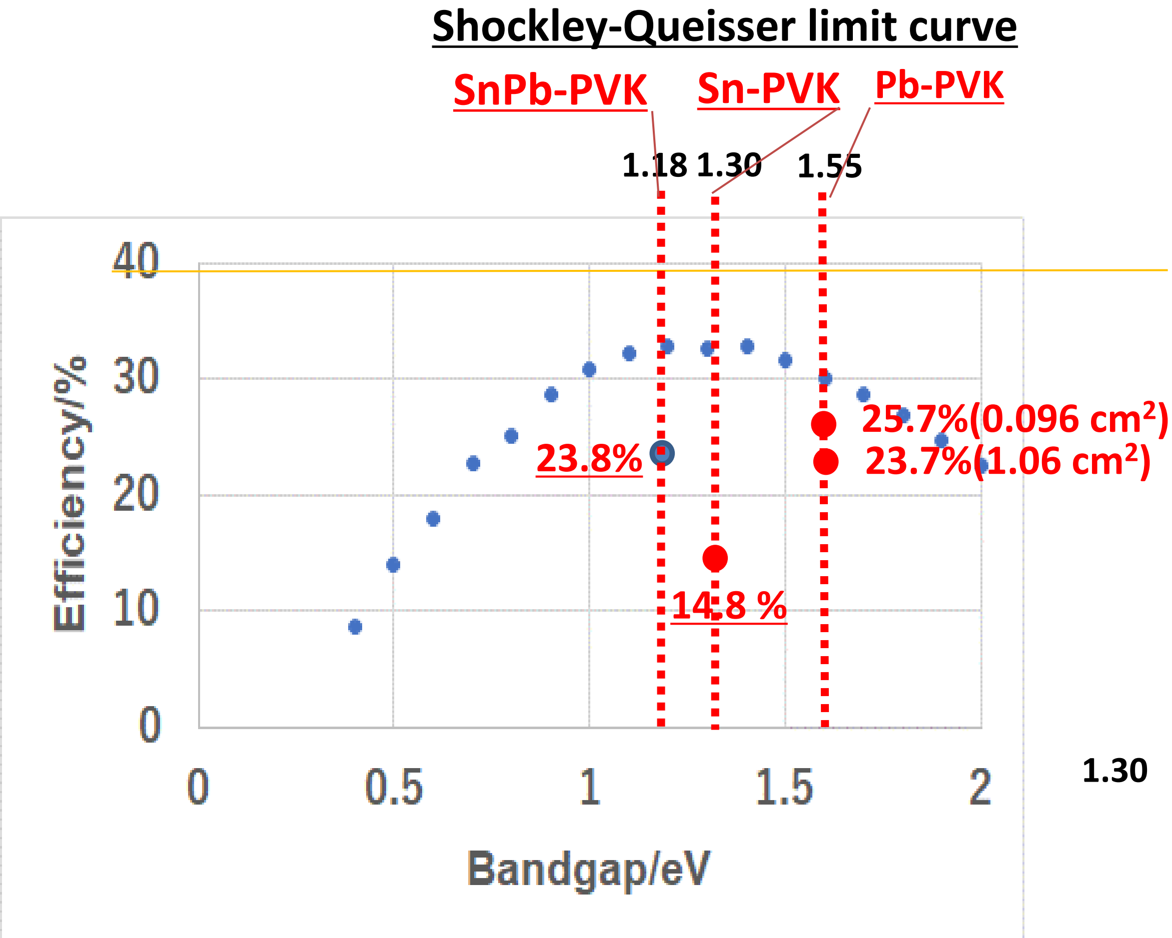
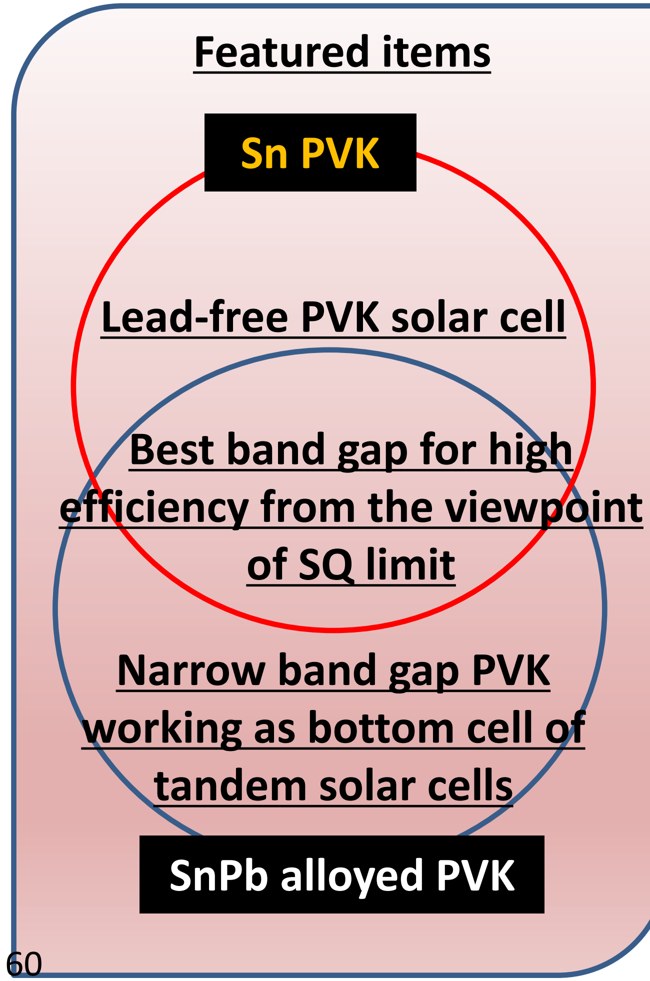
Featured items of Tin based perovskite solar cells

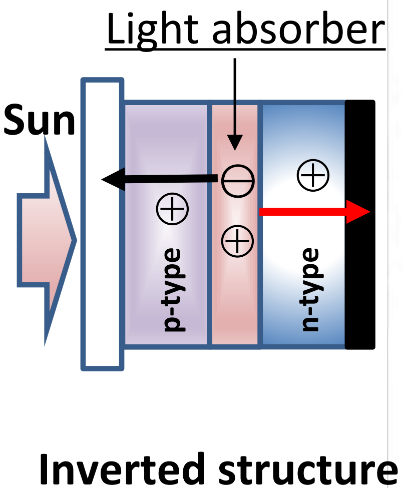


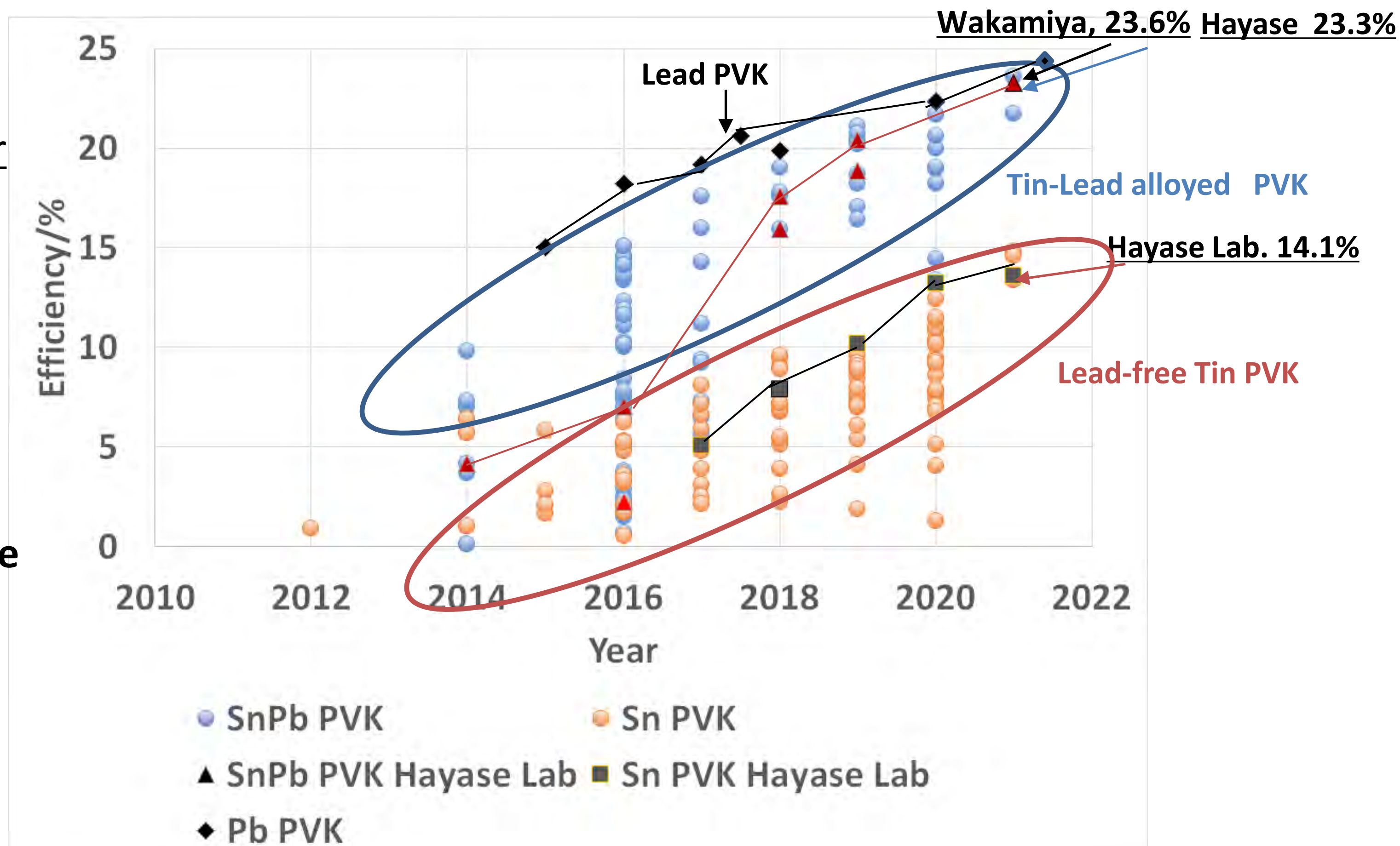
Martin Green, et al., Prog Photovolt Res Appl, 2022;30:687–701.. Efficiency Table 60



Theoretically, Tin and Tin-Lead alloyed perovskites have the best band gap for high efficiency cell. However, the efficiency was still low.

Efficiency trend for Tin and Tin-Lead alloyed perovskite solar cells (Inverted structure)





The efficiency of the Tin-Lead alloyed perovskite solar cell is almost the same as that of the Lead perovskite solar cell. The Lead-free Tin perovskite solar cell efficiency is 14-15% and is improving.

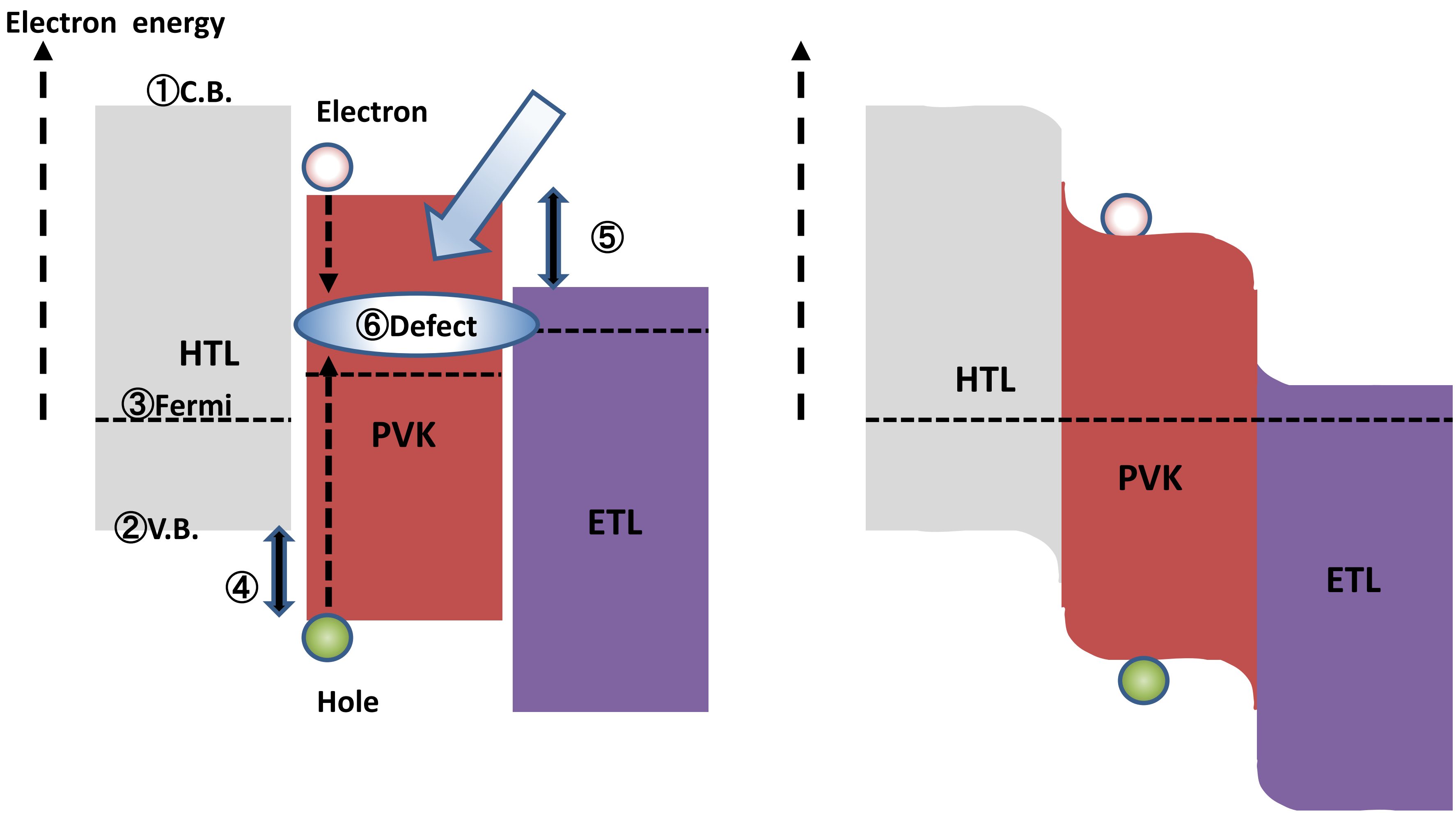
$CH_3NH_3Sn_xPb_{(1-x)}I_3$ Perovskite Solar Cells Covering up to 1060 nm

Yuhei Ogomi*†, Atsushi Morita†, Syota Tsukamoto†, Takahiro Saitho†, Naotaka Fujikawa†, Qing Shen‡∥, Taro Toyoda‡∥, Kenji Yoshino§∥, Shyam S. Pandey†, Tingli Ma†, and Shuzi Hayase*†∥

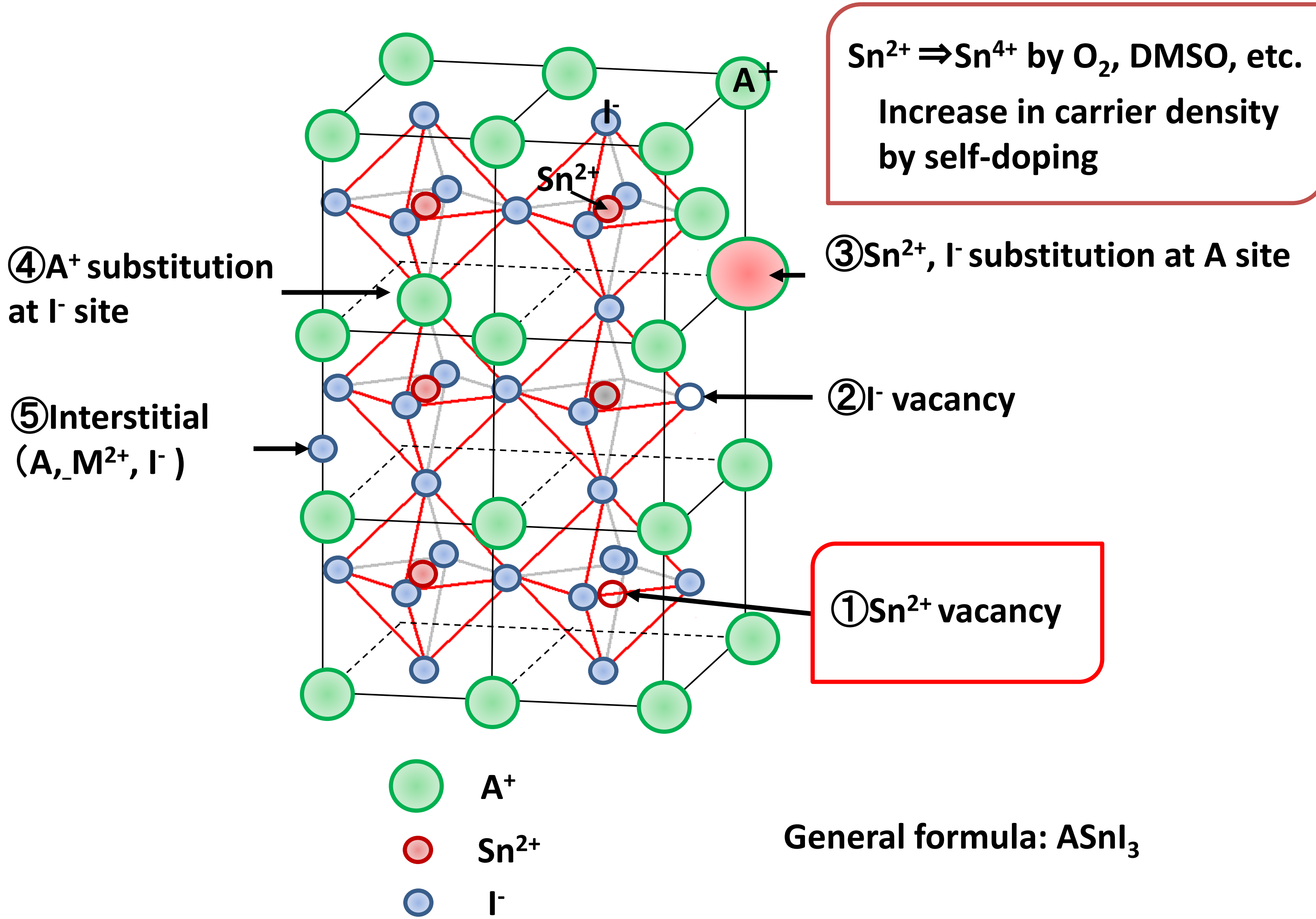
View Author Information

Cite this: *J. Phys. Chem. Lett.* 2014, 5, 6, 1004–1011
Publication Date: March 3, 2014
https://doi.org/10.1021/jz5002117

What are defects?



Defects in Sn perovskite

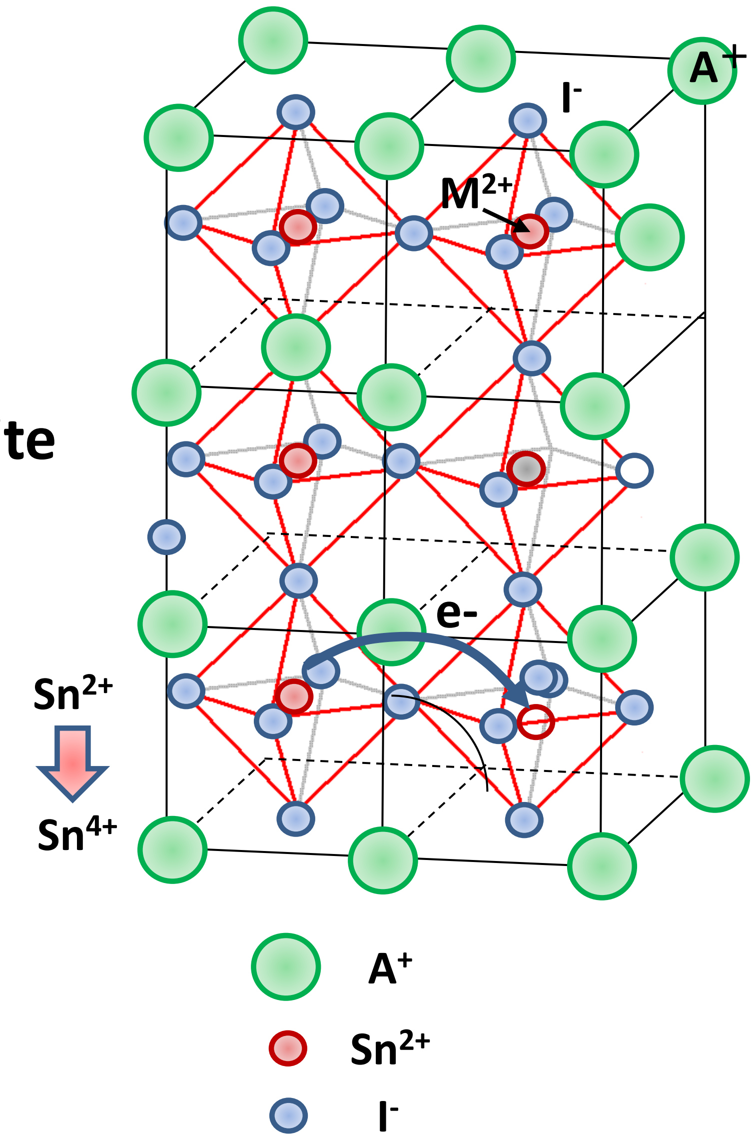


General formula: $ASnI_3$

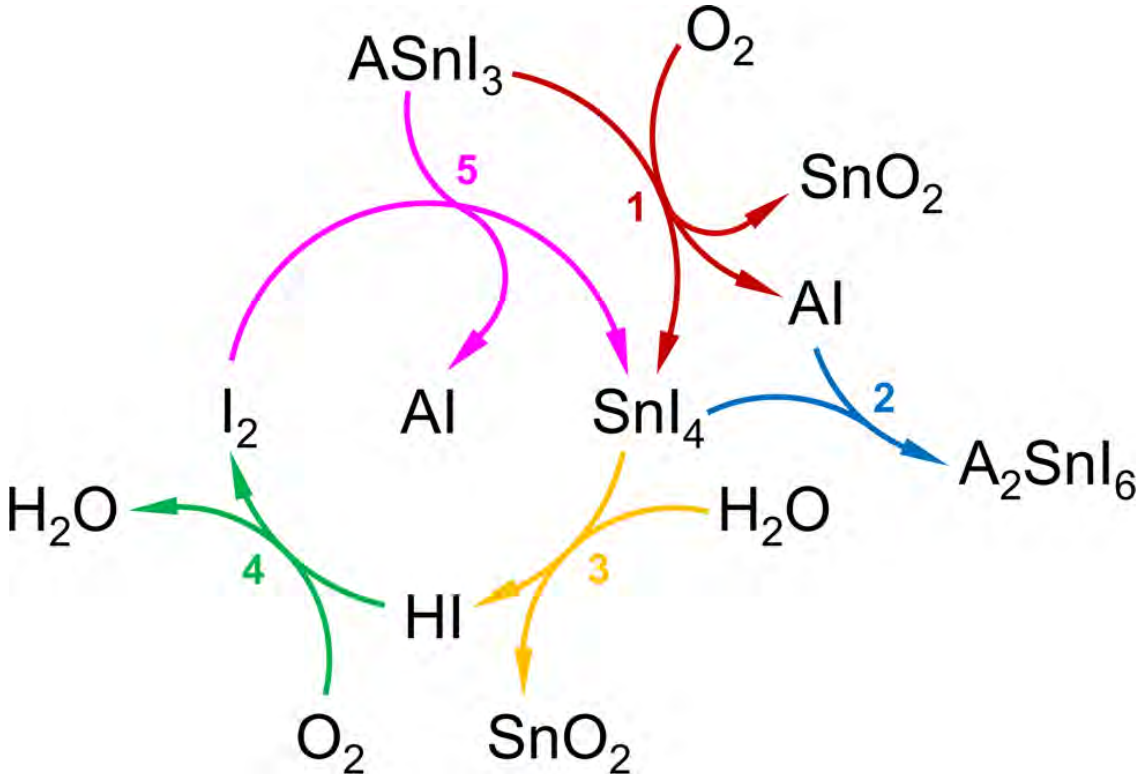
Sn^{4+} formation

- **Material**
- **Perovskite ink during storage**
- **During preparation of perovskite film**
- **Perovskite film in PV**

By solvent such as DMSO
By oxygen
By I_2 formed in perovskite
By Sn^{2+} vacancy



Predicted route for Sn^{4+} formation



L. Lanzetta, T. Webb, N. Zibouche, X. Liang, D. Ding, G. Min, R.J. Westbrook, B. Gaggio, T.J. Macdonald, M.S. Islam, Nat. Commun., 12 (2021) 1-11

To enhance efficiency

1) Defect

- Sn^{4+}
- Sn^{2+} vacancy
- I^- vacancy

2)Band offset

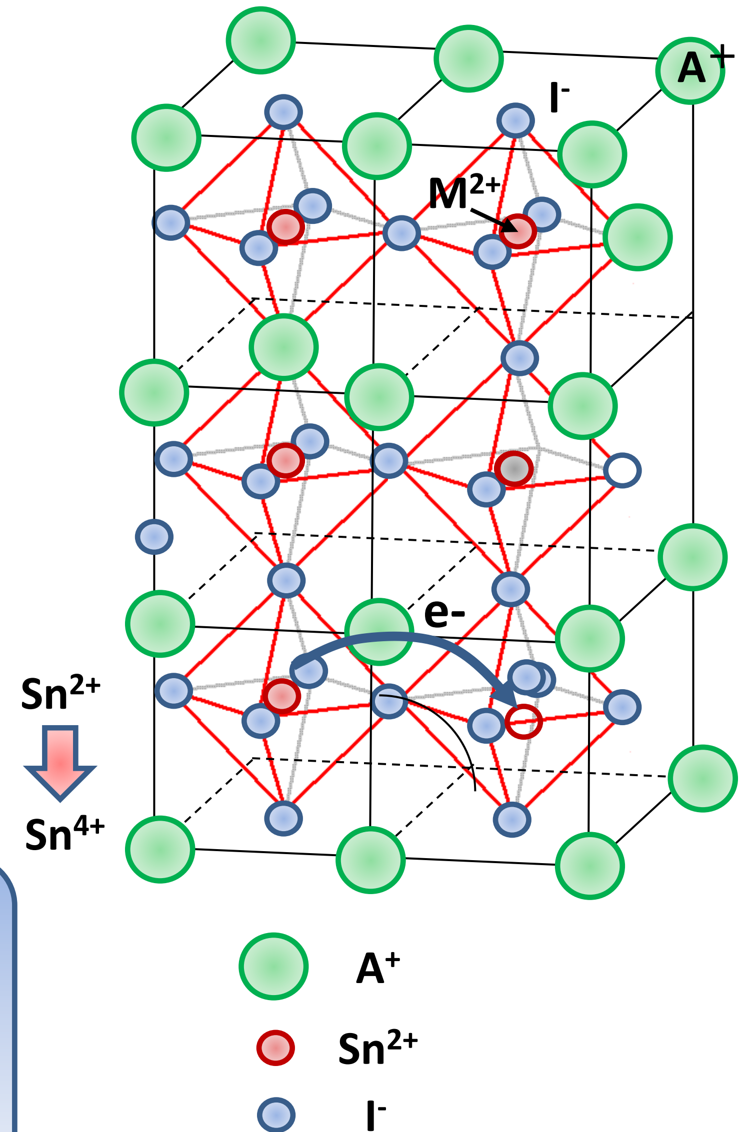
To enhance efficiency

1) Defect
- Sn^{4+}
- Sn^{2+} vacancy
- I^{-} vacancy

2)Band offset

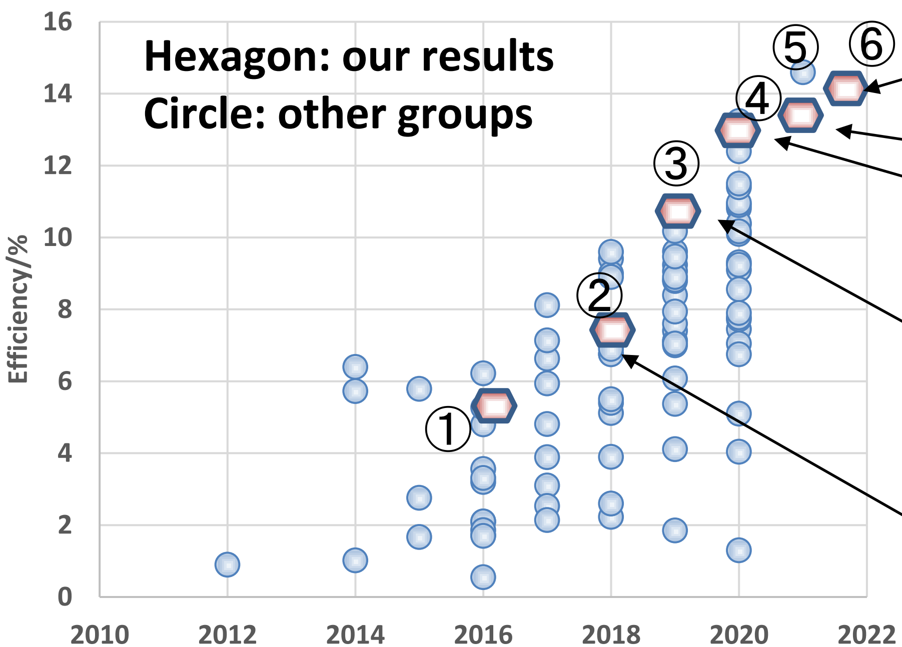
Sn^{4+} formation

- **Material**
- **Perovskite ink during storage**
- **Perovskite film in PV during PV preparation**



By solvent such as DMSO
By oxygen
By I_2 formed in perovskite $Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^-$
By Sn^{2+} vacancy

Progress of efficiency for Tin perovskite solar cells



⑥SnOx p-type layer(14.1%)→14.3%
ACS Energy Lett., 2022, 7, 10, 3703-3708.

⑤Optimization of process (13.6%)

④Decrease in band offset by A site engneering

- ACS Appl. Mater. Interfaces, 2019, 11, 34, 31105-31110
- Nano Energy, 2020, 74, 104858

③Decrease in defect at grain boundary by EDA passivation (I^- defect)

- J. Phys. Chem. Lett. 2019, 10, 17, 5277-5283

②Decrease in Sn^{4+} and passivation by GeI_2 addition

- J. Phys. Chem. Lett., 9, 1682-1688, 2018.
- Nano Energy 2019, 58, 130-137

	Method	Perovskite composition	Solar cell structure
1	Reference	$FA_{0.75}M_{A0.25}SnI_3$	ITO/PEDOPPSS/PVK/PCBM/C60/BCP/Ag/Au
2	GeI_2 addition Decrease in Sn^{4+}	$FA_{0.75}MA_{0.25}SnI_3$ (5 mol % Ge doping)	ITO/PEDOPPSS/PVK/PCBM/C60/BCP/Ag/Au
3	EDA passivation Decrease in surface defect	$FA_{0.98}EDA_{0.01}SnI_3$	FTO/PEDOPPSS/PVK/C60/BCP/Ag/Au
4	Ge + EDA passivation+Et sub. Less Lattice disordering, Less band offset	$(EA_{0.1}FA_{0.9})_{0.98}EDA_{0.01}SnI_3$(5mol% GeI_2 doped)	FTO/PEDOPPSS/PVK/C60/BCP/Ag/Au

Sn^{4+} reduction to Sn^{2+} by Ge^{2+}

Redox potential

Strong oxidation reagent

$T_2 + 2e \rightarrow T^-$	0.485
$Ge^{2+} + 2e \rightarrow Ge$	0.25
$Sn^{4+} + 2e \rightarrow Sn^{2+}$	0.15
$Ge^{4+} + 2e \rightarrow Ge^{2+}$	0
$2H^{+} + 2e \rightarrow H_2$	0
$Pb^{2+} + 2e \rightarrow Pb$	-0.13
$Sn^{2+} + 2e \rightarrow Sn$	-0.14
$Sm^{3+} + e \rightarrow Sm^{2+}$	-0.77
$H_2 + 2e \rightarrow H^-$	−2.24

Strong reducing reagent

Electronic properties before and after Ge^{2+} ion addition

Composition	Carrier concentration cm^3	Mobility $cm^2/v/s$	Lifetime ns	Diffusion length nm
Sn-PVK w/o SnF_2	4.1×10^{20}	1.05	-	-
Sn-PVK with SnF_2	9.11×10^{17}	12.49	3.51	352.9
GeI_2 doped Sn-PVK with SnF_2	1.69×10^{15}	98.27	5.09	1191.8
ref. $MAPbI_3$	10^{13-15}	up to 60	3,000	120-175,000

Ref: Samuel D. Henry J. Snaith, et al Science, 2013, 342, 6156, 341-344,
Igal Levine, Isaac Balberg, et al., J. Phys. Chem. Lett. 2016, 7, 24, 5219–5226,

C.-H. Ng, S. Hayase, et.al., Nano Energy, 2019, 58, 130-137.

Ge^{2+} addition decreased carrier concentration and increased mobility

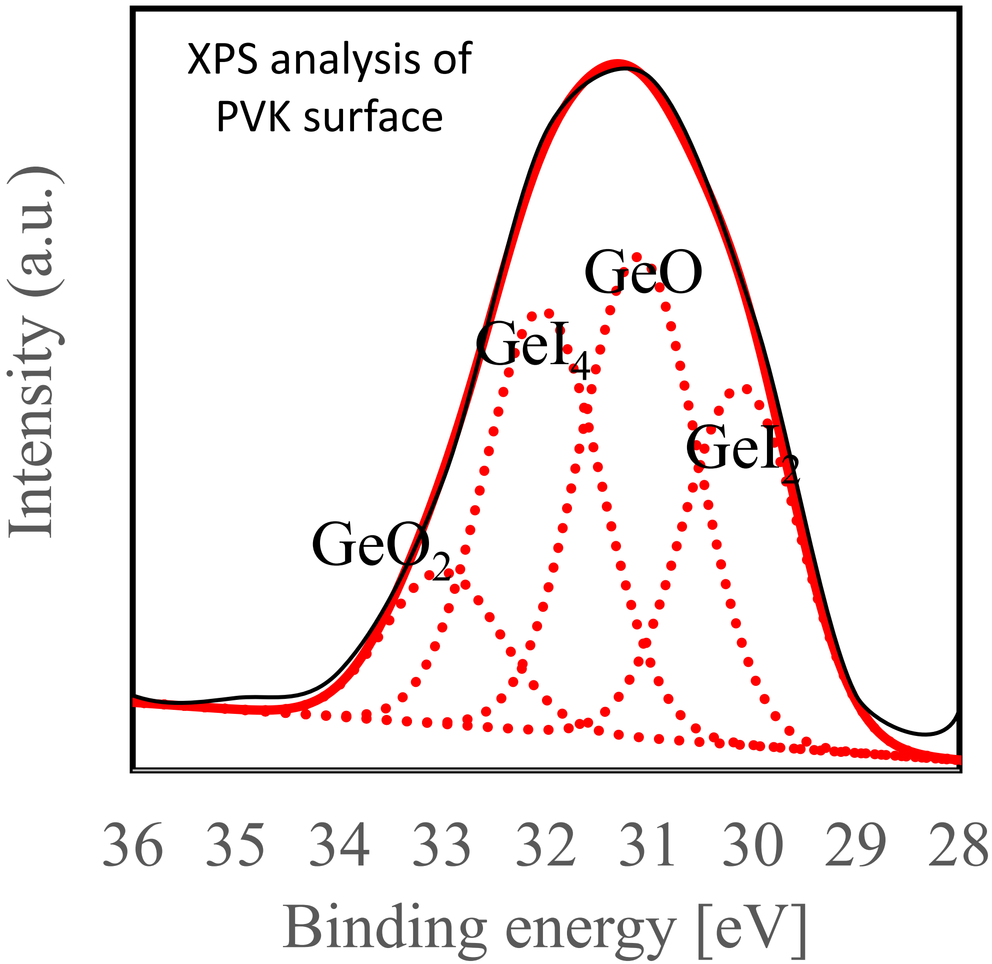
Efficiency of Sn-PVK-PV vs GeI_2 addition

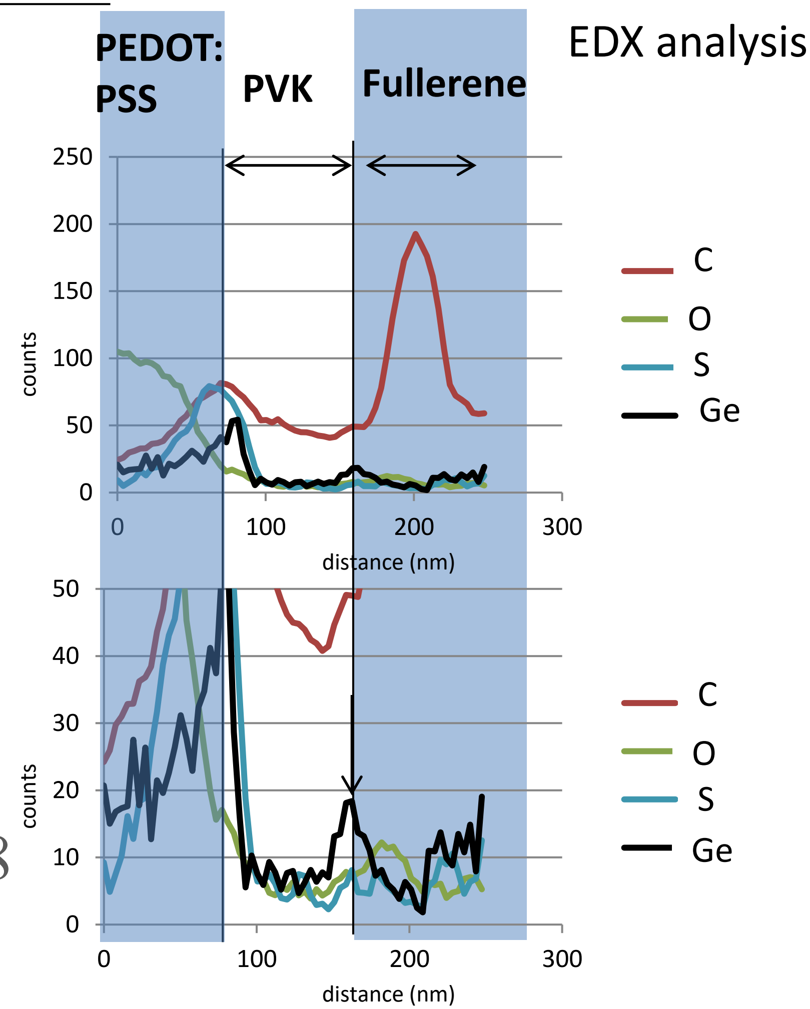
$FA_{0.75}MA_{0.25}Sn_{1-x}Ge_xI_3$

Perovskites	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
$FASnI_3$ (FSI)	17.99	0.34	0.64	3.86
FPSGI (0Ge)	16.27	0.36	0.68	3.92
FPSGI (2.5Ge)	19.85	0.43	0.69	5.84
FPSGI (5.0Ge)	19.84	0.47	0.72	6.80
FPSGI (7.5Ge)	21.92	0.46	0.73	7.45
FPSGI (10.5Ge)	10.85	0.26	0.40	1.14

Huey, Hayase et al, J. Mater. Chem. A, 2020,8, 2962-2968

Ge distribution in cross-section of solar cell

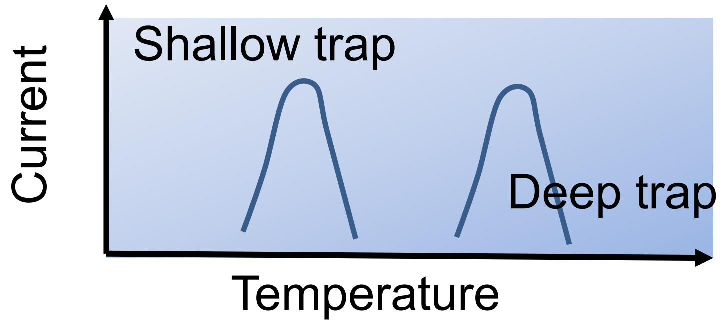


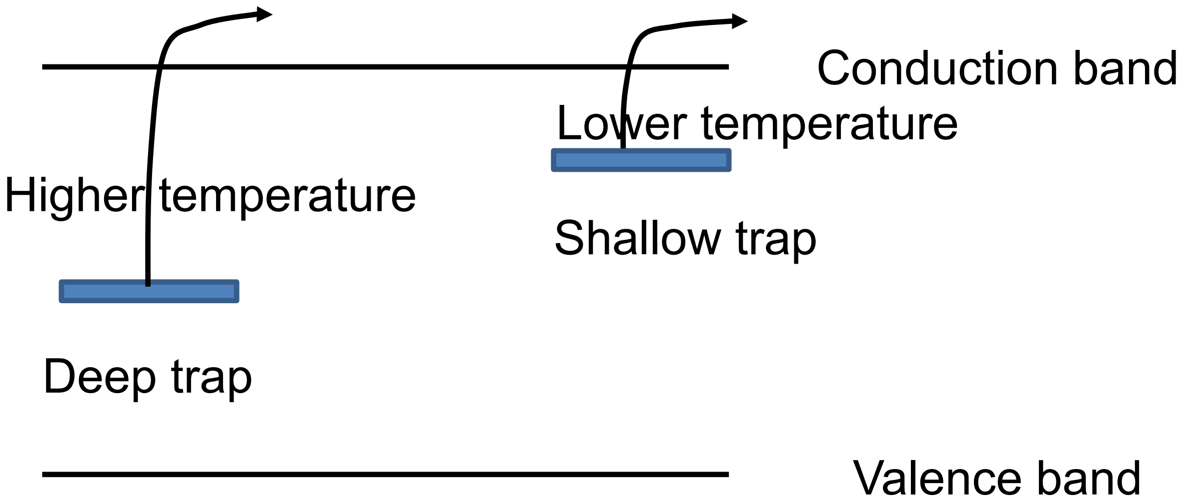


Hayase, S., Sn-based Halide Perovskite Solar Cells, Chapter 10, 293-319, 2021, Perovskite Photovoltaics and Optoelectronics, Edited by Miyasaka, T., Eiley-VCH,

Higher concentration area of Ge was detected at both interfaces of ETL and HTL

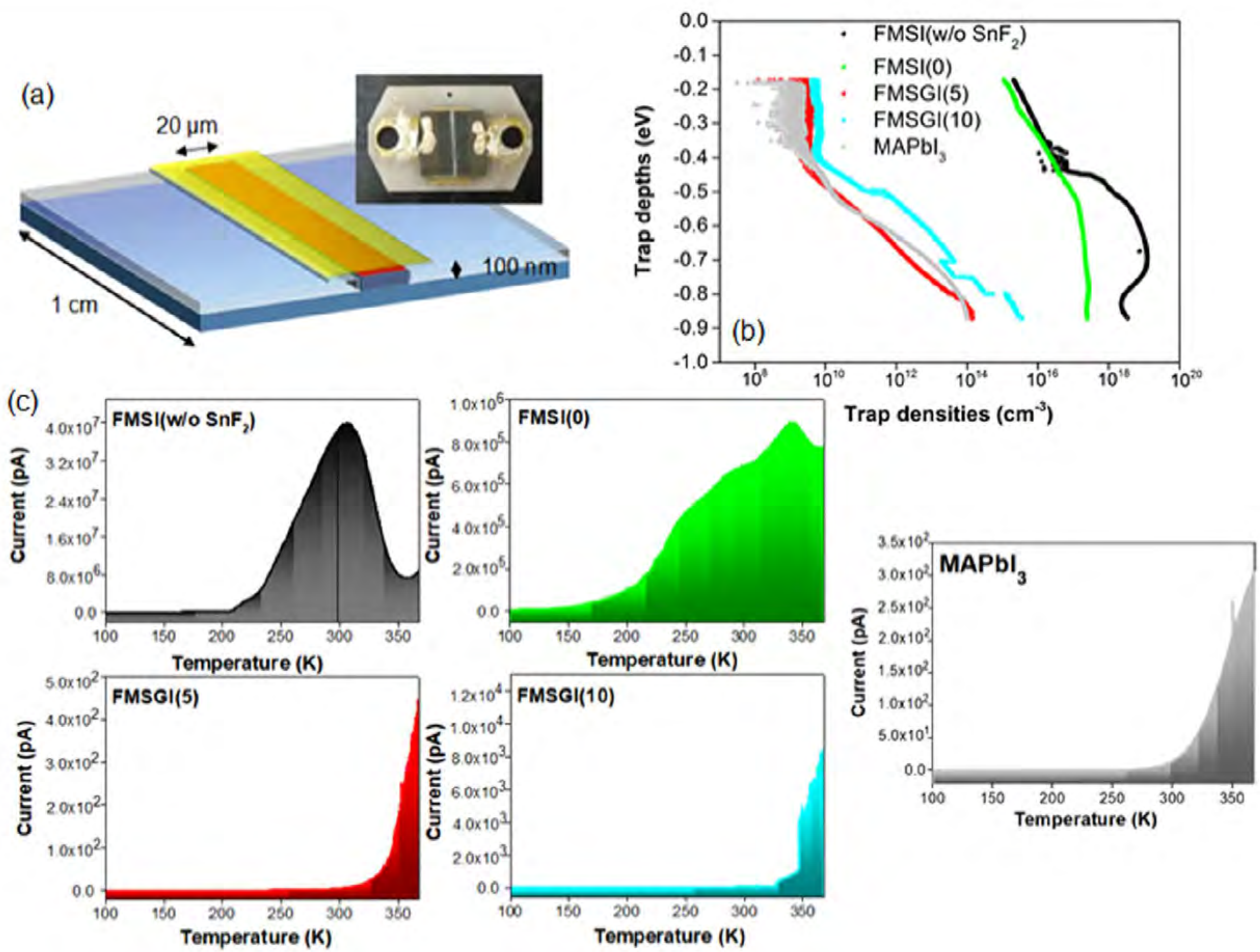
Thermally stimulated current



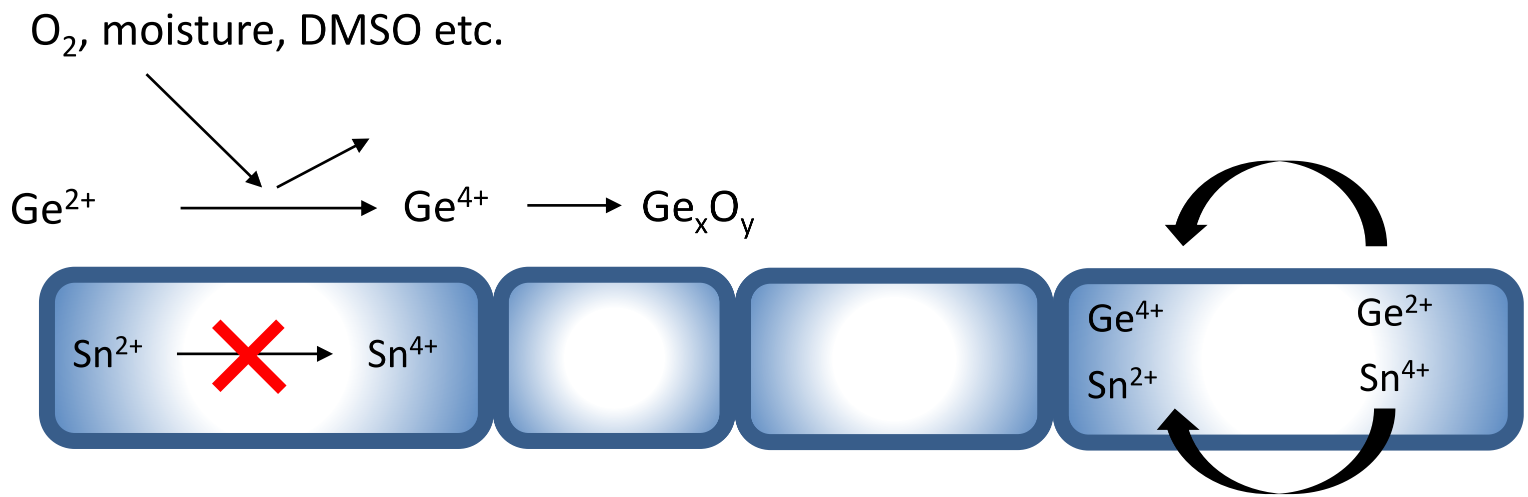


Thermally stimulated current after GeI_2 addition

Ng, C.H., Hayase, S., et al., Nano Energy, 2019, 58, 130-137.



Role of Ge^{2+} doping



Ge ion

- decreases Sn^{4+} concentration by working as reducing agent.
- decreases Sn^{2+} vacancy site by inserted in the lattice
  because Sn^{2+} vacancy formation energy becomes larger after Ge^{2+} was inserted.
- becomes G_xO_y on the surface (and grain boundary) and protects the inside of the perovskite layer

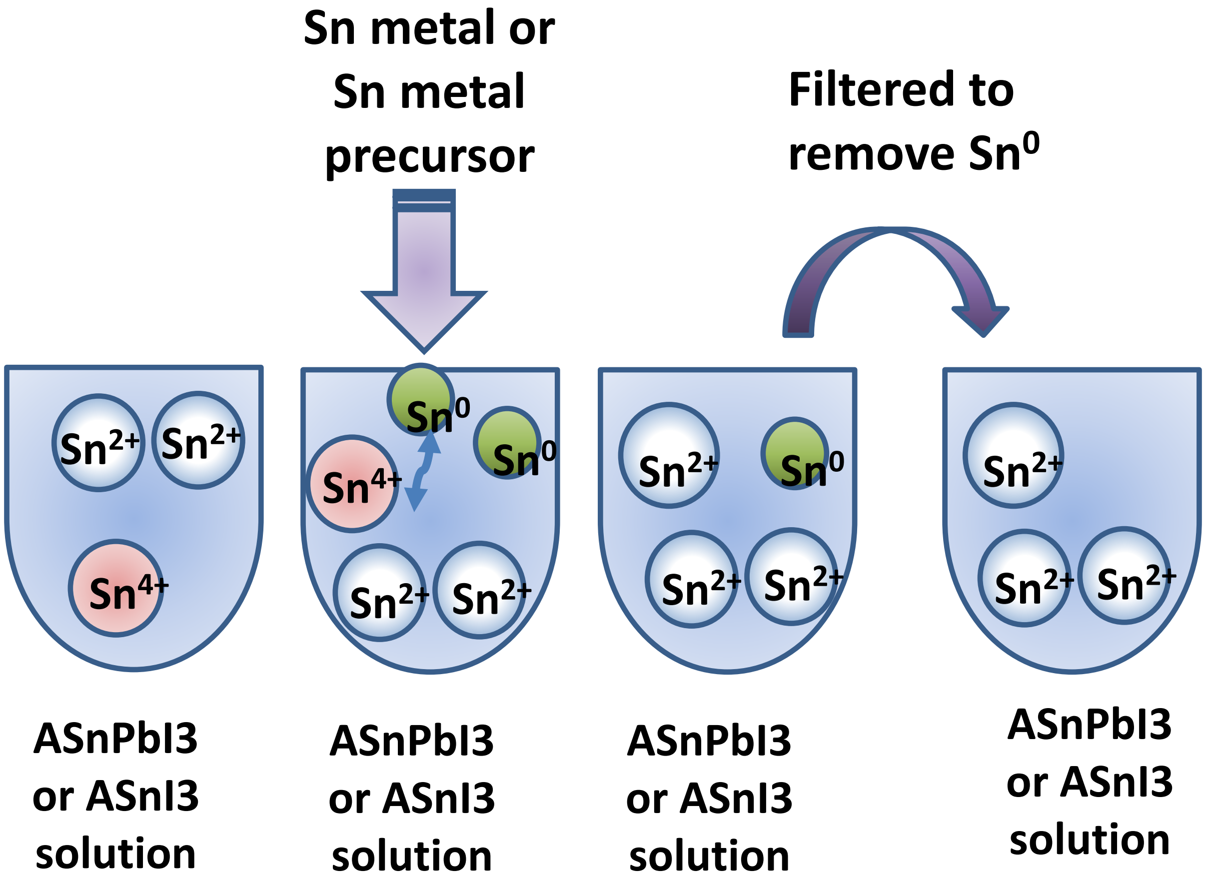
Sn^{4+} reduction to Sn^{2+} by Ge^{2+}

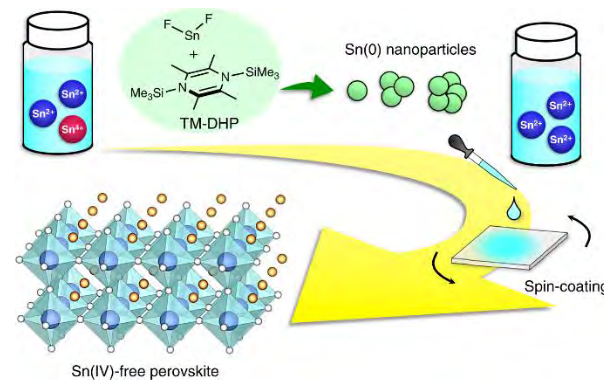
Strong oxidation reagent

Reaction	Redox potential
$T2 + 2e \rightarrow T-$	0.485
$Ge^{2+} + 2e \rightarrow Ge$	0.25
$Sn^{4+} + 2e \rightarrow Sn^{2+}$	0.15
$Ge^{4+} + 2e \rightarrow Ge^{2+}$	0
$2H^{+} + 2e \rightarrow H_2$	0
$Pb^{2+} + 2e \rightarrow Pb$	-0.13
$Sn^{2+} + 2e \rightarrow Sn$	-0.14
$Sm^{3+} + e \rightarrow Sm^{2+}$	-0.77
$H_2 + 2e \rightarrow H^{-}$	−2.24

Strong reducing reagent

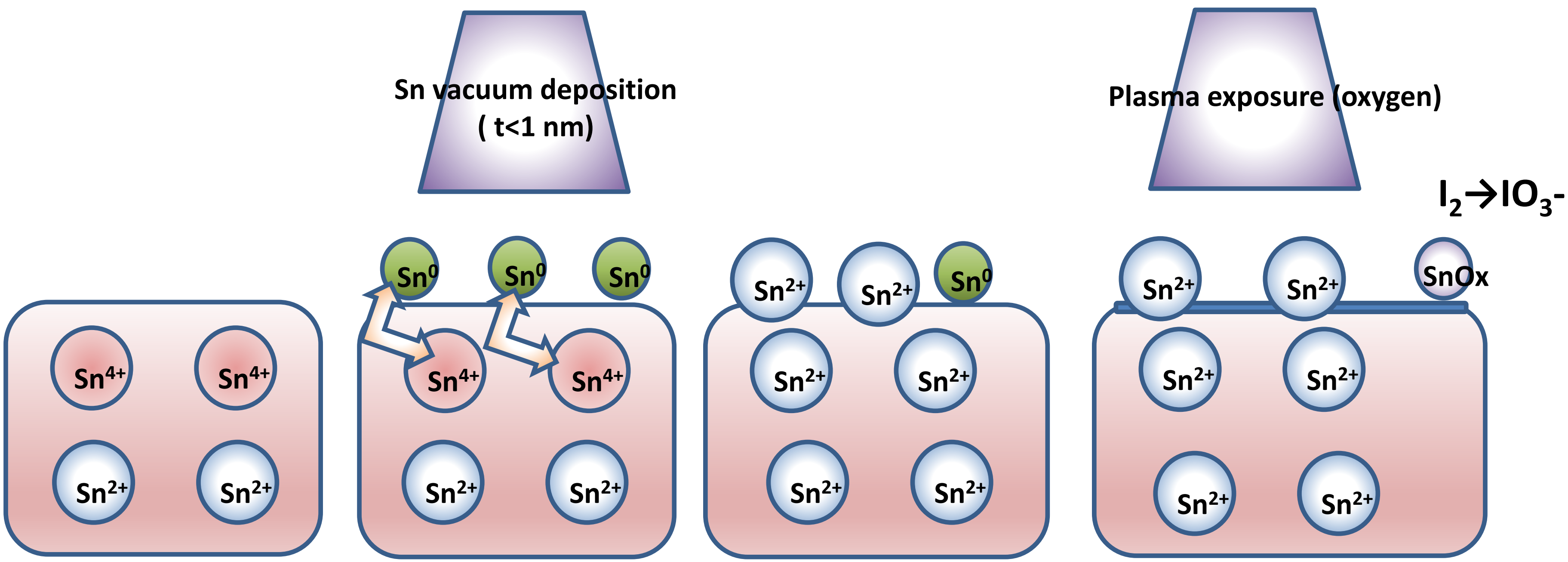
Previous report: Decrease in Sn^{4+} concentration in precursor solution





Jiang, T., et al., Solar RRL., 2019, 10.1002/solr.201900467.
Nakamura, T., et al., Nature Communications, 2020, 11, 3008.

Direct metal deposition on Sn-PVK layer
(Expected effect)

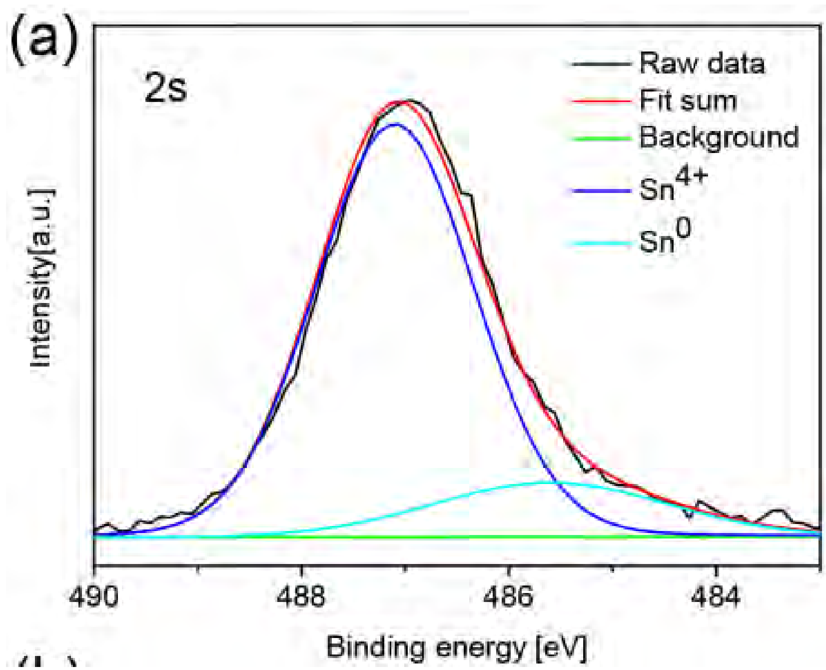


$ASnI_3$ film

Decrease in Sn^{4+} concentration by XPS

Purpose of O_2 plasma exposure
- **Oxidation of Si metal surface**
- **Oxidation of I_2**

1nm Sn metal exposed by 2 sec. plasma

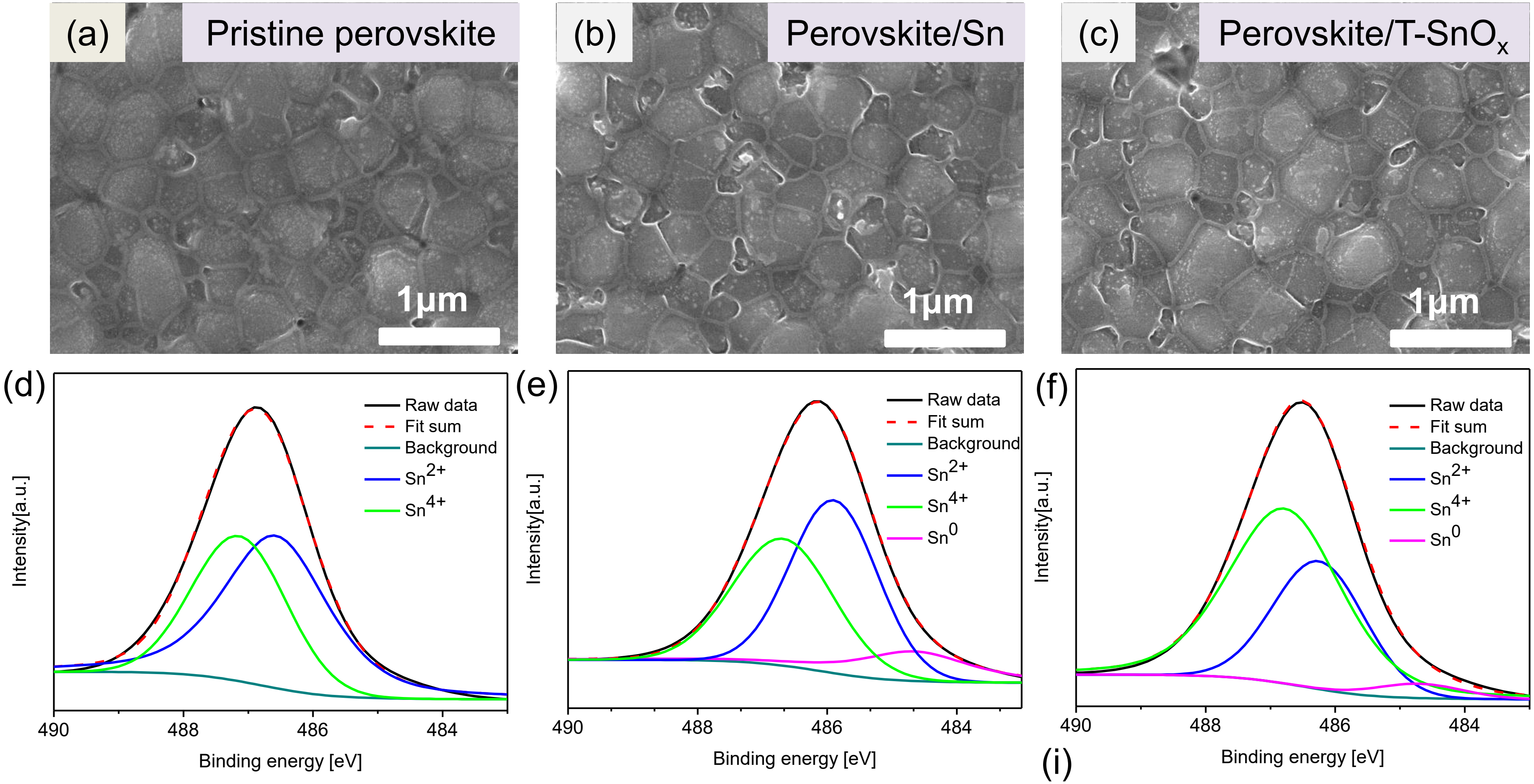


SnOx prepared by plasma exposure

Wang Lian, Shuzi Hayase, et al., ACS Energy Lett., 2022, 7, 10, 3703-3708.

Only Sn^{4+} and Sn metal were detected.

SEM and XPS analysis: Peroskite layer



Sn^{4+}/Sn^{2+}=0.96

Sn^{4+}/Sn^{2+}=0.70

Sn^{4+}/Sn^{2+}=1.87

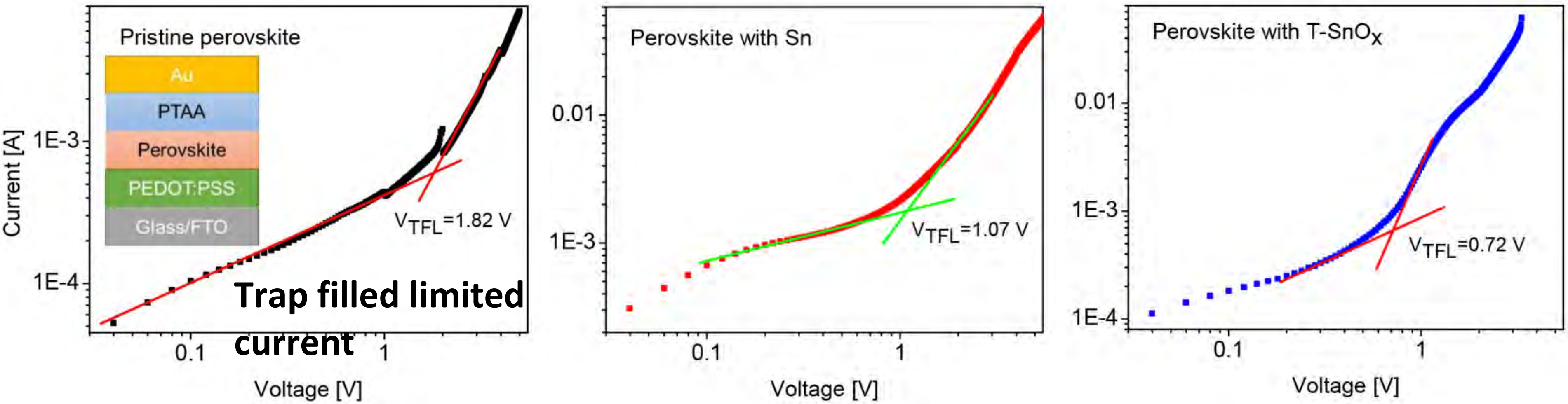
$Sn^{4+}+Sn \rightarrow Sn^{2+}$

$Sn+Plasma \rightarrow Sn^{4+}$

Wang Lian, Shuzi Hayase, et al., ACS Energy Lett., 2022, 7, 10, 3703-3708.

Trap density of perovskite layer

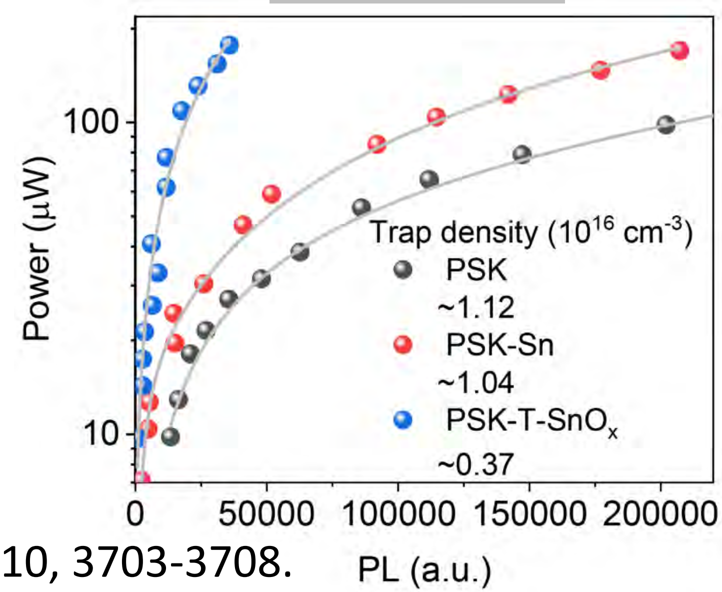
Method: 1 **SCLC:Space charge limited current**



$$N_{defects} = 2\varepsilon\varepsilon_0 V_{TFL}/eL^2$$

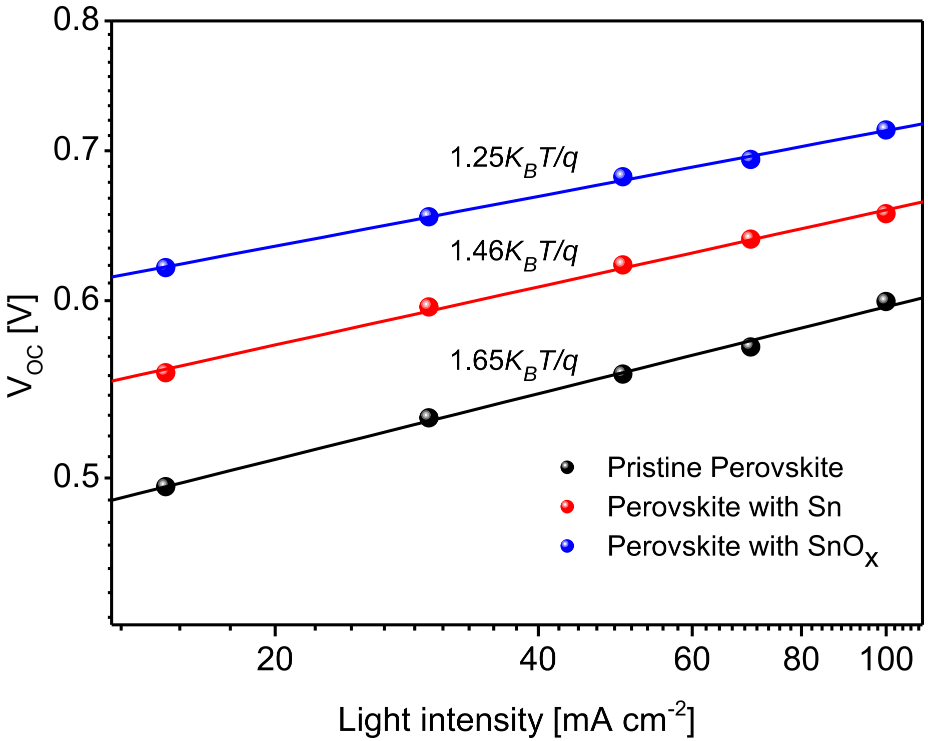
	V_{TFL}/V	Trap density/10^{16} cm^{-3}
Pristine perovskite	1.82	2.41
Perovskite-Sn	1.07	1.42
Perovskite-T-SnO_x	0.72	0.72

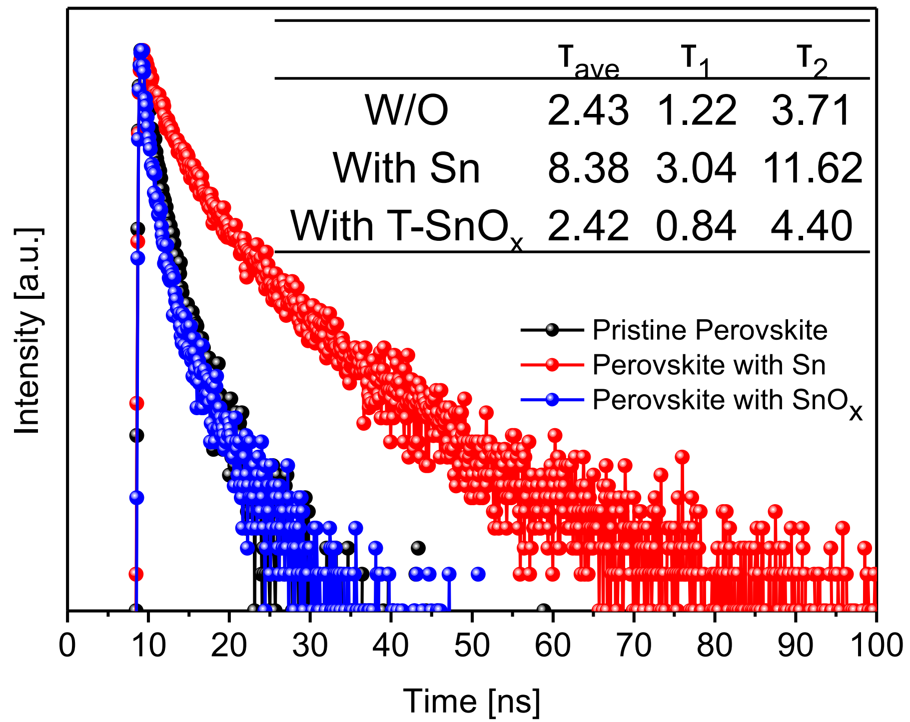
Method: 2



Wang Lian, Shuzi Hayase, et al., ACS Energy Lett., 2022, 7, 10, 3703-3708.

Recombinaition inhibitation and fast carrier transport





Wang Lian, Shuzi Hayase, et al., ACS Energy Lett., 2022, 7, 10, 3703-3708.

Redox potential of each ion

Strong oxidation reagent

	Redox potential	
$T2 + 2e \rightarrow T^-$	0.485	
$Ge^{2+} + 2e \rightarrow Ge$	0.25	
$Sn^{4+} + 2e \rightarrow Sn^{2+}$	0.15	
$Ge^{4+} + 2e \rightarrow Ge^{2+}$	0	
$2H^+ + 2e \rightarrow H_2$	0	
$Pb^{2+} + 2e \rightarrow Pb$	-0.13	
$Sn^{2+} + 2e \rightarrow Sn$	-0.14	
$Sm^{3+} + e \rightarrow Sm^{2+}$	-0.77	Chem. Lett., 2019, 48, 836-839
$H_2 + 2e \rightarrow H^-$	−2.24	$PhSiH_3$ (submitted)

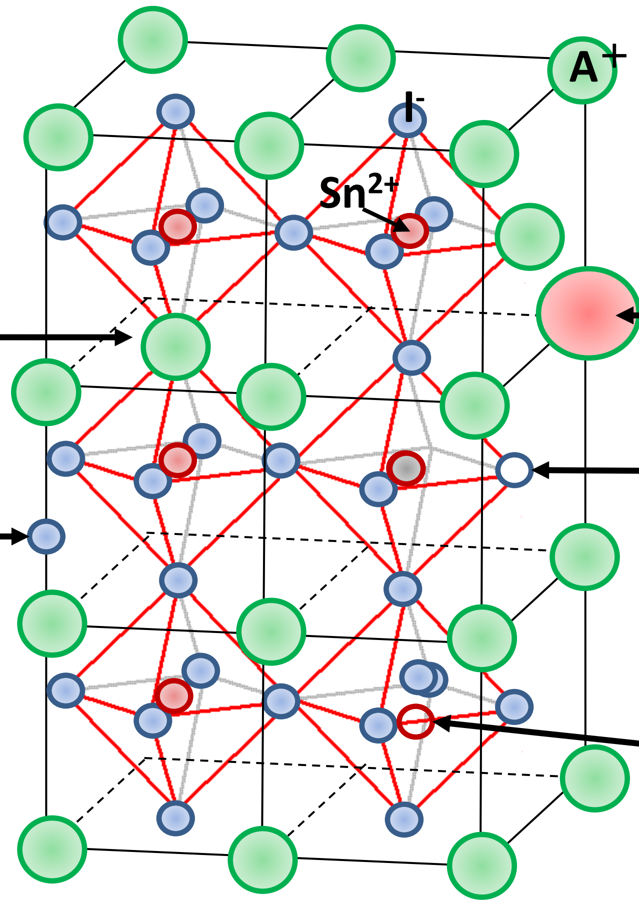
Strong reducing reagent

Reports on decreasing Sn^{4+} concentration by adding perovskite ink

Addition of reducing agents such as SnF_2[1)]、GeI_2[2-4)], Nano Sn particle [5)] and their related material[6)]、benzyl azide salts[7)], and removal of low boiling point Sn^{4+} salts by heating[8)]。

1. Kumar, M., Advance Materials, 2014, 5, 26, 7122-7.
2. Ito, N., Journal of Physical Chemistry, Letters, 2018, 9, 1682-1688.
3. Ng, C., J. Mater. Chem. A., 2020, 8, 2962-2968.
4. Ng, C.H., Nano Energy, 2019, 58, 130-137.
5. Jiang, T., Solar RRL., 2019, 10.1002/solr.201900467.
6. Nakamura, T., Nature Communications, 2020, 11, 3008.
7. Wang, C., Advanced Materials, 2020, 32, 1907623.
8. Zhou J., Matter, 2021,https://doi.org/10.1016/ j.matt.2021.12.013.

Defects in metal perovskite



Sn²⁺ ⇒ Sn⁴⁺ by O₂, DMSO, etc.

Increase in carrier density by self-doping

③Sn^{2+}, I^- substitution at A site

④A^+ substitution at I^- site

②I^- vacancy

⑤Interstitial (A, M^{2+}, I^-)

①Sn^{2+} vacancy

A^+

Sn^{2+}

I^-

General formula: $ASnI_3$

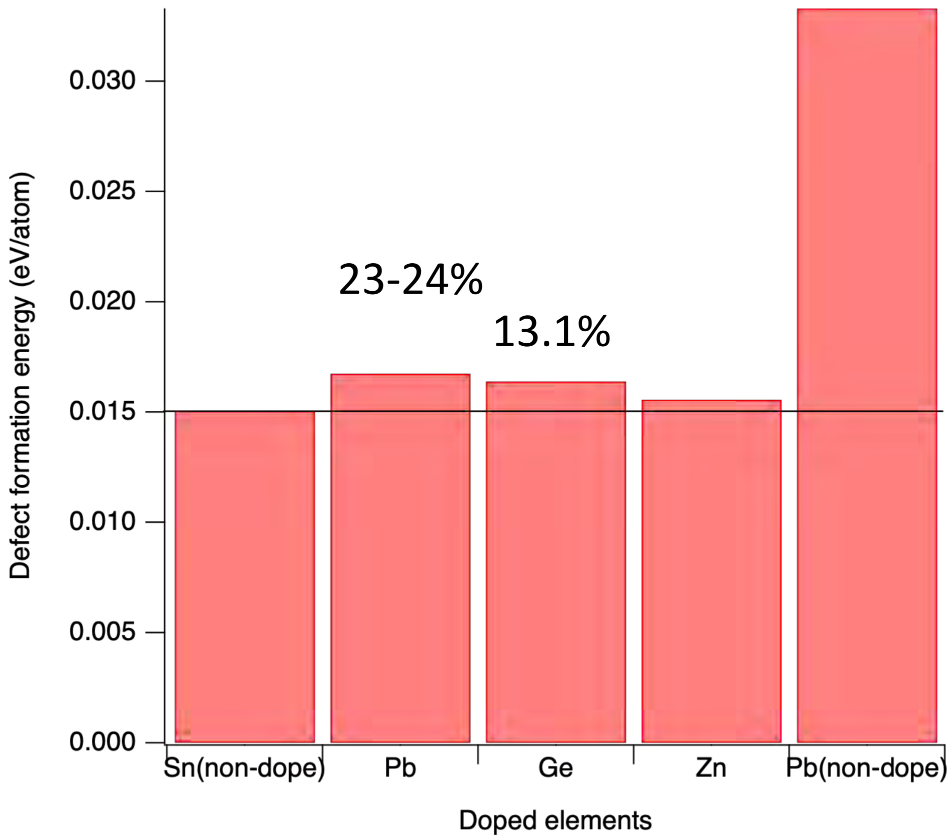
To enhance efficiency

1) Defect

- Sn^{4+}
- Sn^{2+} vacancy
- I^- vacancy

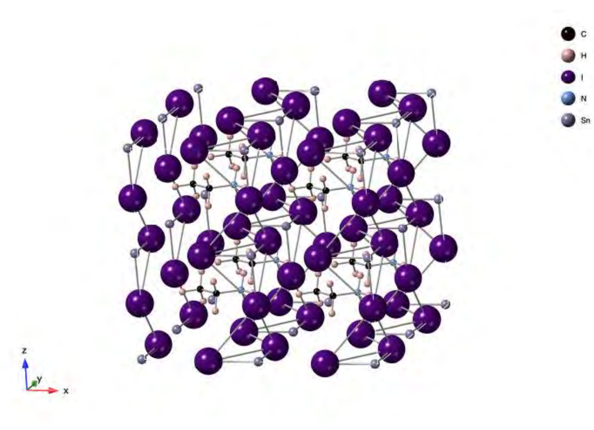
2)Band offset

Defect formation energy of Sn^{2+}



$$E_{form} = E_{tot}^{PVK-Sn} - E_{tot}^{PVK} + E_{tot}^{Sn}$$

S. Iikubo, et al., Jpn. J. Appl. Phys. **61** 031003



Initial motivation: Ge ion doping would decrease the defect formation energy of Sn^{2+} , resulting in the decrease in the Sn^{2+} vacancy concentration.

To enhance efficiency

1) Defect

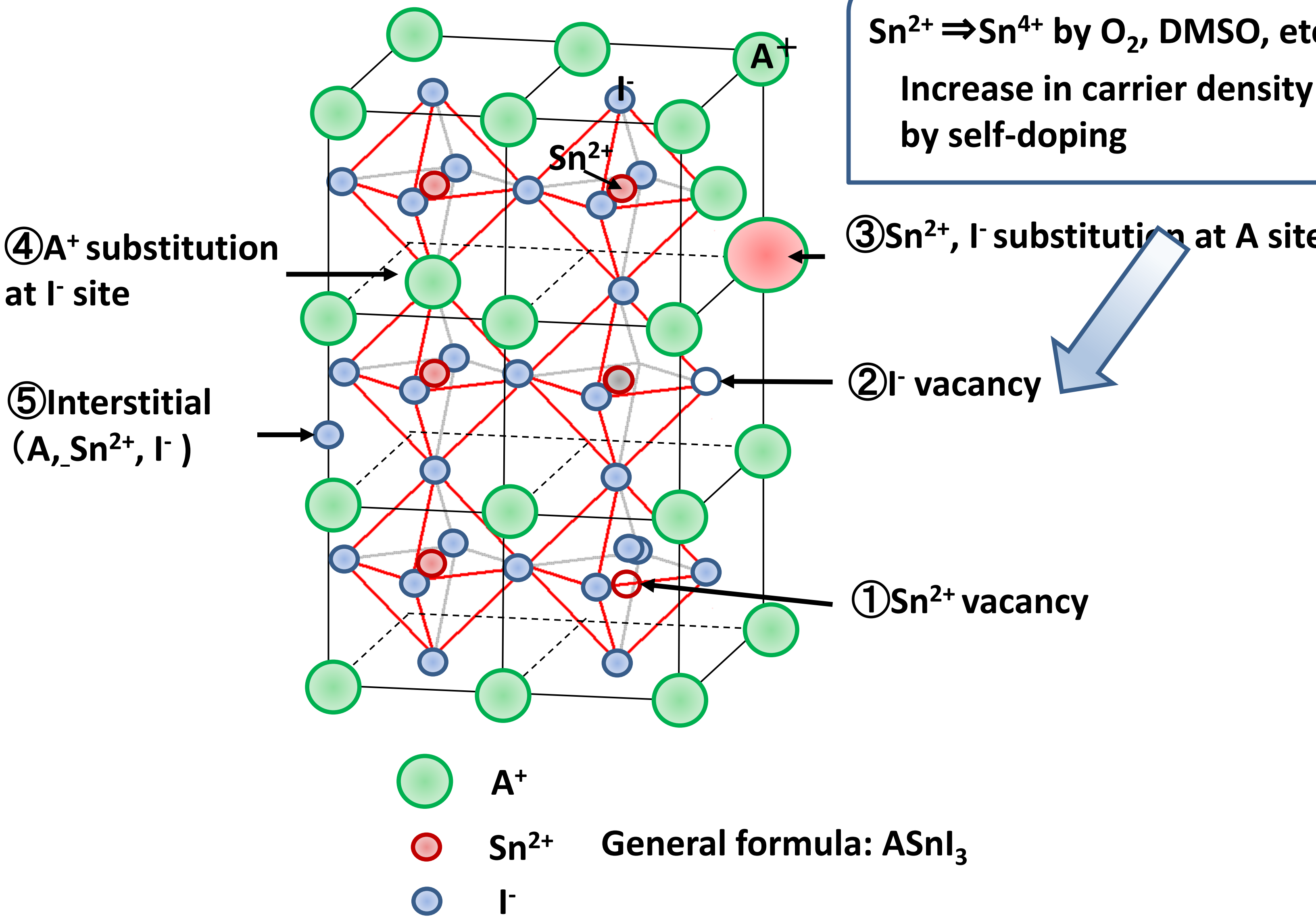
- Sn^{4+}
- Sn^{2+} vacancy
- I^{-} vacancy

2)Band offset

Defects in Tin perovskite and Tin-Lead alloyed perovskite

$Sn^{2+} \Rightarrow Sn^{4+}$ by O_2, DMSO, etc.

Increase in carrier density by self-doping

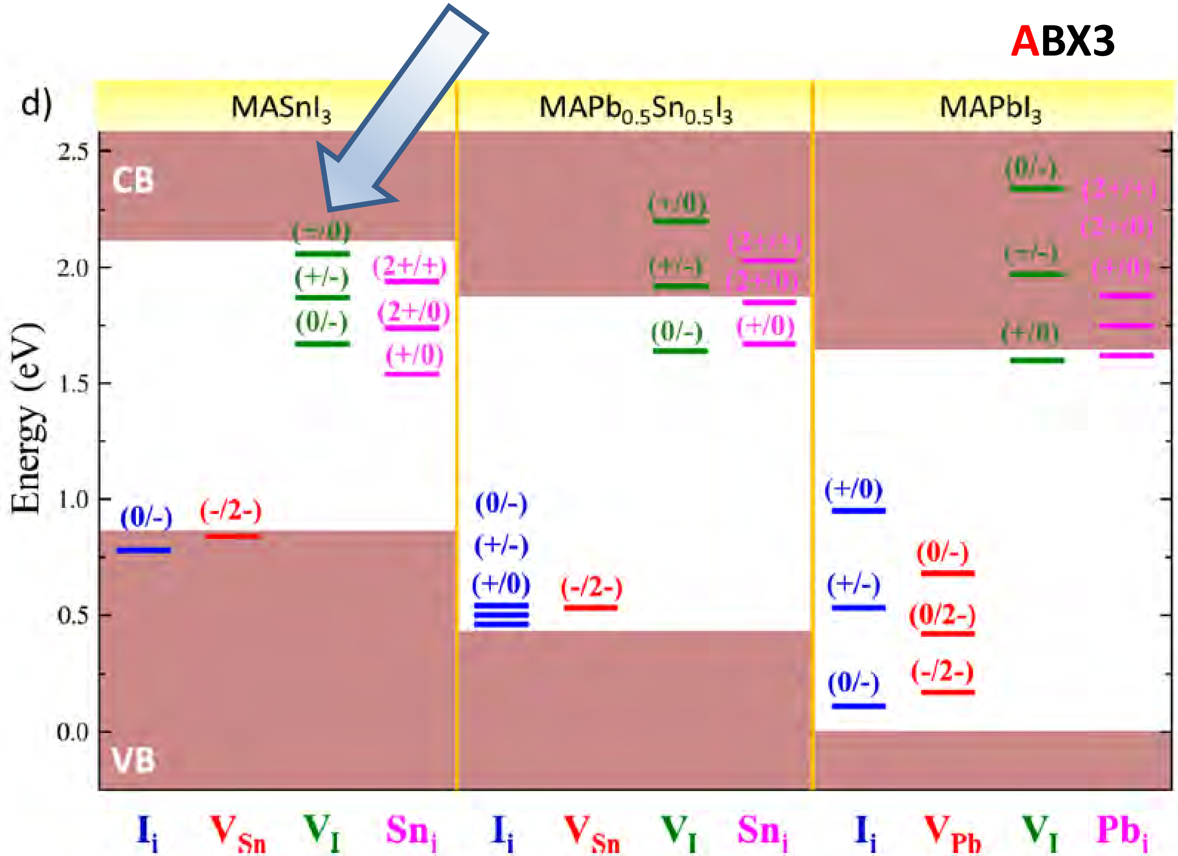


General formula: $ASnI_3$

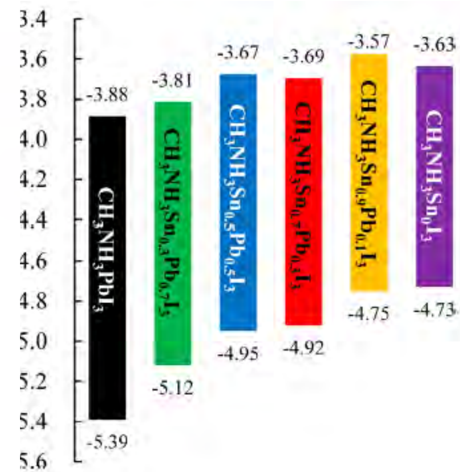
Defect energy level for $MAPbI_3$ MASnPb and $MASnI_3$

(Heat of formation and trap depth)

ABX3



Experimental results

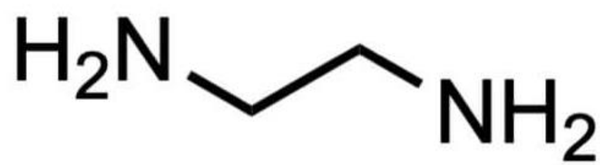


Y. Ogomi, S. Hayase, et al.
***J. Phys. Chem. Lett.* 2014, 5, 1004-1011**

Thermodynamically unstable (large formation energy)

Daniele Meggiolaro, Damiano Ricciarelli, Ahmed A. Alasmari, Fatmah A. S. Alasmary, and Filippo De Angelis, Journal of Physical Chemistry Letter, 2020, 11, 3546-3556

Effect of EDA passivation

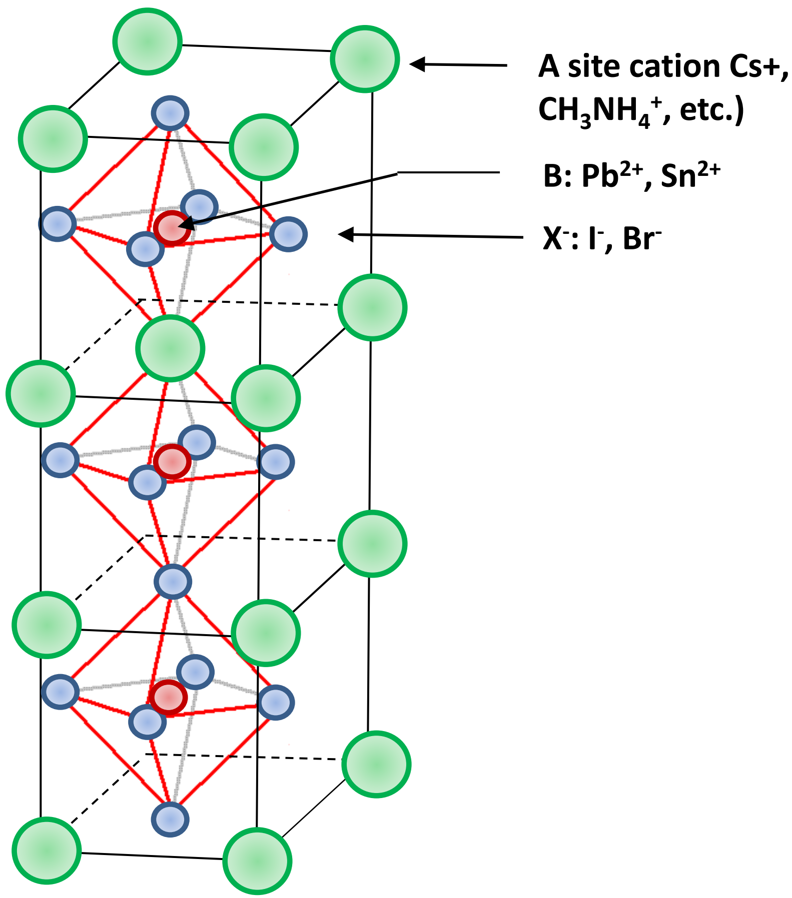


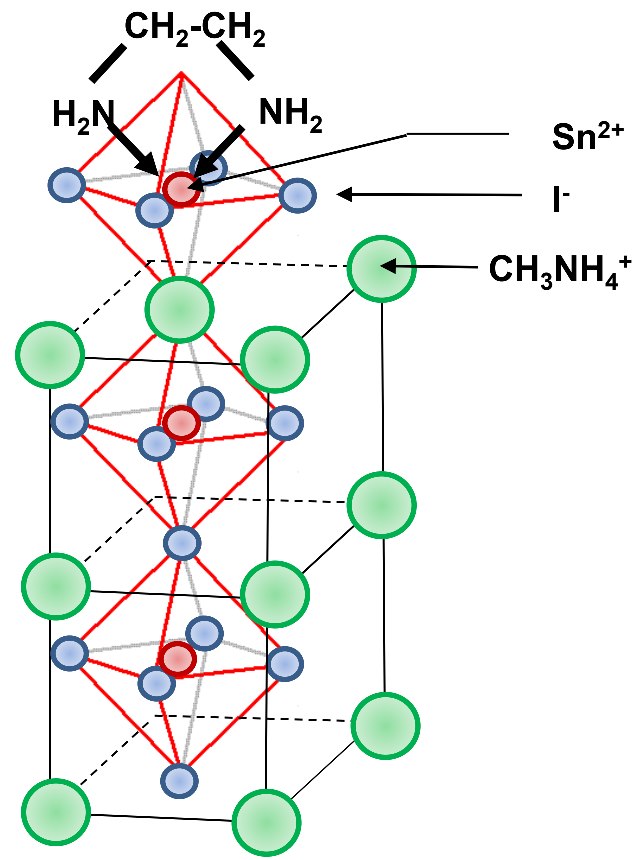
Ethylenediammonium salts addition to perovskite precursor (not passivation)

- Jokar, E., Chien, C., Tsai, C., Fathi, A., Diau, ERobust Tin-Based Perovskite Solar Cells with Hybrid Organic Cations to Attain Efficiency Approaching 10%, Advanced Materials, 2019, 31, 1804835.

- Ke, W., Stoumpos, C., Spanopoulos, I., Chen, Wasielewski, M., Kanatzidis, M. Diammonium Cations in the FASnI3 Perovskite Structure Lead to Lower Dark Currents and More Efficient Solar Cells. ACS Energy Lett., 2018, 3, 7, 1470–1476.

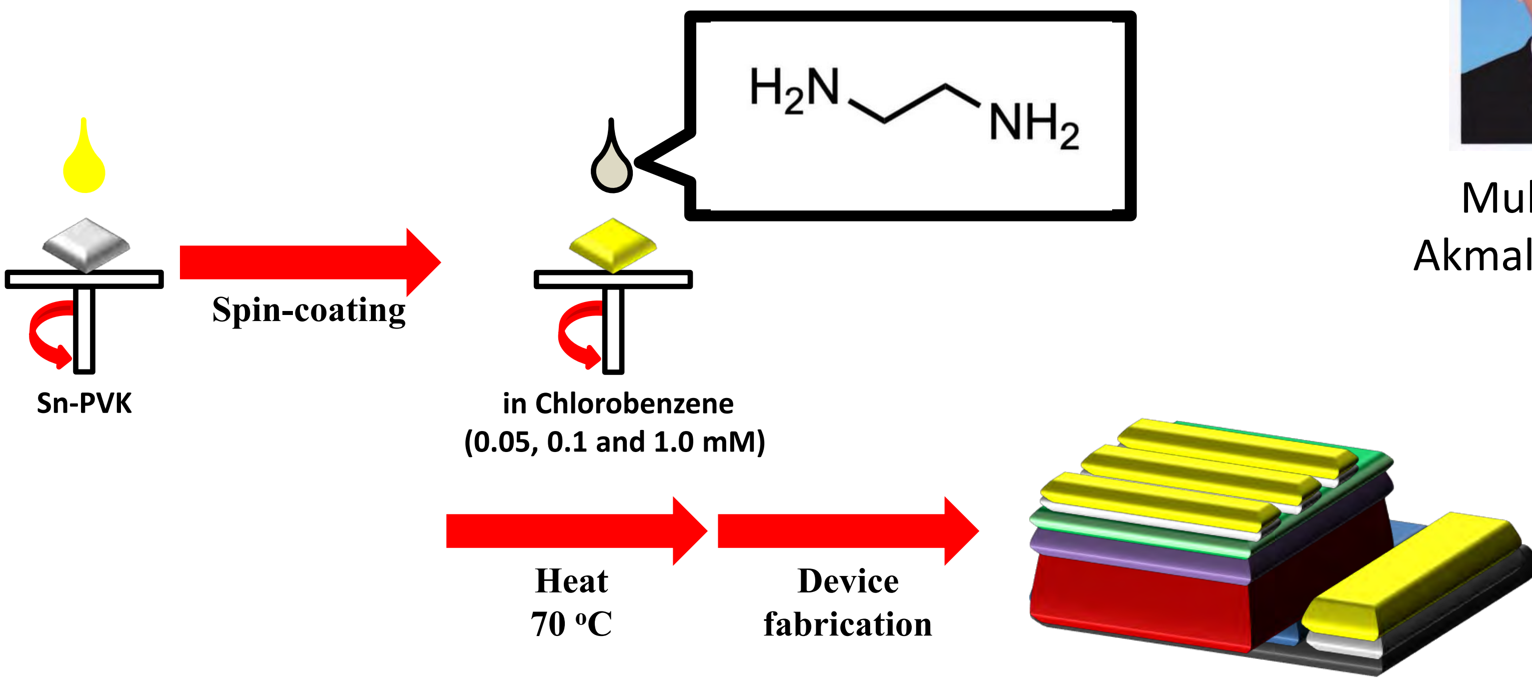
One of possible explanations on EDA passivation





Coordination model

Ethylene diamine passivation process

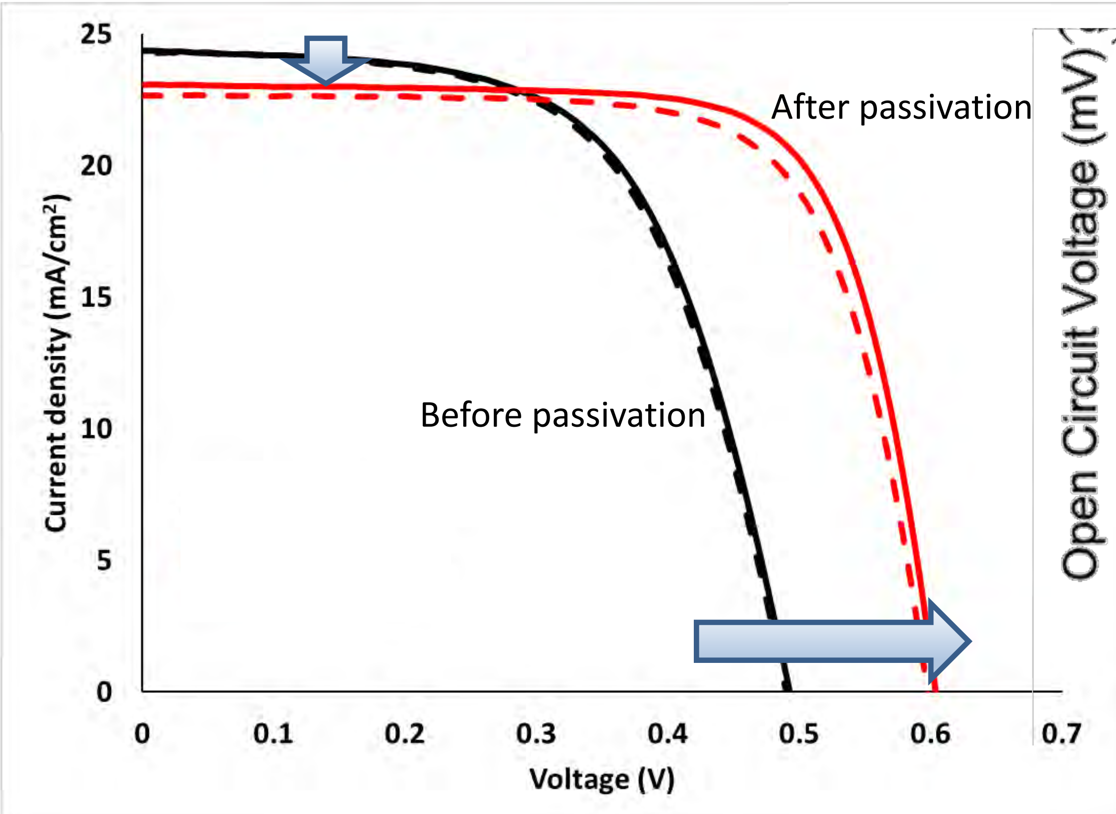


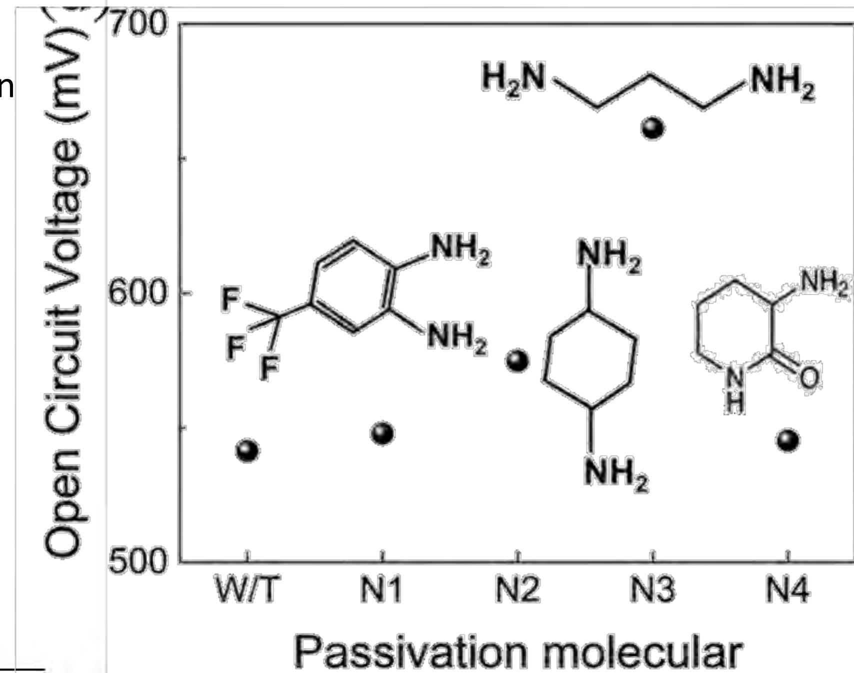
Muhammad
Akmal Kamarudin

$(EA_{0.1}FA_{0.9})_{0.98}EDA_{0.01}SnI_{3}$(5mol% GeI_2 doped)
ITO/PEDOT:PSS/Perovskite/C60/BCP/Ag/Au

M. A. Kamarudin, S. Hayase, et.al., Journal of Physical Chemistry, Letter,
J. Phys. Chem. Lett. 2019, 10, 17, 5277-5283,DOI:10.1021/acs jpclett.9b02024, 2019

I-V curves of Sn perovskite solar cells before and after DEA passivation



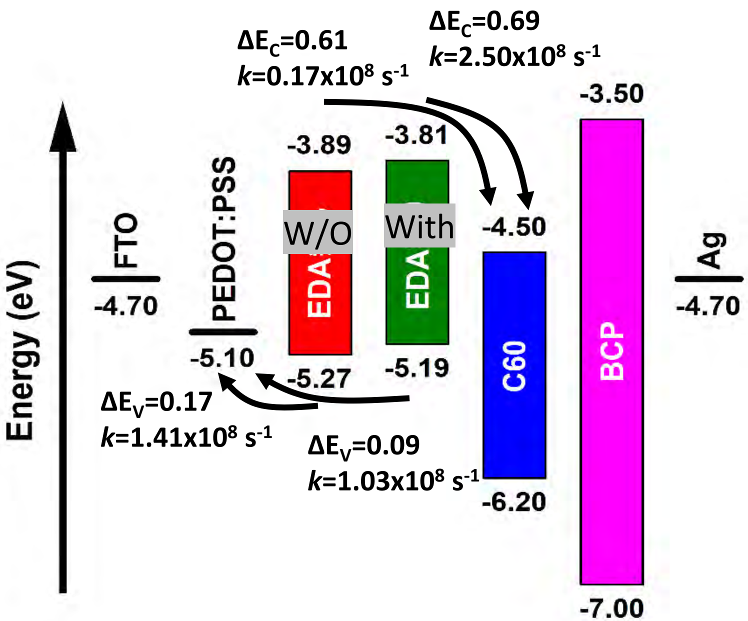


ITO/PEDOT:PSS/Perovskite/C60/BCP/Ag/Au

Sn perovskite composition: $FA_{0.98}EDA_{0.01}SnI_3$

Shuzi Hayase, Sn based and Pb free perovskite solar cells, Chapter 10 in Perovskite photovoltaics and optoelectronics, Wiley-VCH, Edited by Tsutomu Miyasaka, 2021.

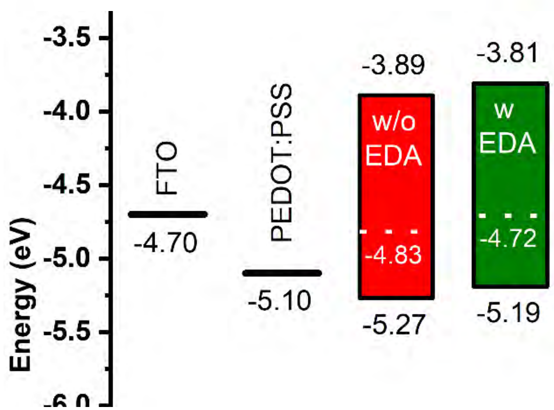
Charge injection balance between holes and electrons after EDA passivation



EDA: ethylenediamine

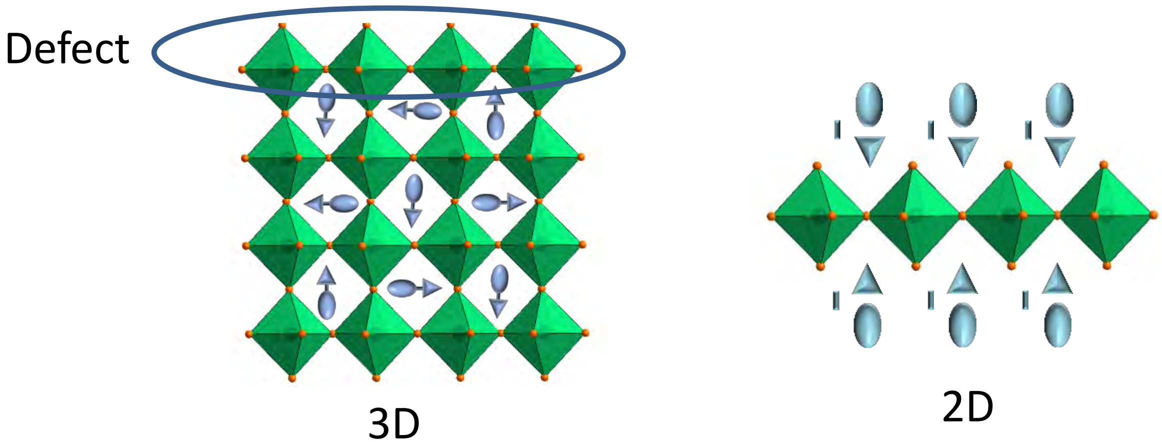
Sample	Electron injection (s^{-1})	Hole injection (s^{-1})
W/O EDA	0.17 x 10^8	1.41 x 10^8
With EDA	2.50 x 10^8	1.03 x 10^8

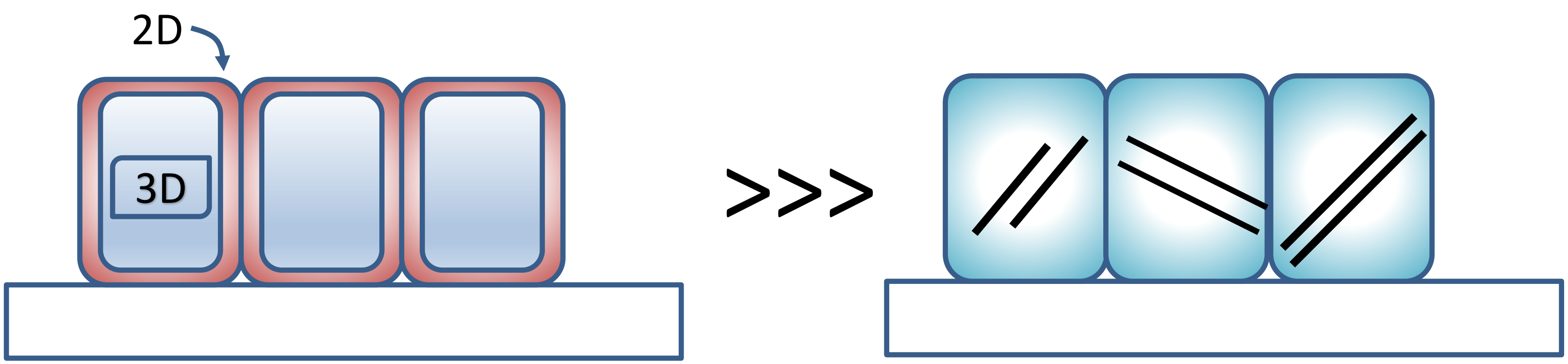
$FA_{0.98}EDA_{0.01}SnI_3$ + 5 mol% GeI_2



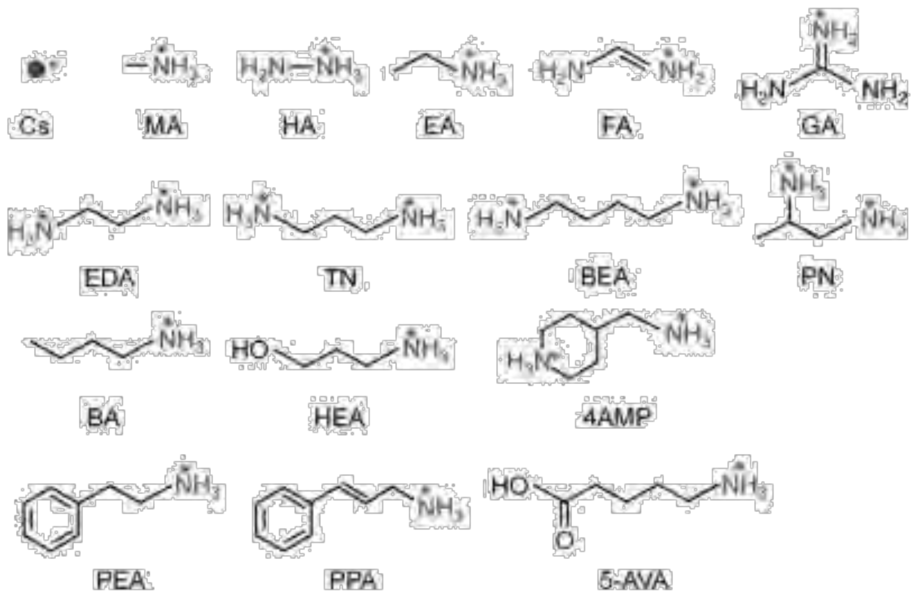
EDA passivation made Fermi level of the surface shallower and improved electron injection into C60, resulting in balanced charge injection between holes and electrons.

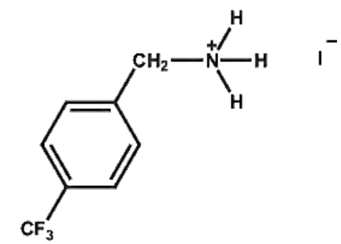
Surface passivation by decreasing surface defect
Optimized 2D/3D structure

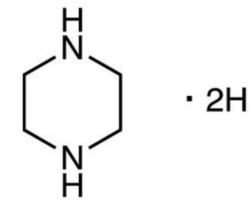


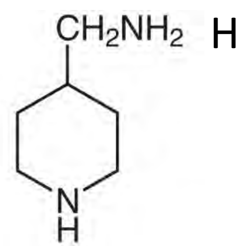


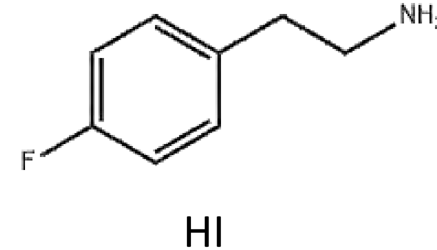
Examples of additives or substitution of A site in Sn-PVK-PV

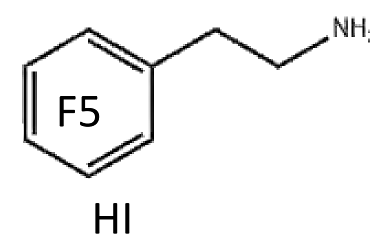












Examples of additives or substitution of A site in Pb-PVK-PV

Passivator type	PCE	Passivator type	PCE
Alkylamine ligands (AALs) [22]	23.0%	DMAI-TFMPHC [23]	21.4%
Phenethyl ammonium iodide (PEAI) [24]	20.31%	Dicyandiamide (DICY) [25]	20.05%
1-Ethyl-3-methylimidazolium (EMIMX) [26]	20%	2-Amino-5-iodobenzoic acid (AIBA) [27]	20.23%
Phenethylammonium chloride (PEACl) [28]	22.7%	Multifunctional pyridine unit [29]	22%
1,4 -Phenyl mercaptan (PHMT) [30]	21.11%	Tetra-n-octadecyl ammonium bromide (TODB) [31]	20.36 %
Poly(styrene-co-acrylonitrile) (PS-PAN) polymer [32]	22.02%	p-Chlorobenzenesulfonic acid (CBSA) [33]	21.8%
2-Mercaptobenzimidazole (MBI) [34]	21.20%	Amine, 3,4,5-trifluorobenzylamine (TFBA) [35]	20.39%
Benzylammonium thiocyanate + MACl [36]	22.3%	3-Hydrazinobenzoic acid (3-HBA) [37]	23.5 %
Homologous PbI_2 [38]	22.13%	Sulfonyl and ammonium [39]	21.76%
Methylamine cyanate (MAOCN) molecules [40]	21.28%	Benzenebutanammonium iodide (PBAI) [41]	23.33%
2-Phenylethylammonium iodide (PEAI) [15]	21.00%	4-Chloro-phenylethylammonium iodide (Cl-PEAI) [15]	22.64%
4-Fluoro-phenylethylammonium iodide (F-PEAI) [15]	23.32%	Piperazinium iodide (PI) [42]	23.37%

Qamar Wali et al., J. Mater. Chem. C, 2022, DOI: 10.1039/d2tc02592b

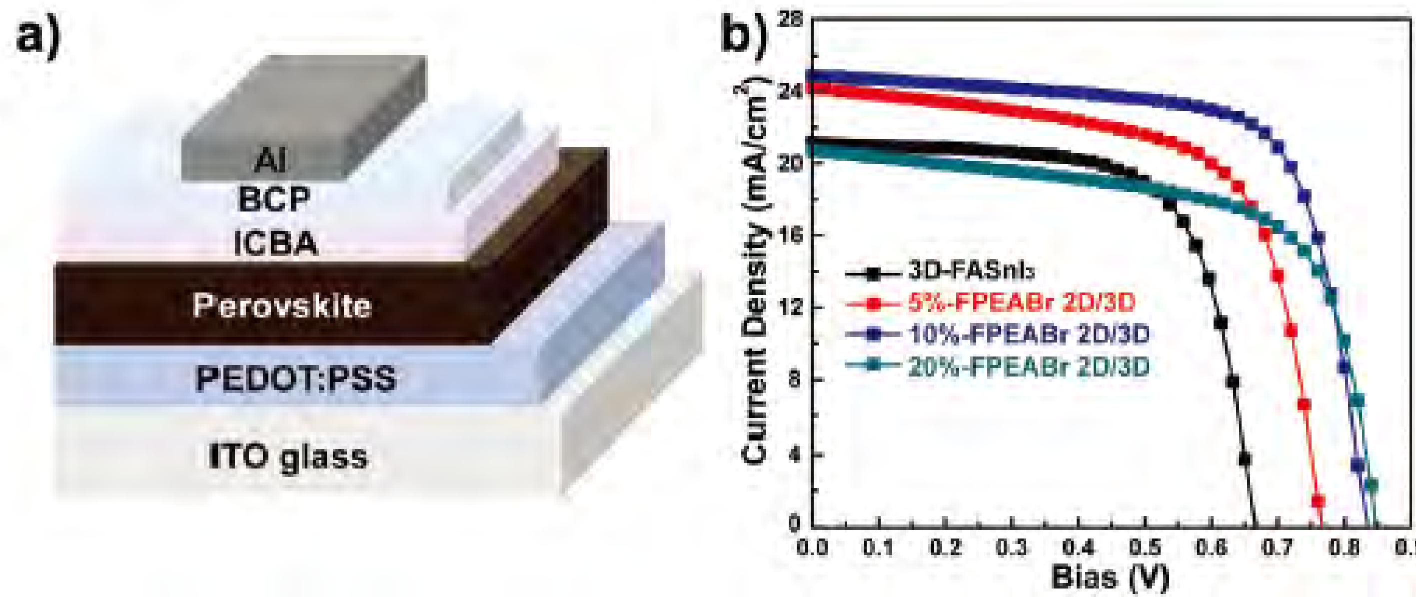
To enhance efficiency

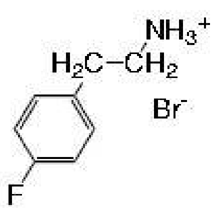
1) Defect
- Sn^{4+}
- Sn^{2+} vacancy
- I^{-} vacancy

2)Band offset

Top efficiency reported so far
Tin perovskite solar cells with 14.8% efficiency

Band offset optimization





4-fluoro-phenethylammonium bromide

Surface passivation

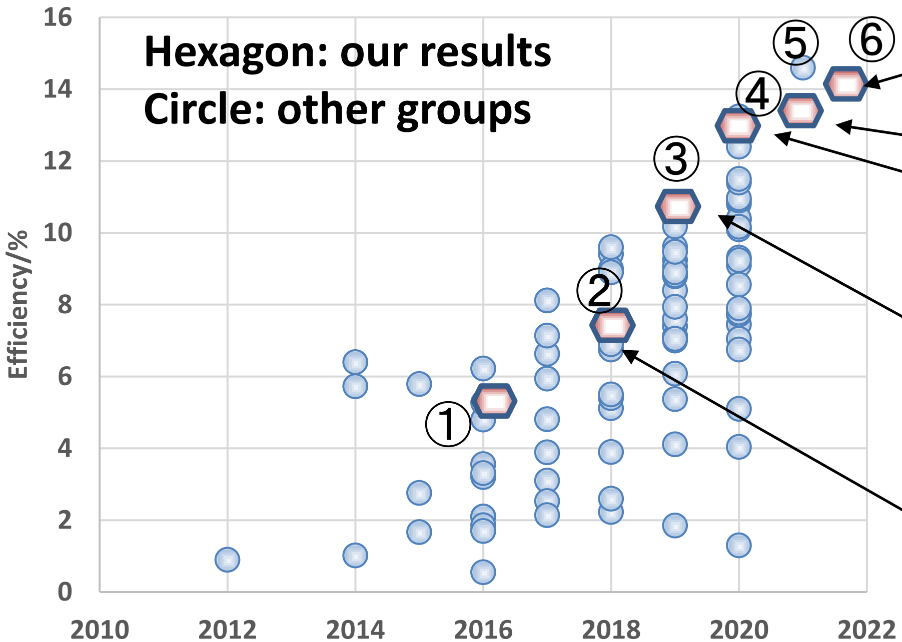
Bin-Bin Yu, Zhenhua Chen, Yudong Zhu, Yiyu Wang, Bing Han, Guocong Chen, Xusheng Zhang, Zheng Du, and Zhubing He, Adv. Mater, 2021, 2102055

Examples of reports on Tin perovskite solar cells with efficiency higher than 13%

Year	Efficiency	Composition	Title	Authors	Paper
2020	13.24	$(FAEA)EDASnI_3$	Lead-free Tin-halide Perovskite Solar Cells with 13% Efficiency (passivation and Reducing agent)	K Nishimura, S. Hayase, et al.	Nano Energy, 2020, 74, 104858
2021	13.4	$FASnI_3$	Perovskite Solar Cell under Coordinated Control of Phenylhydrazine and Halogen Ions (Reducing agent)	Chengbo Wang, et al.	Matter, 2021, 4, 709-721
2021	14.6	$FA(EDA)SnI_3(Br)$	One-Step Synthesis of SnI2・(DMSO)x Adducts for High-Performance Tin Perovskite Solar Cells (Purification)	Xianyuan Jiang, et al.	JACS, https://doi.org/10.1021
2021	14.8	$FA(FPEABr)SnI_3$	Heterogeneous 2D/3D Tin-halides perovskite solar cells with certified conversion efficiency braking 14%(Passivation)	Bib-Bin Yu	Adv. Mater, 2021, 2102055
2021	14.7	$FA_{0.75}MA_{0.25}SnI_3$	Chemo-Thermal Surface Dedoping for High-performance Tin Perovskite Solar Cells (Purification)	J. Zhou, Y. Zhou et al.,	Matter, 2021, https://doi.org/10.1016/j.matt.2021.12.013.
2022	13.8	$FASnI_3$	Heterogenerous FASnI3 absorber with enhance Electric field for high-performance lead-free perovskite solar cells (Band optimization)	T. Wu, L. Han, et al.,	Nano-Micro Letters, 2022, 14:99
2022	14.07	$Cs_{0.02}(FA_{0.9}DEA_{0.1})_{0.98})_{0.98}EDA_{0.01}I_3$	SnOx as Bottom Hole Extraction Layer and Top In-situ Protection Layer Yields over 14% Efficiency in Sn-based Perovskite Solar Cells (Hole collector+ reducing agent)	Liang Wang, Shuzi Hayase, et al.,	ACS Energy Lett., in press

The efficiency is being enhanced step by step.

Progress of efficiency for Tin perovskite solar cells



⑥SnOx p-type alyer(14.1%)→14.3%
ACS Energy Lett., 2022, 7, 10, 3703-3708.

⑤Optimization of process (13.6%)

④Decrease in band offset by A site engneering

- ACS Appl. Mater. Interfaces, 2019, 11, 34, 31105-31110
- Nano Energy, 2020, 74, 104858

③Decrease in defect at grain boundary by EDA passivation

- J. Phys. Chem. Lett. 2019, 10, 17, 5277-5283

②Decrease in Sn^{4+} By GeI_2 addition

- J. Phys. Chem. Lett., 9, 1682-1688, 2018.
- Nano Energy 2019, 58, 130-137

	Method	Perovskite composition	Solar cell structure
1	Reference	$FA_{0.75}MA_{0.25}SnI_3$	ITO/PEDOPPSS/PVK/PCBM/C60/BCP/Ag/Au
2	GeI_2 addition Decrease in Sn^{4+}	$FA_{0.75}MA_{0.25}SnI_3$ (5 mol % Ge doping)	ITO/PEDOPPSS/PVK/PCBM/C60/BCP/Ag/Au
3	EDA passivation Decrease in surface defect	$FA_{0.98}EDA_{0.01}SnI_3$	FTO/PEDOPPSS/PVK/C60/BCP/Ag/Au
4	Ge + EDA passivation+Et sub. Less Lattice disordering, Less band offset	$(EA_{0.1}FA_{0.9})_{0.98}EDA_{0.01}SnI_3$(5mol% GeI_2 doped)	FTO/PEDOPPSS/PVK/C60/BCP/Ag/Au

Summary

Sn PVK PV

- To decrease Sn^{4+}concentration：reduced reagents
- Grain boundary defect: Introduction of 2D structure
- To deacrease Sn^{2+} defect：Ge^{2+} addition
- To decrease I^- defect：ethylenediamine
- To decrease band offset：A site optimization of $ASnX_3$
- To improve carrier injection: Heterointerface modification
- Charge injection balance optimization

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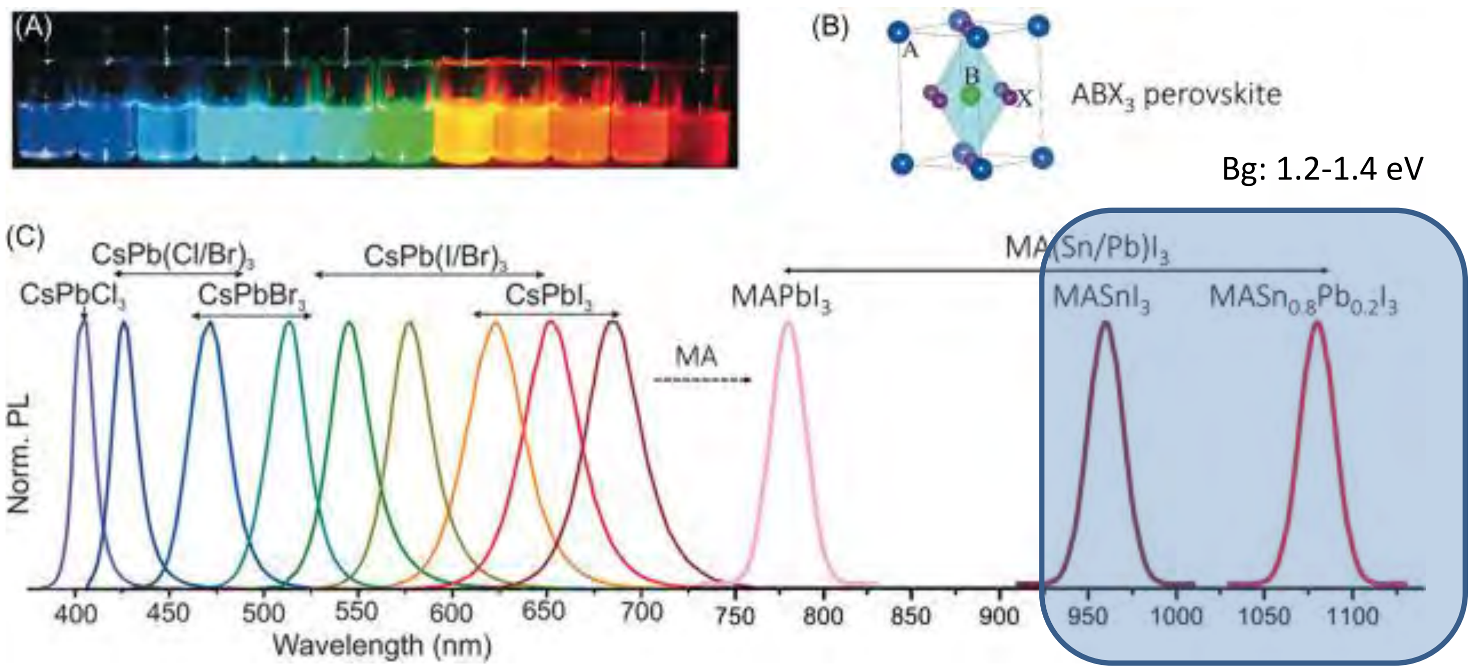
Band gap control

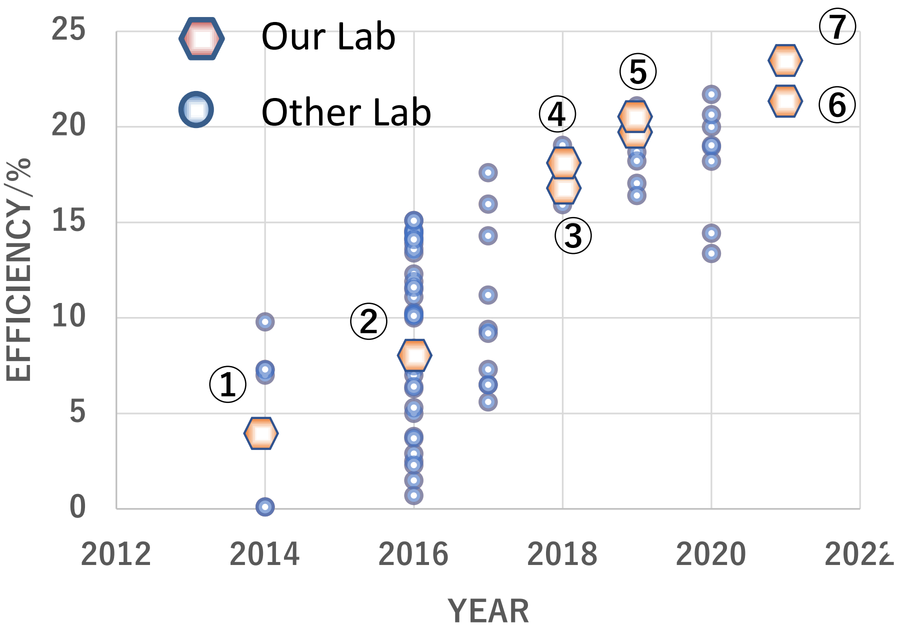
Characterization Techniques for Perovskite Solar Cell Materials, Micro and Nano Technologies, 2020, Pages 1-22
Somayeh Gholipour, Michae lSaliba, https://doi.org/10.1016/B978-0-12-814727-6.00001-3



Top cell　　Bottom cell

- **Pb perovskite: APbX3: Large size A site⇒Narrow band gap, X site Br substitution⇒wide band gap**
- **Sn perovskite: ASnX3: Large size A site⇒Wide band gap**

Efficiency progress of SnPb perovskite solar cell



②J. Phys. Chem. Lett. 2014, 5 (6), 1004–1011.

②ACS Appl. Mater. Interfaces 2020, 12, 1776-17782

③J. Phys. Chem., C: 2018, 122, 27284–27291

④Nano Letters, 18, p.3600-3607, 2018

⑤ACS. Energy Lett., 2019, 4, 1991－1998

⑥Advance Energy Materials ,doi.org/10.1002/aenm.2021010692021) (21.7%)

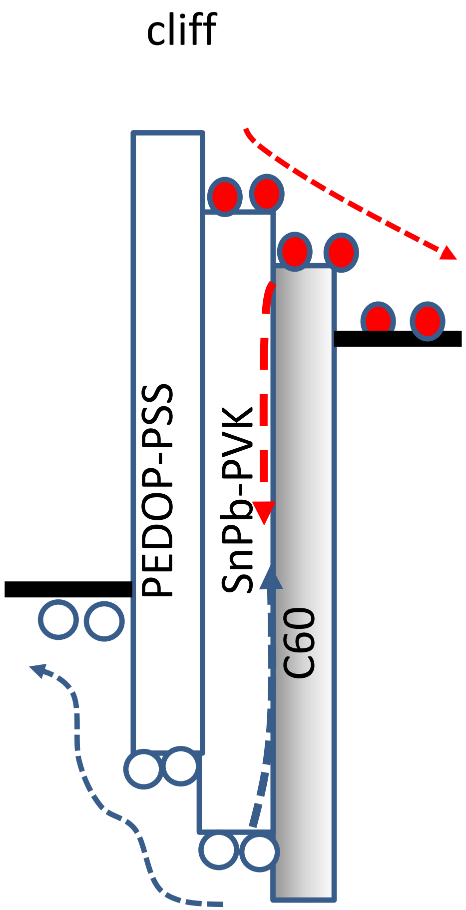
⑦ ACS. Energy Lett., 2022, 7, 3, 966–974.(23.3%)

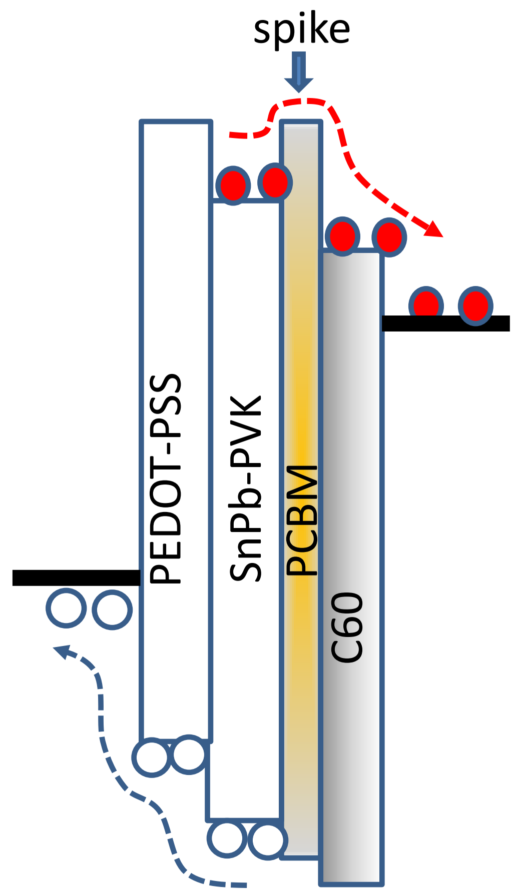
Method		PVK	Cell structure
normal	1	$MASn_{0.5}Pb_{0.5}I_3$	FTO/TiO_2/PVK/P3HT/Au
inverted	2	$MASn_{0.5}Pb_{0.5}I_3$	ITO/PEDOTPSS/PVK/C60/BCP/Ag
DMSO complex	3	$MASn_{0.5}Pb_{0.5}I_3$	ITO/PEDOTPSS/PVK/C60/BCP/Ag
Spike structure	4	$FA_{0.5}MA_{0.5}Sn_{0.5}Pb_{0.5}I_3$	ITO/PEDOTPSS/PVK/PCBM/C60/BCP/Ag
FTO structure	5	$FA_{0.5}MA_{0.5}Sn_{0.5}Pb_{0.5}I_3$	FTO/PEDOTPSS/PVK/PCBM/C60/BCP/Ag
Lattice strain+EDA	6	$Cs_{0.025}FA_{0.475}MA_{0.5}Sn_{0.5}Pb_{0.5}I_3$	FTO/PEDOTPSS/PVK/PCBM/C60/BCP/Ag

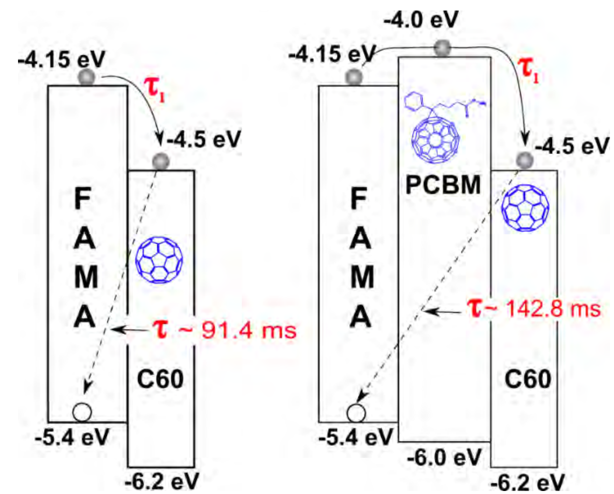
Direction:

Low defect density, low lattice strain, band structure for retarding charge recombination

Spike and Cliff band structure at SnPb-PVK and C60 interfaces





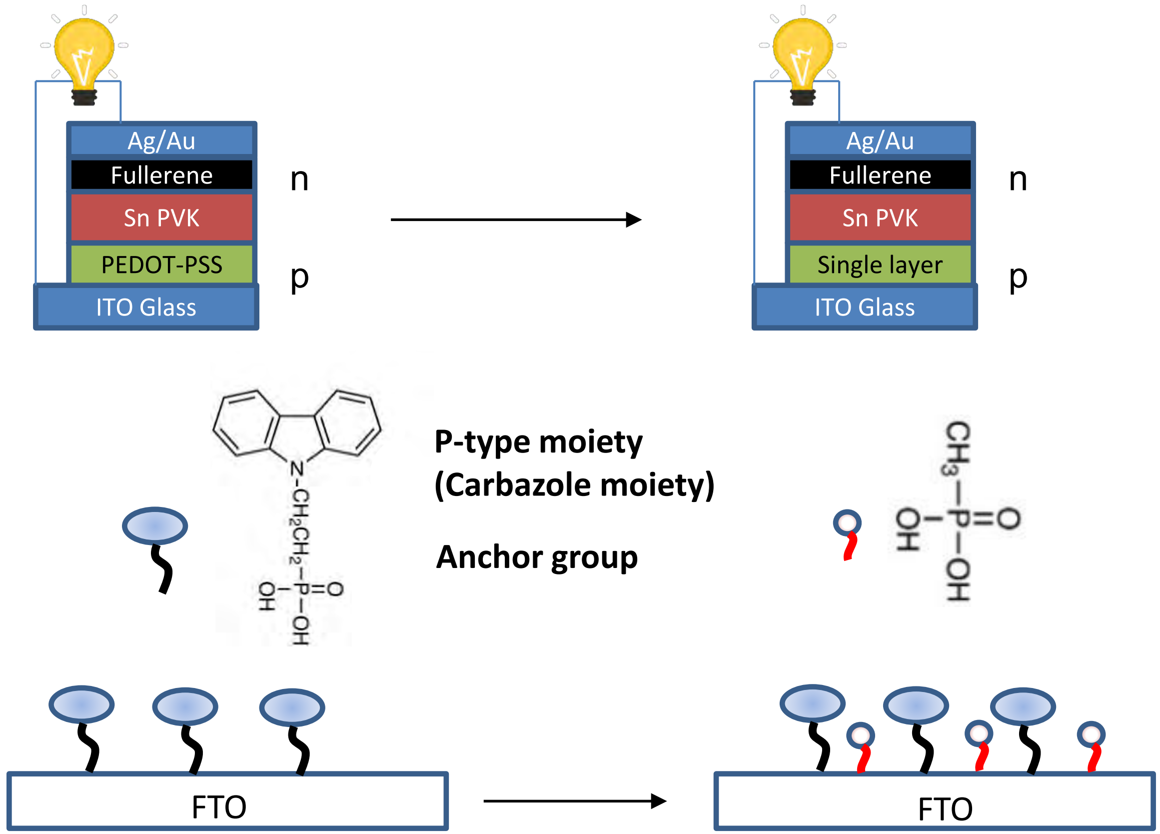


Previously recommended
(cascade structure)

Band structure tried
Recommended from CIGS study

G. Kapil, H. Segawa, S. Hayase , Nano Lett., 2018, 18 (6), pp 3600–3607

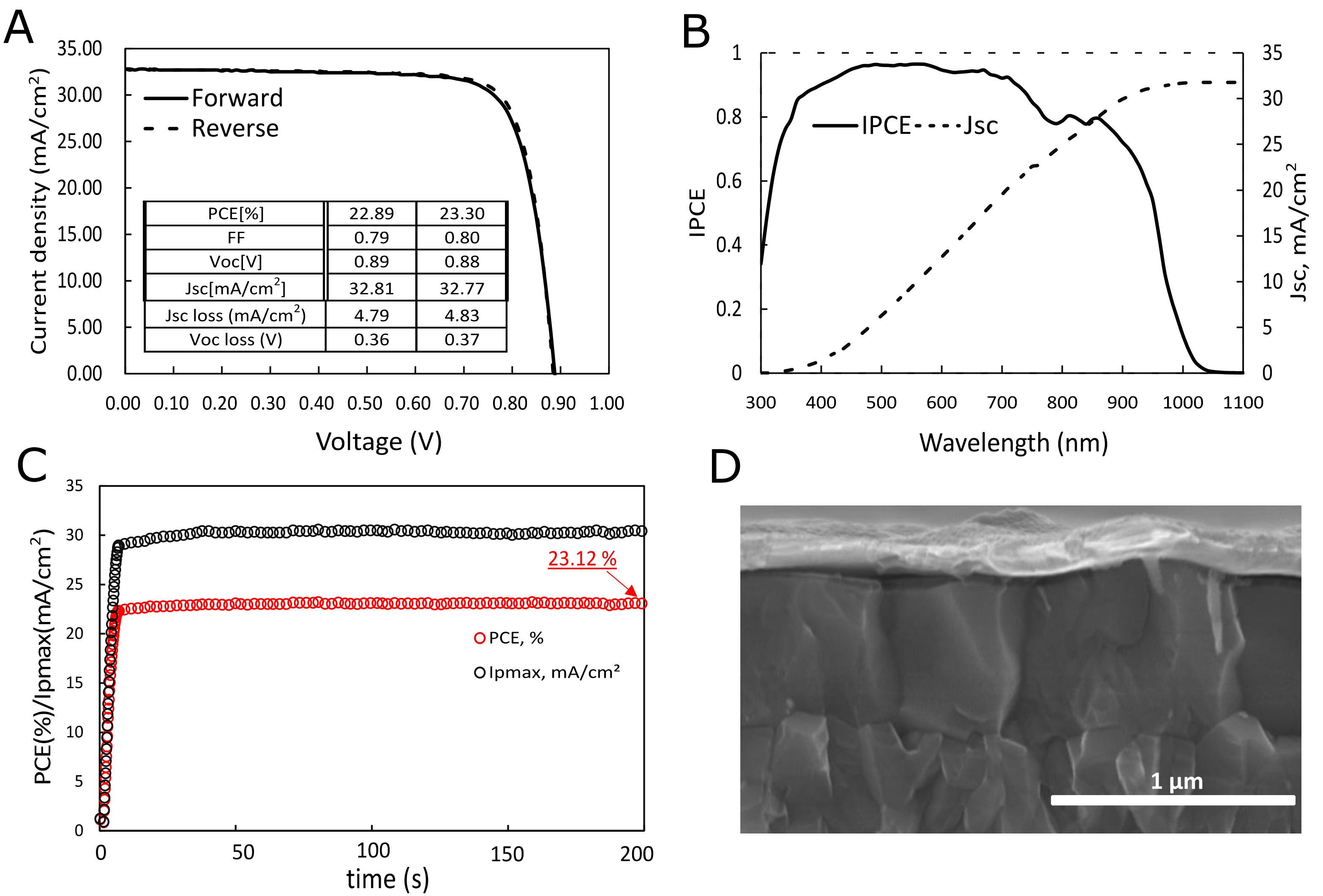
Increase in surface coverage with p-type monomolecular layer



Conventional monolayer

Mixed monolayer enhanced the efficiency of Tin-Lead alloyed perovskite solar cells

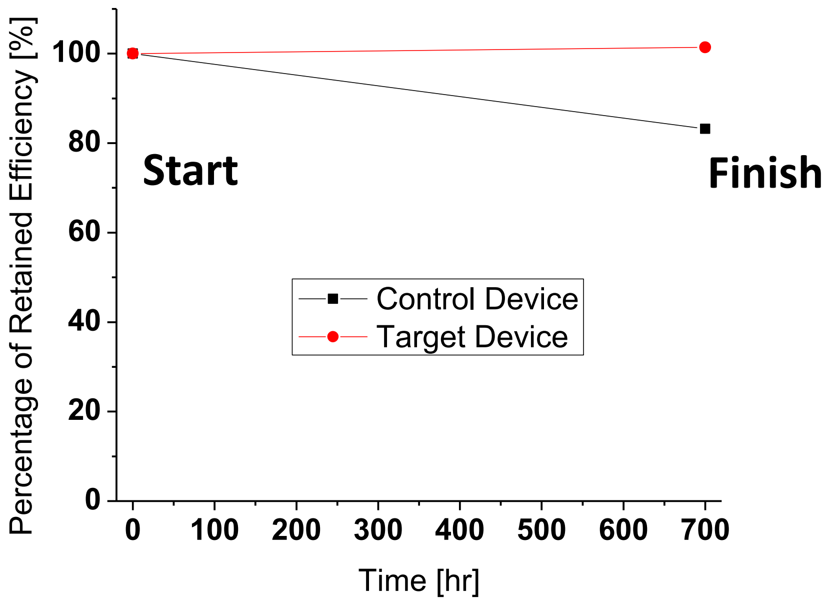
Optimized device



PCE[%]	22.89	23.30
FF	0.79	0.80
Voc[V]	0.89	0.88
Jsc[mA/cm^2]	32.81	32.77
Jsc loss (mA/cm^2)	4.79	4.83
Voc loss (V)	0.36	0.37

G. Kapil, S. Hayase, et al., ACS Energy Letters, 2022, 7, 3, 966–974.

Thermal stability of SnPb PVK solar cells



Condition for thermal stability test: Samples were placed on a hotplate at 85 degree Celsius in dark storage, nitrogen atmosphere for over 700 hrs.

The detail will be presented in Japan Society of Applied Physics spring meeting by Shahrir Razey Sahamir

No degradation of efficiency was observed after 85°C for 700 hrs after optimization of the devaice structure.

summary

Tin Lead alloyed PVK PV

- Decrease in defect density
- Introduction of spike structure to reduce heterointerface charge recombination
- Decrease in distortion of ABX3 by A site optimization
- Increase in surface coverage of ITO or FTO by co-adsorption of SAM moleculres

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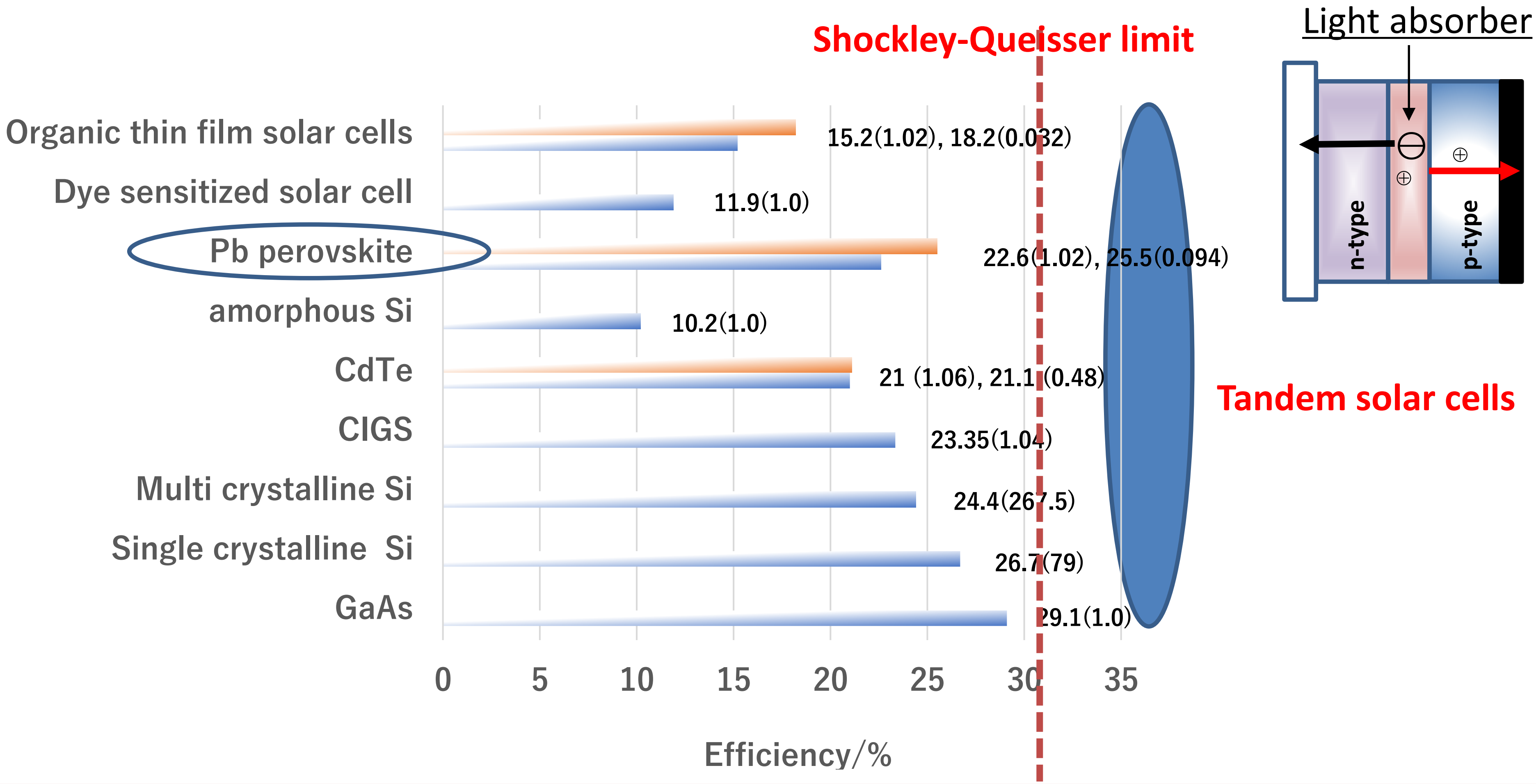
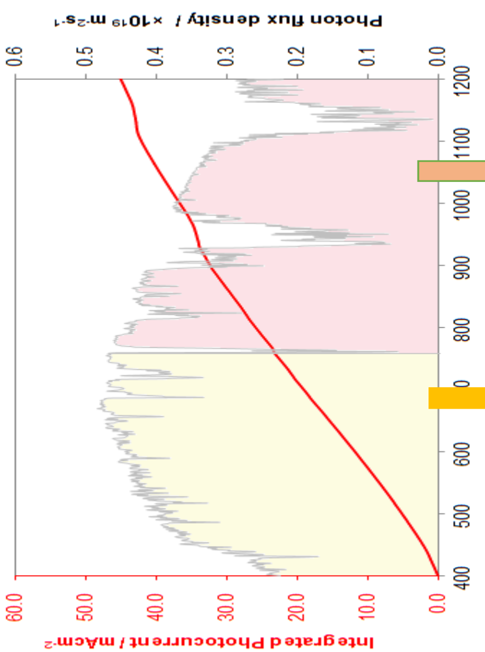
Certified efficiency for various solar cells larger than 1cm^2



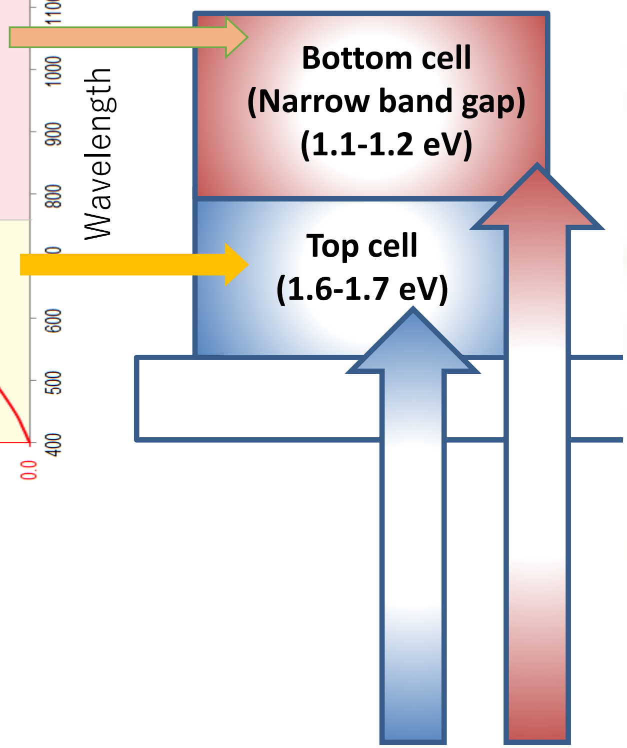
Martin Green, Ewan Dunlop, Jochen Hohl-Ebinger, Masahiro Yoshita, Nikos Kopidakis, Xiaojing Hao, Prog Photovolt Res Appl2021;1-11. Efficiency Table 58

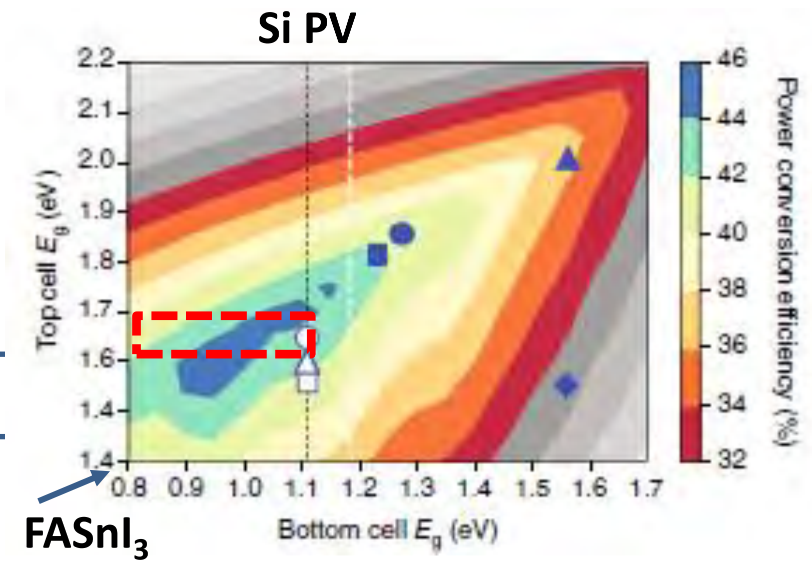
Efficiency of PVK is close to that of Si solar cell even though the cell is prepared at 100 ℃ process.

Perovskite tandem solar cells



A



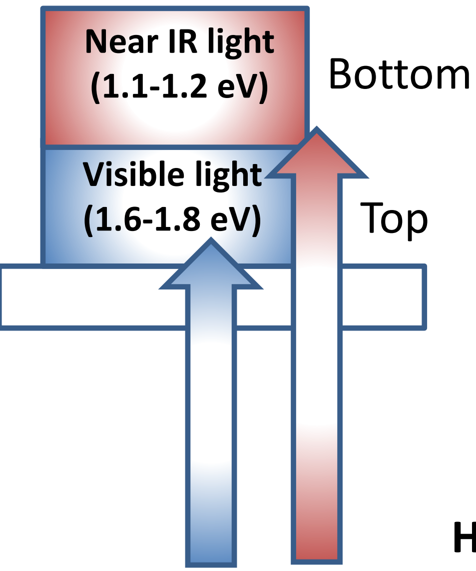


T. Leijtens et al, Nature Energy, 2018, 3, 828-838

Tandem Voc = V1 + V2, Tandem Jsc = Jsc

Tin perovskite with 1.6 – 1.7 eV wide band gap is needed.

Perovskite tandem solar cell efficiency



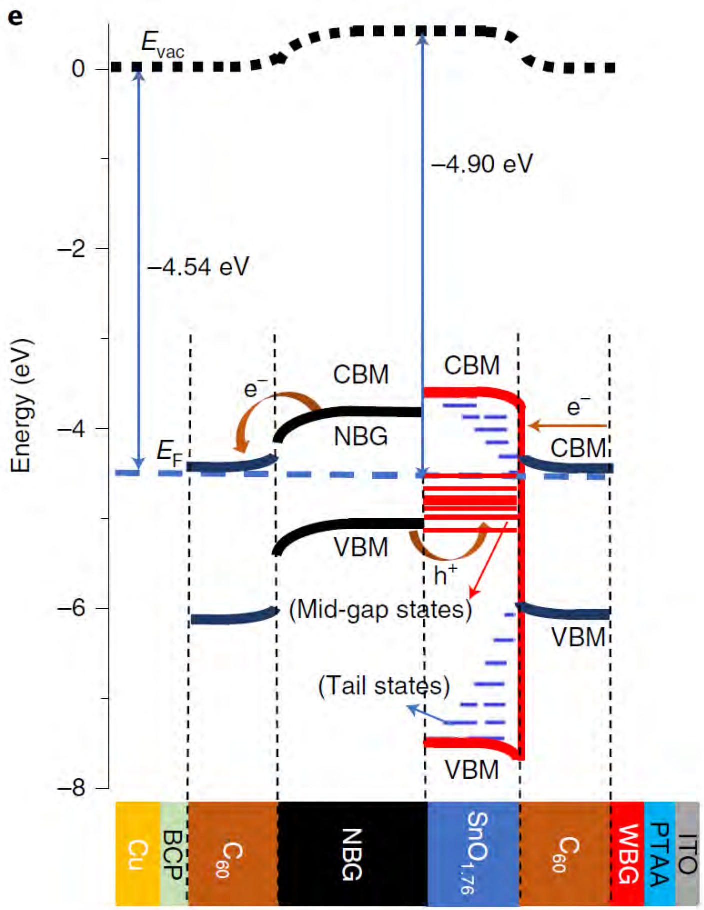
Tandem	Efficiency %	Area cm^2	Institute
Pb PVK(top)/Si(Bottom)	32.5→33.2		HZB→KAUST
Pb PVK(top)/Si(Bottom)	31.3	1.17	EPFL/CSEM
Pb-PVK/CIGS	24.2	1.045	HZB
Pb-PVK/SnPb-PVK	26.4	1.04	SichuanU/EMP
Pb-PVK/SnPb-PVK	28.0	0.0495	Nanjin Univ.
Si(single) PV	26.8	79	ISFH
Pb PVK PV	25.7	0.096	UNIST

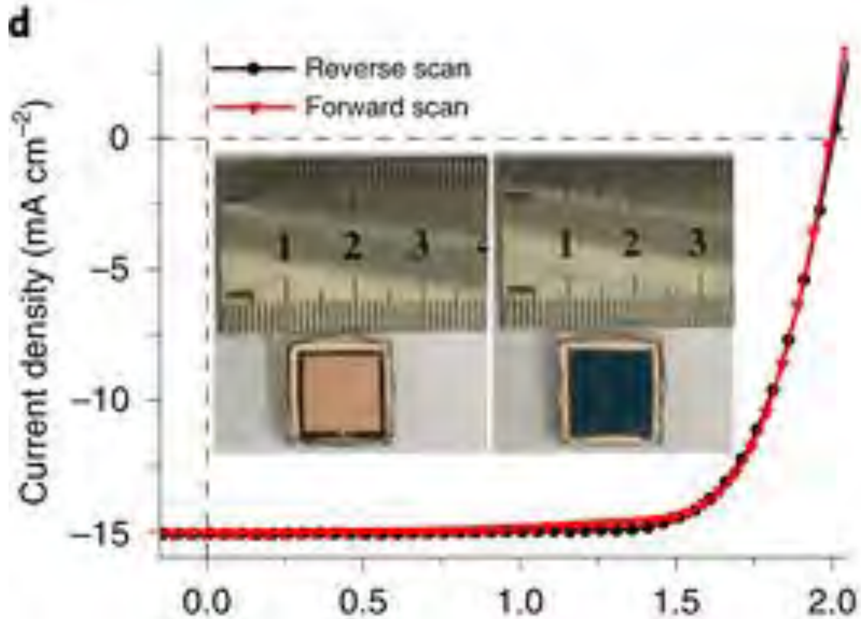
Hayase Lab. Perovskite/perovskite tandem solar cells: 26.5% (2023/4)

Advantage of the all-perovskite tandem solar cells over others
⇒Flexible tandem solar cells

Perovskite tandem solar cells with efficiency higher than 30% is now realized

Charge recombination layer with ALD SnOx/C60

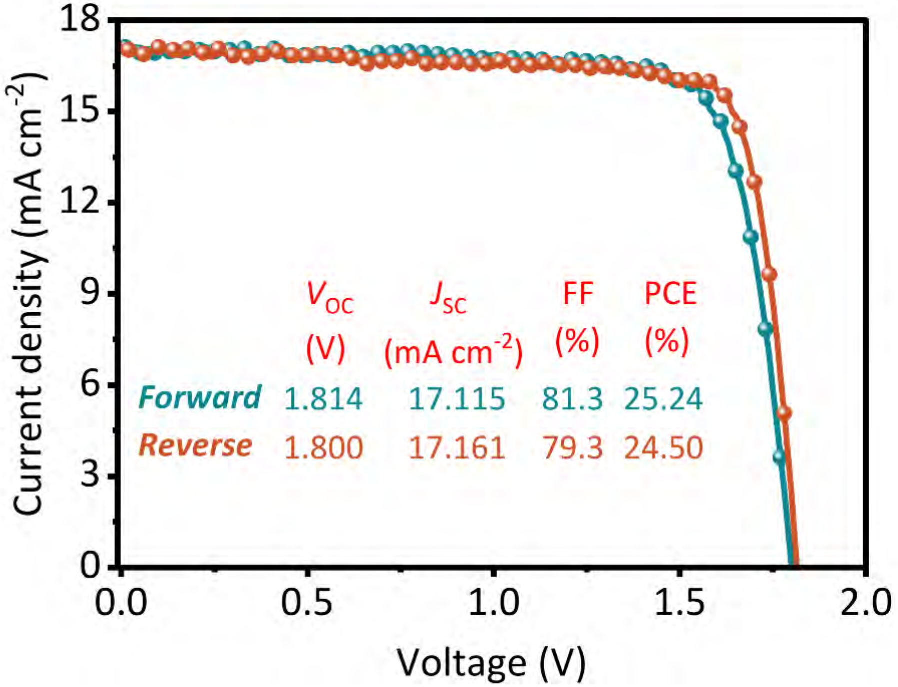




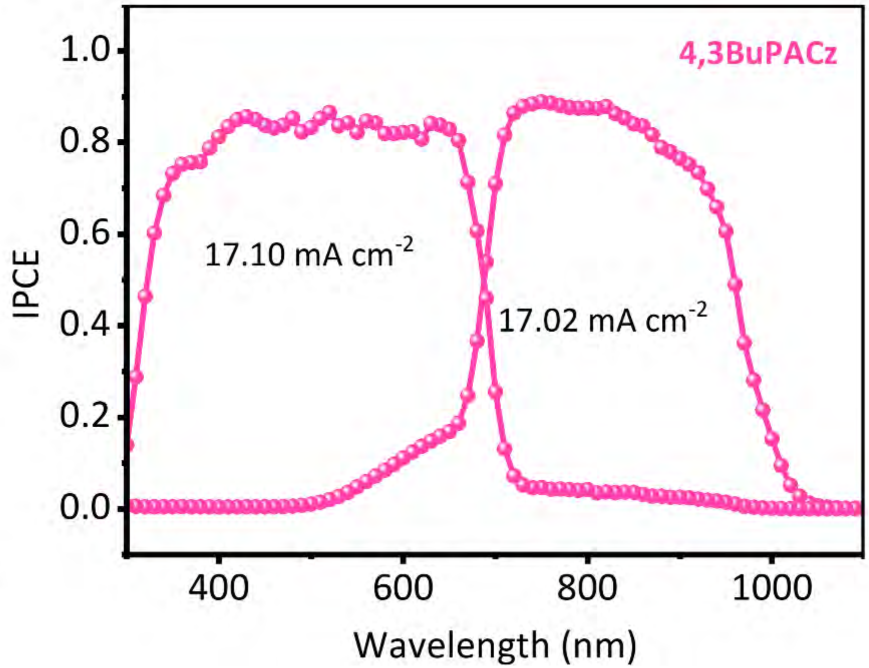
Small-area tandem cells (5.9 mm2) and large-area tandem cells (1.15 cm2) to 24.4% and 22.2%

Zhenhua Yu, et al., Nature Energy, 2020, 5(9):1-9

Our perovskite/perovskite tandem soalr cells

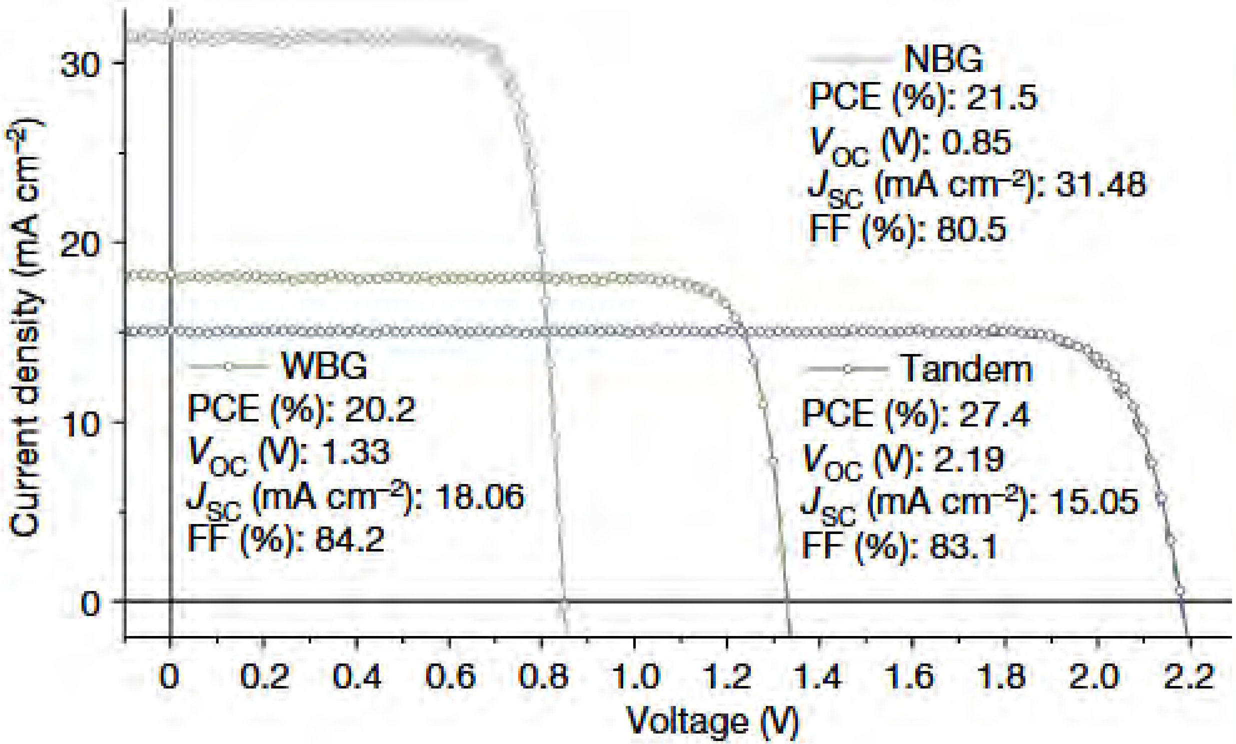


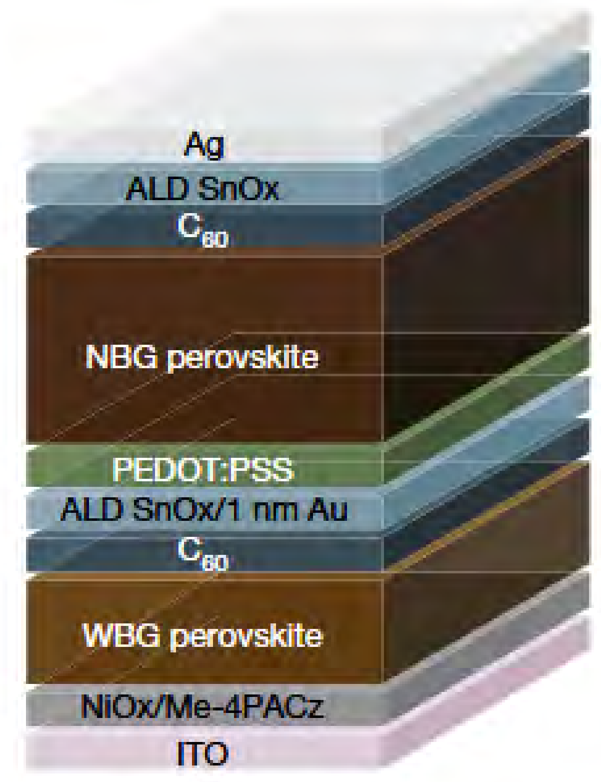
(c)



H. Bi, H. Segawa, S. Hayase, et al., Advanced Functional Materials, 2023, just accepted.

Highest all perovskite tandem cell published so far!





Area= 0.049cm^2

H. Chen and E. Sargent al., Nature volume 613, pages676-681 (2023)

Summary

Perovskite tandem solar cels

- **Top cell-bandgap: 1.6-1.8 eV**
- **Bottom cell-bandgap: 1.1-1.2eV**
- **Pb PVK (top)/Si PV(bottom): 33.2%**
- **All-perovskite tandem solar cell: Pb PBK(top)/SnPb PVK PV(bottom): 28%**
- **All-perovskite solar cells has advantage over other solar cells from view point of flexibility.**

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Research trends in Feb. 2023

Current situation

- Sn-Pb alloyed perovskite: 23.3% in Hayase Lab (world: 23.6%) which is almost the same as that of Pb perovskite(Inverted structure).
- Sn-PVK: 14.3 % in Hayase Lab (World:14.8%)

Solution

- Decrease in carrier concentration (Ge(II) ion addition)
- Decrease in defects of grain boundary (EDA passivation)
- Conduction band and valence band energy level optimization (A site engineering)
- Decrease in Lattice disordering (A site engineering)
- Surface passivation by 2D structure
- Charge injection balance (EDA passivation)

Tandem

- Perovskite/Perovskite tandem solar cells 28% (world) (our Lab. 26.8%)
- Perovskite/Si tandem aiming at 35% (present: 33.2%) (our Lab. 27-28%)

Thank you for kind attention!