

Effect of Binary Metal Fluoride (MF_x) on Tin Perovskite Solar Cells

Dhruba B. Khadka[1],

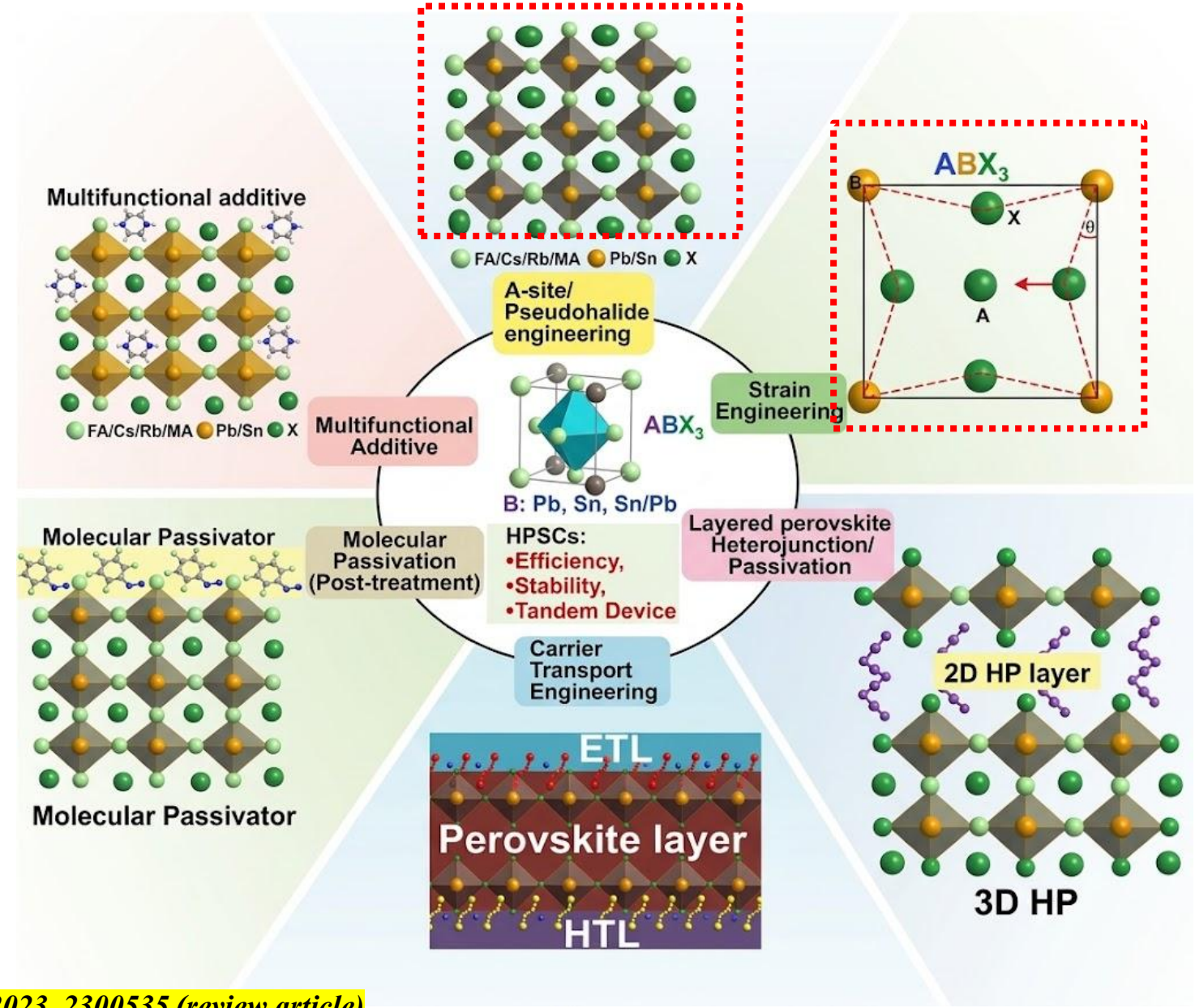
A. Shukla, M.Otake[2], M. Yanagida[1], K. Yamashita, Azusa Muraoka[2], Yasihiro Shirai

[1]***Photovoltaic Materials Group***
Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN)
National Institute for Materials Science (NIMS), Tsukuba, Japan

[2]*Graduate School of Science, Japan Women's University, Japan*

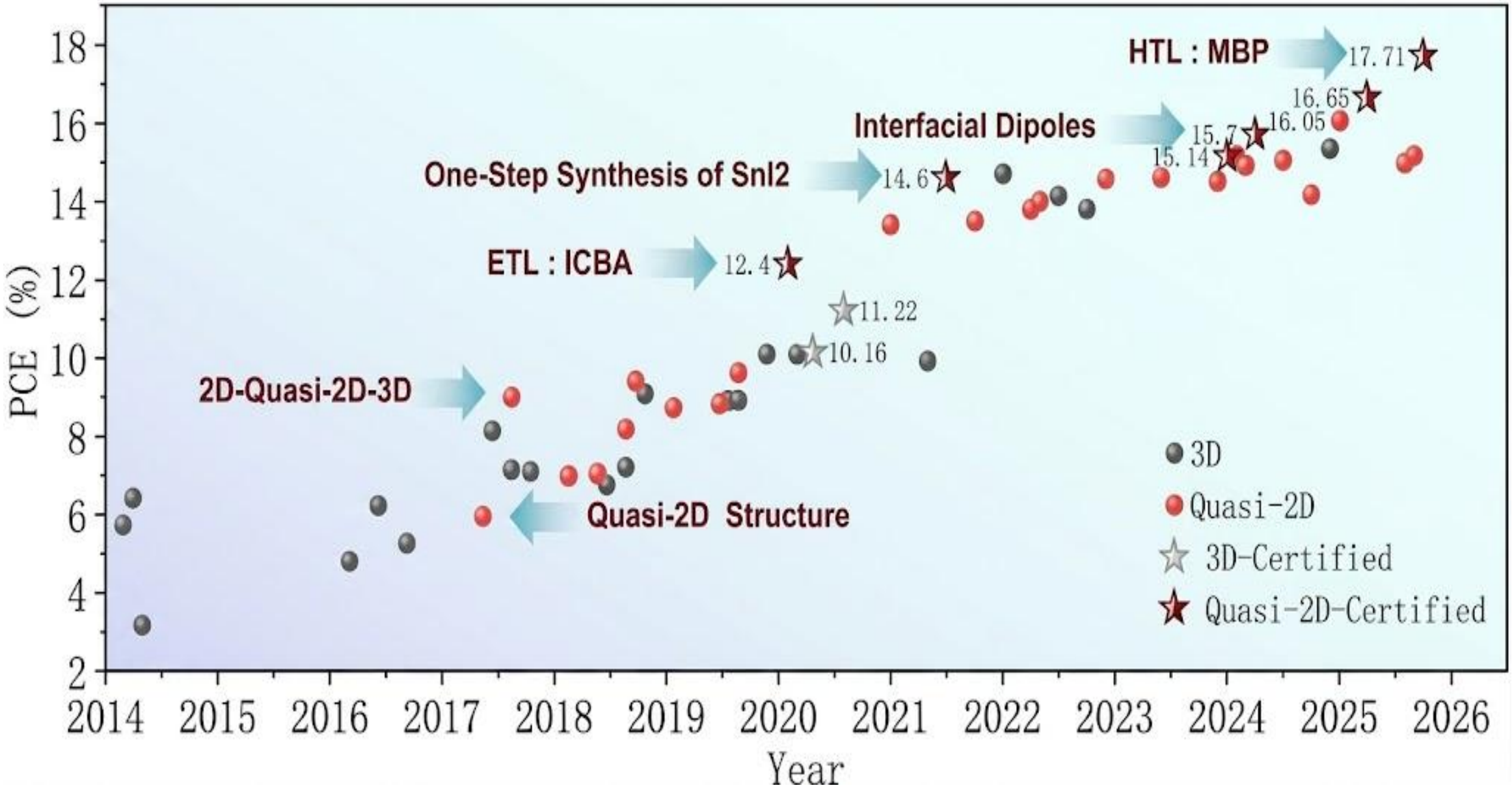
9/8(Tue.) >E201会場(Room E201)

Strategies for Perovskite Solar Cell Optimization



Khadka et al. Sol. RRL 2023, 2300535 (review article)

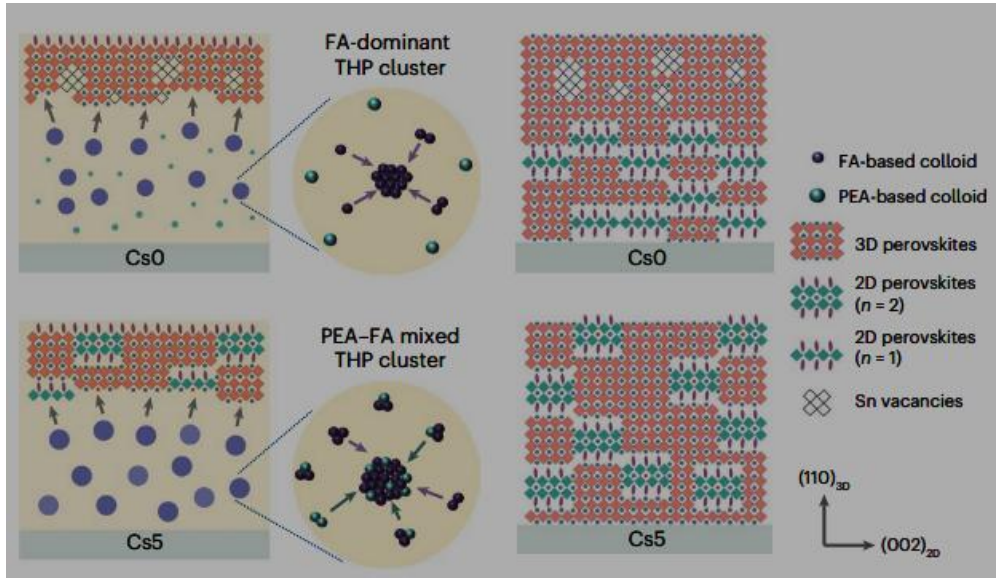
Strategies for Tin Perovskite Solar

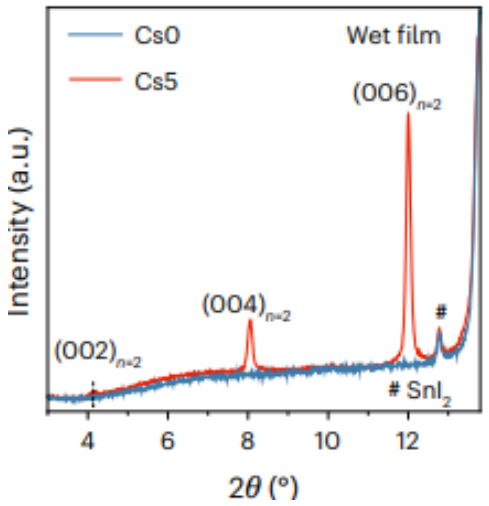


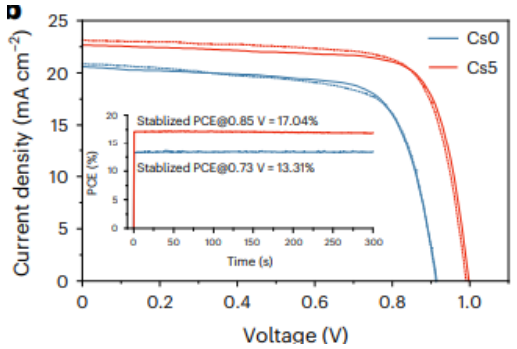
ACS Energy Lett. 2026, 11, 180

Sn-PSCs: Reports

Caesium-PEA-FA –based colloid-regulated 2D/3D Sn-perovskite



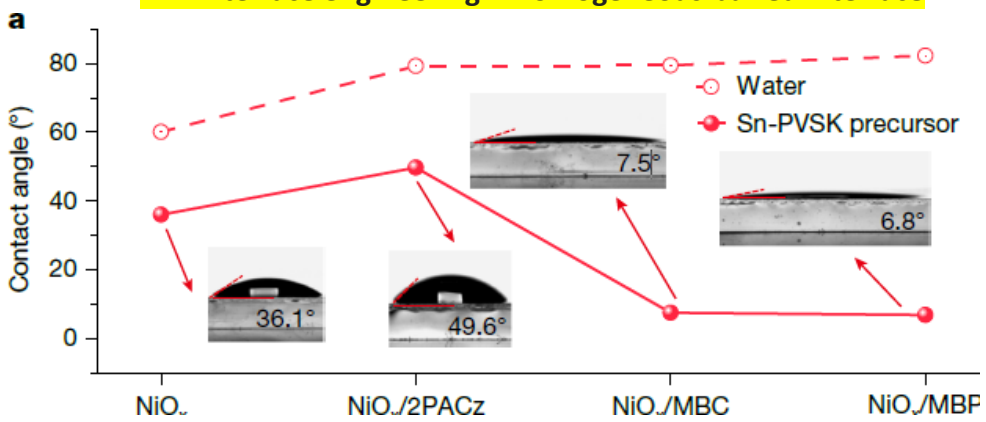


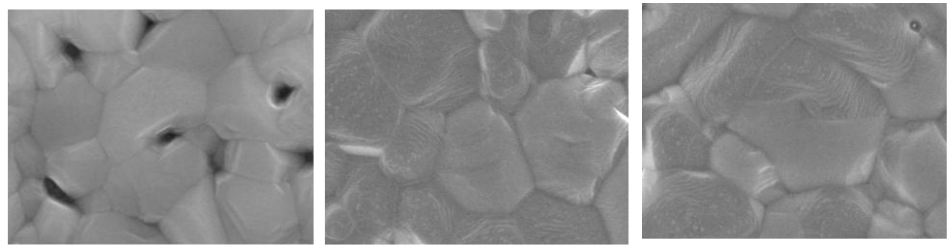


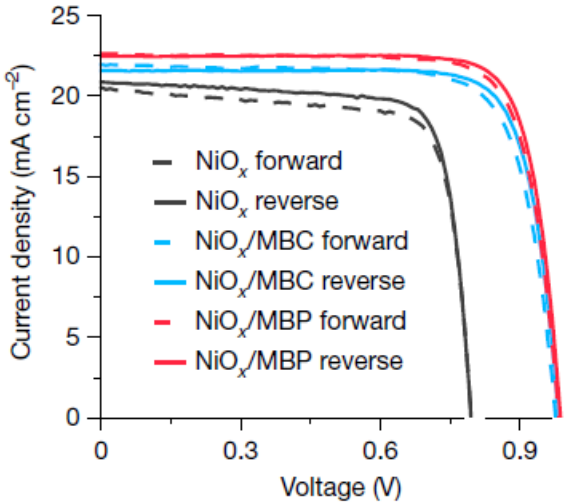
>16.65%

Steele *et al. Nat. Nanotechnol.* **2025, 20, 779**

HTL interface engineering > Homogeneous buried interface







>17.71%

Wang, *et al. Nature*, 2025, **648**, 84

B-Site Doping: Report

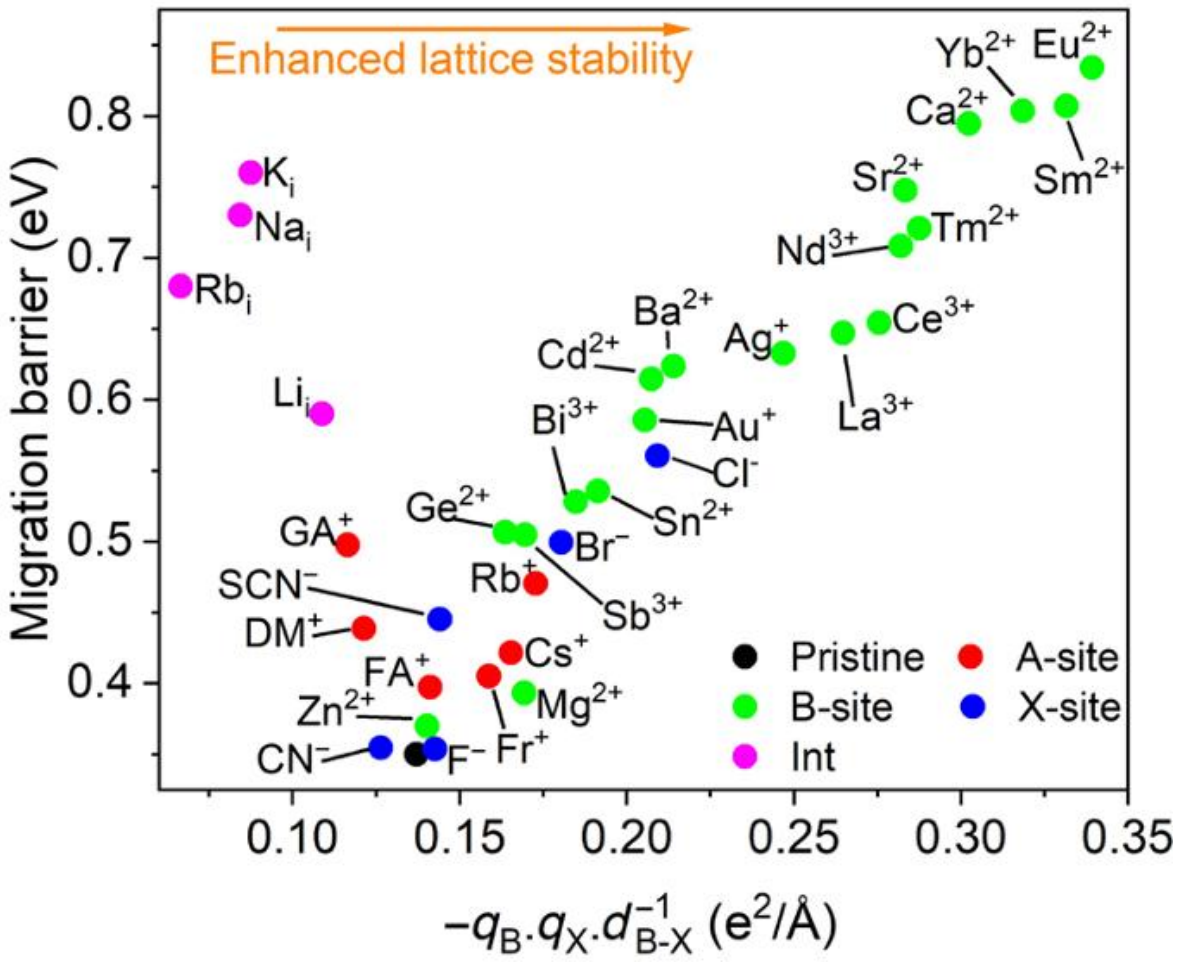
SCIENCE ADVANCES | RESEARCH ARTICLE

PHYSICAL SCIENCES

Multiple B-site doping suppresses ion migration in halide perovskites

Yuhang Liang[1,2], Feng Li[2]*, Xiangyuan Cui[3]*, Catherine Stampfl[2], Simon P. Ringer[3], Xudong Yang[4,5,6], Jun Huang[1]*, Rongkun Zheng[2]*

Lead halide perovskites hold great promise for photovoltaics and optoelectronics, yet ion migration continues to challenge their long-term stability. Here, combining first-principles calculations and machine learning molecular dynamics, we unravel the interplay between perovskite octahedral lattice dynamics and energy barrier associated with ion migration. Our results show that B-site substitution, particularly with alkaline-earth and lanthanide elements, notably strengthens lattice interactions, restrains octahedral oscillation, and increases iodine-migration barriers, outperforming the commonly used A-site and X-site substitutions and interstitial doping. Moreover, the enhanced barrier aligns with the geometric factor of μτ (tolerance-octahedral product), underlining the superior effectiveness of co- and multiple-element B-site doping in lattice stabilization and ion migration suppression. Experimental validation with exemplary hysteresis-free Eu-Ca–doped perovskite single crystals demonstrates remarkable improvements in ambient stability and transport properties. These findings highlight B-site engineering as an effective microstructural strategy for controlling ion migration, with important implications for stable and lead-reduced perovskite devices.



Lattice ionic interaction

>B- site engineering as an effective microstructural strategy for controlling ion migration.

Effect of SrI_2- doping in Sn-perovskite

ACS Energy LETTERS

Open Access

This article is licensed under CC-BY 4.0

http://pubs.acs.org/journal/aelccp

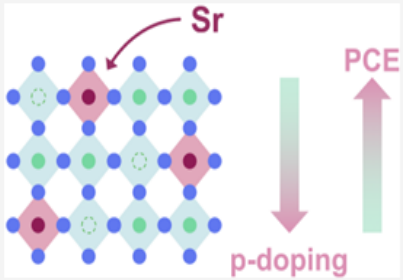
Mitigation of Self-p-Doping and Off-Centering Effect in Tin Perovskite via Strontium Doping

Chiara Frasca, Paola Alippi, Renè Schwiddessen, Karunanantharajah Prashanthan, Giuseppe Nasti, Shengnan Zuo, Muhammad Okash Ur Rehman, Mahmoud Hussein Aldamasy, Noor Titan Putri Hartono, Artem Musiienko,* and Antonio Abate*

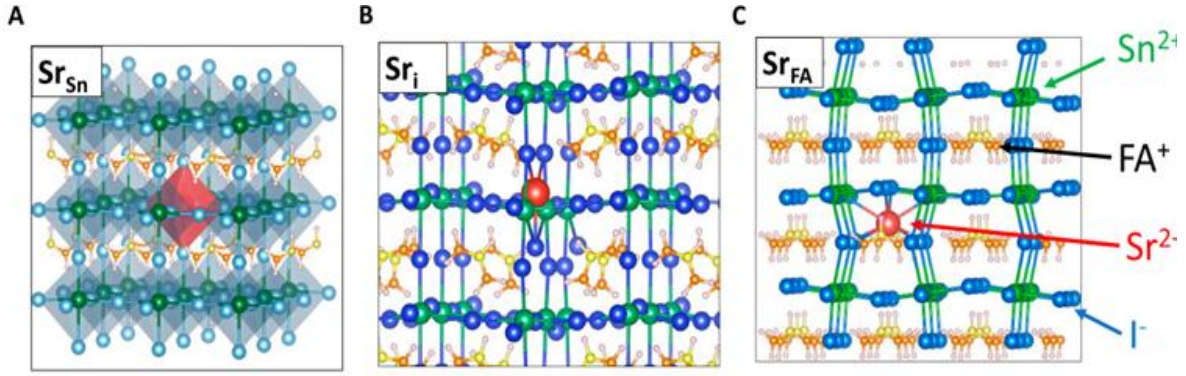
Cite This: *ACS Energy Lett.* 2025, 10, 526–533 Read Online

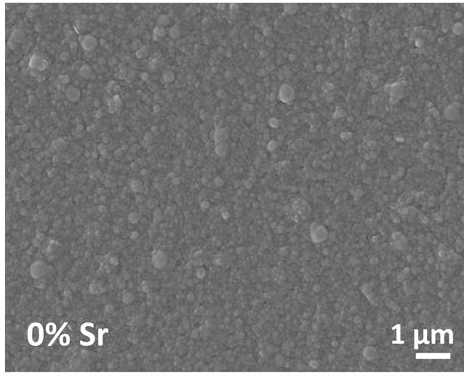
ACCESS | Metrics & More | Article Recommendations | Supporting Information

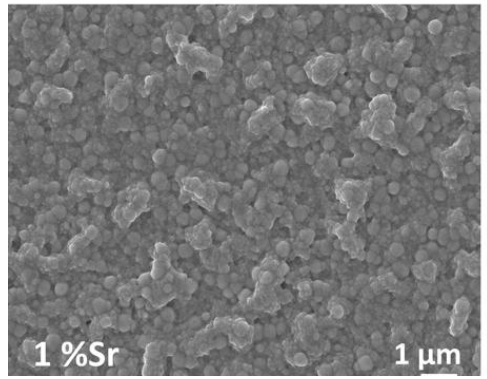
ABSTRACT: Tin-based perovskite solar cells offer a less toxic alternative to their lead-based counterparts. Despite their promising optoelectronic properties, their performances still lag behind, with the highest power conversion efficiencies reaching around 15%. This efficiency limitation arises primarily from electronic defects leading to self-p-doping and stereochemical activity of the Sn(II) ion, which distorts the atomic arrangement in the material. In this study, we investigate the effect of strontium doping in tin-based perovskite on the distortion of the material's structure and its optoelectronic properties. Using a combination of Density Functional Theory calculations and experiments, we demonstrate that strontium doping reduces p-doping and structural strain. This approach improves the efficiency from 6.3% in undoped devices to 7.5% in doped devices without relying on dimethyl sulfoxide, a harmful solvent for tin-based perovskites. This method could enable precise control of tin off-centering and self-p-doping, advancing the development of efficient and stable tin perovskite solar cells.



Sr-doping-defect passivation



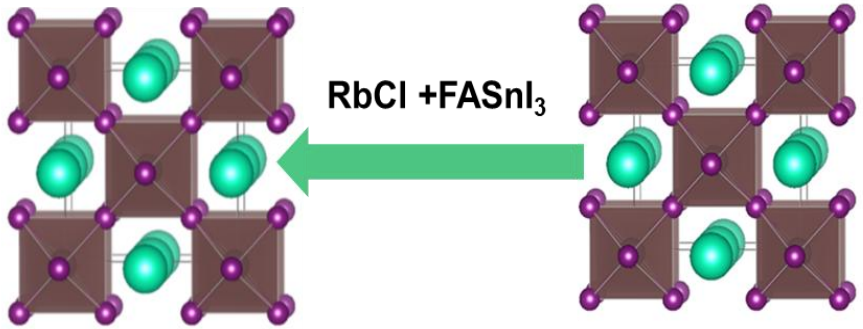




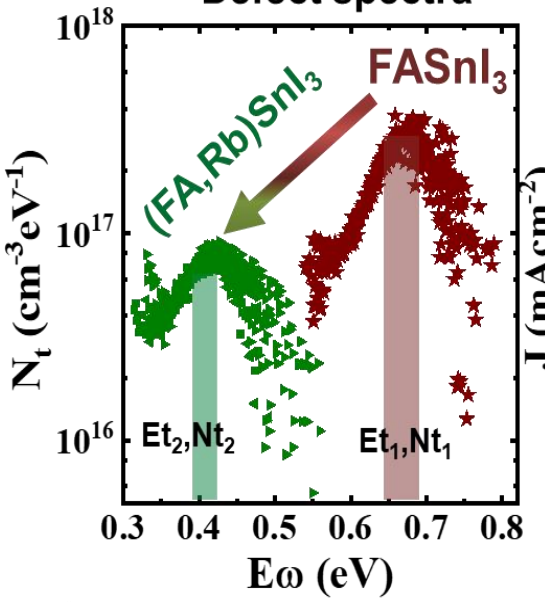
Modulation in film morphology

Our reports on Sn-PSCs

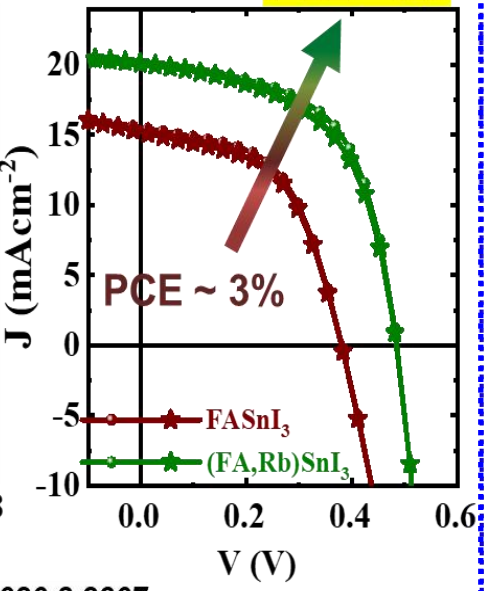
Structural regulation



Defect spectra

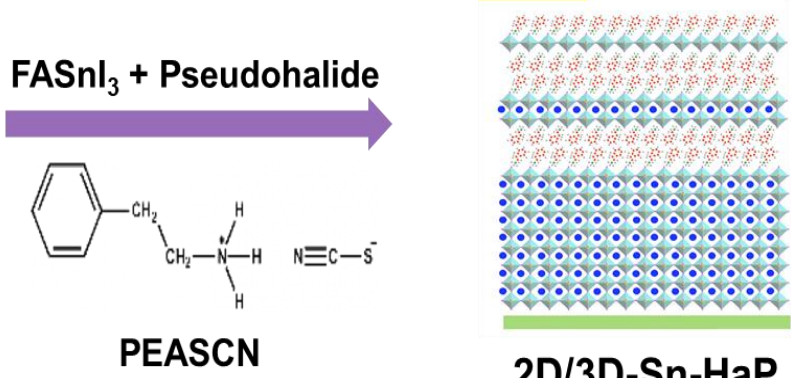


PCE~ 6%

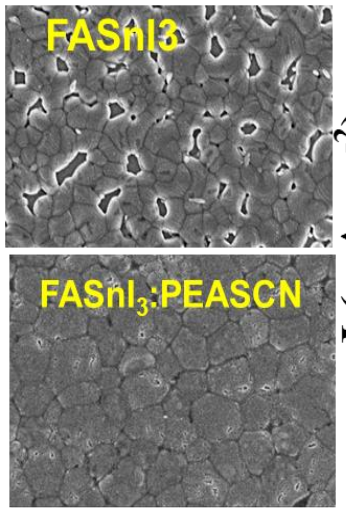


Khadka* et al. Mater. Chem. C,2020,8,2307

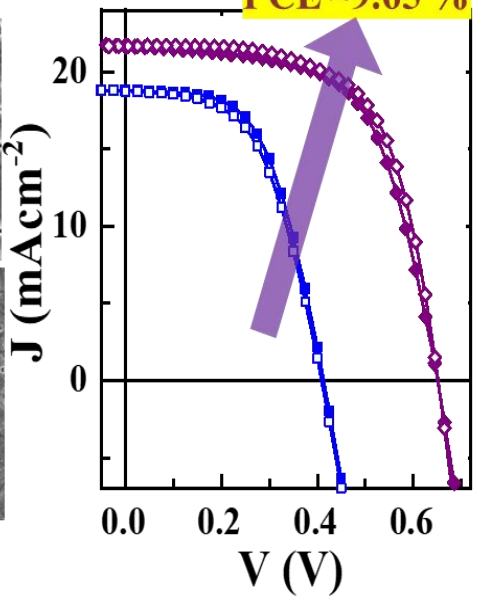
Pseudohalide additive effect



Film growth

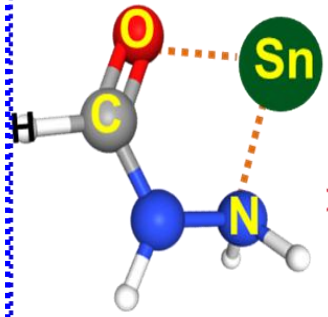


PCE ~9.65 %



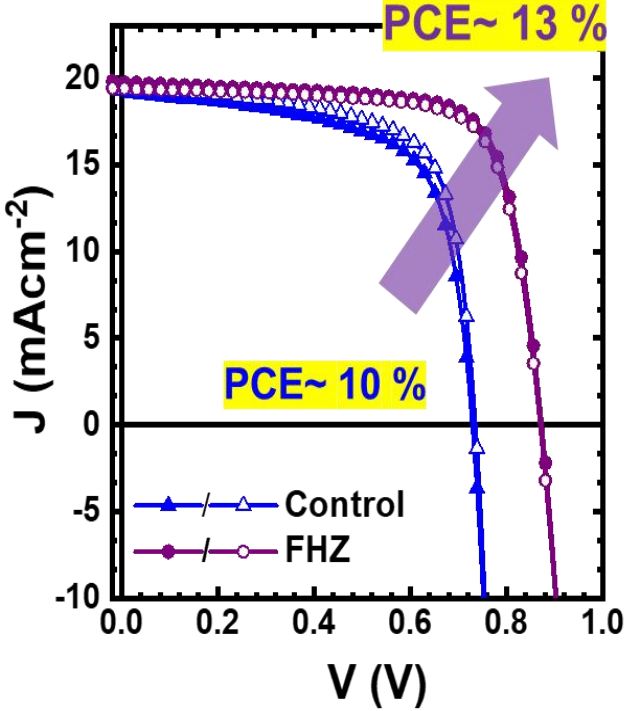
Khadka* et al. *ACS Appl. Energy Mater. 2021, 4, 12819*

Multi-functional ligand-additive



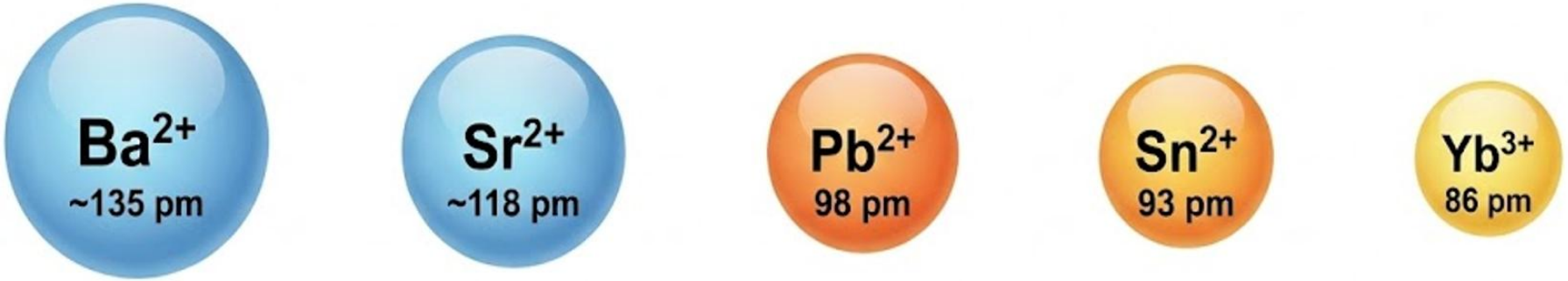
Formohydrazide (FHZ)
>Bidentate ligand

PCE~ 13 %



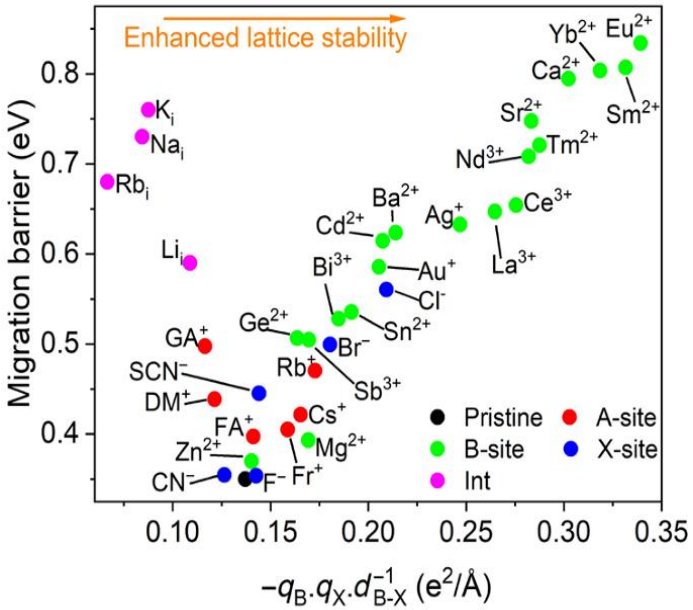
Khadka et al. Chem. Mater. 2023,35, 4250*

B-site doping Effect: Schematic of Ionic Size



Increasing Size ← **Observed Size Trend: $Ba^{2+} > Sr^{2+} > Pb^{2+} > Sn^{2+} > Yb^{3+}$** → Decreasing Size

Increasing Cation Charge (+3 > +2)	Greater Electrostatic Pull	Smaller Radius **Yb^{3+}**
Period Progression (Same Charge/Group)	Higher Principal Quantum Number	Larger Radius (Pb^{2+} [P6] > Sn^{2+} [P5])
Lanthanide Contraction Factor	Inefficient *4f* Electron Shielding	Unexpectedly Small Radius for Period 6 **Yb^{3+}**

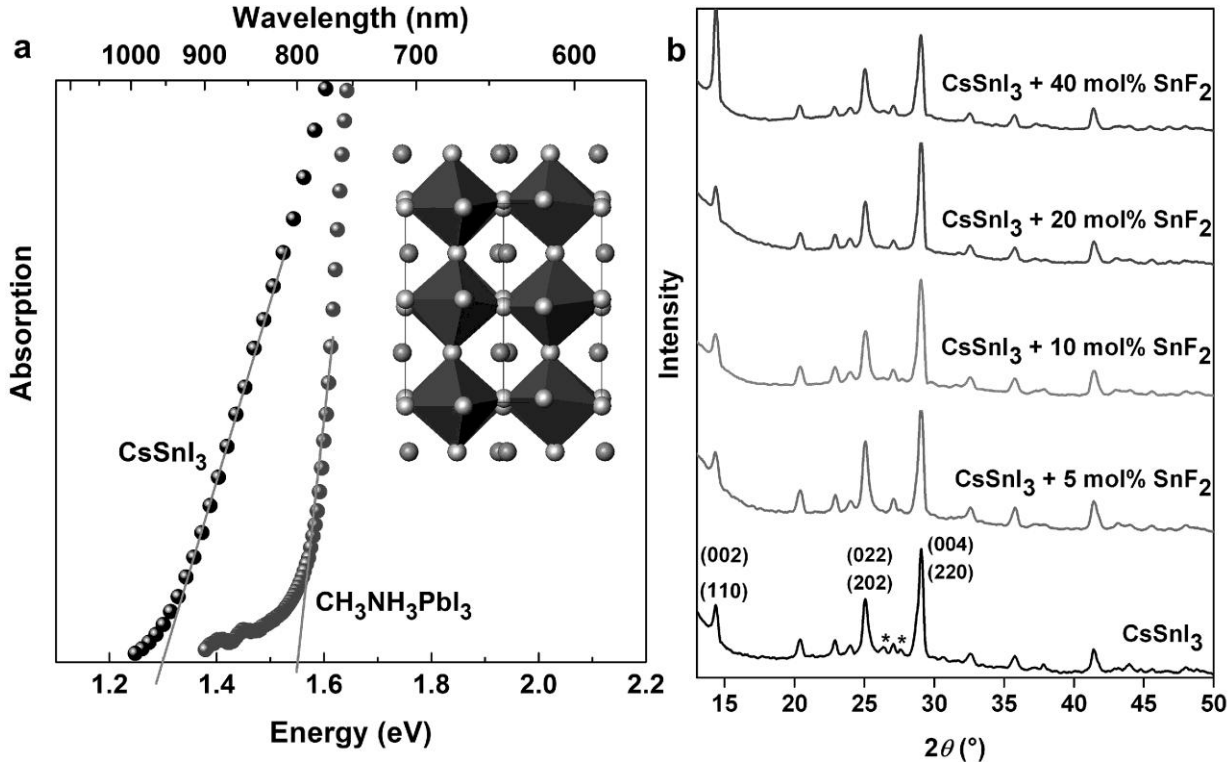


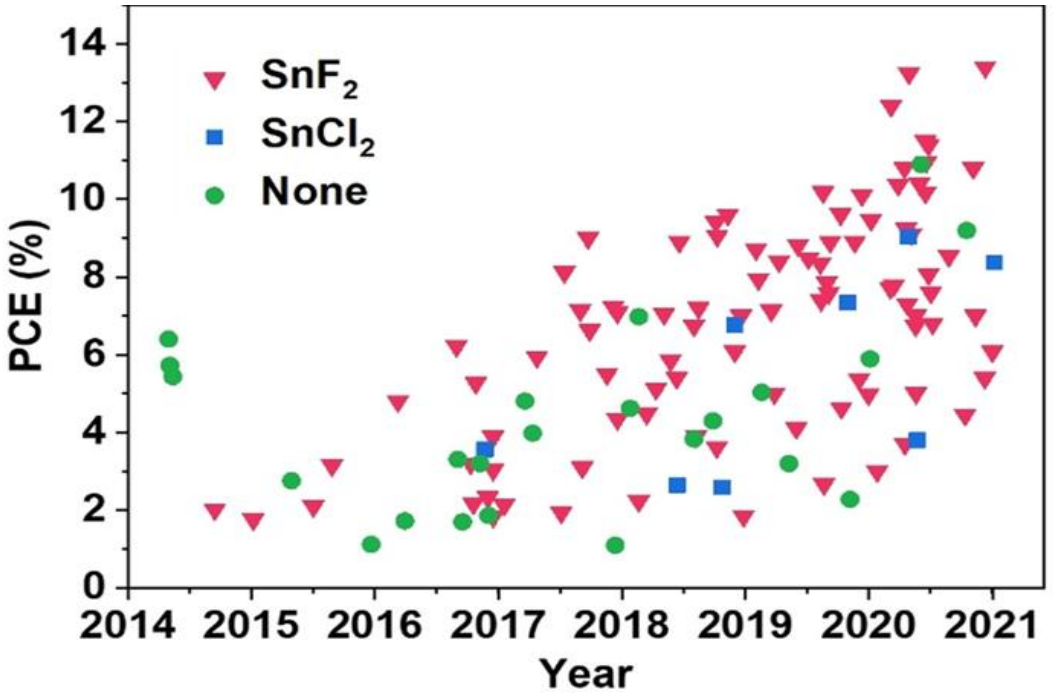
SnF_x additive -Sn-perovskite

Lead-Free Halide Perovskite Solar Cells with High Photocurrents Realized Through Vacancy Modulation

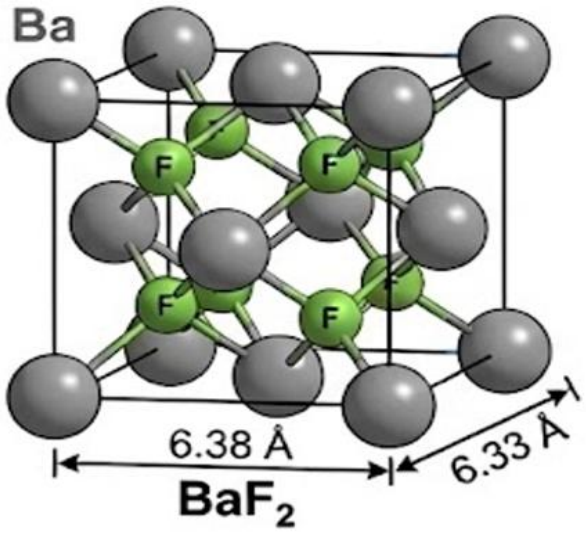
Mulmudi Hemant Kumar, Sabba Dharani, Wei Lin Leong, Pablo P. Boix, Rajiv Ramanujam Prabhakar, Tom Baikie, Chen Shi, Hong Ding, Ramamoorthy Ramesh, Mark Asta, Michael Graetzel, Subodh G. Mhaisalkar, Nripan Mathews ... See fewer authors

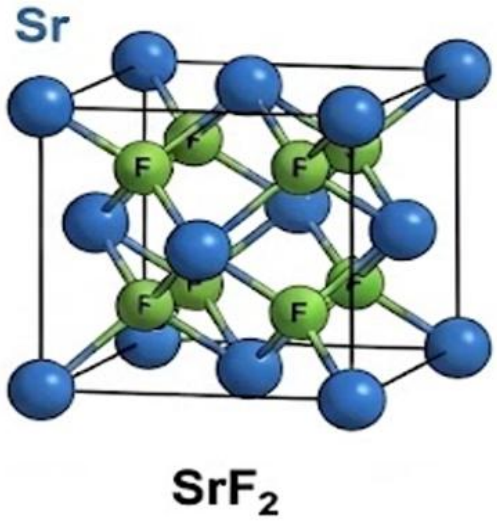
SnF_2 has achieved remarkable success as an additive in the Sn-PSCs.

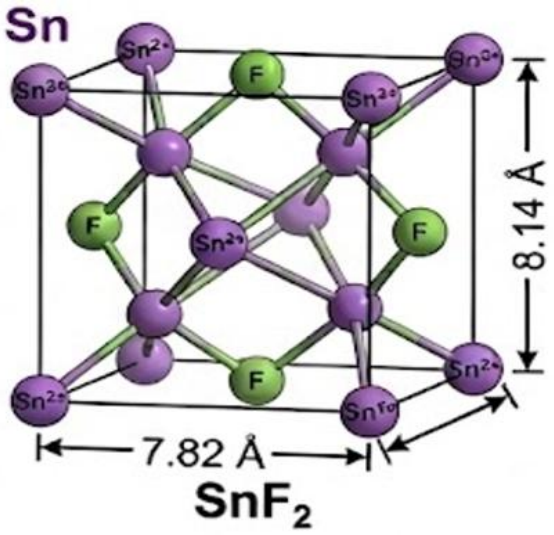


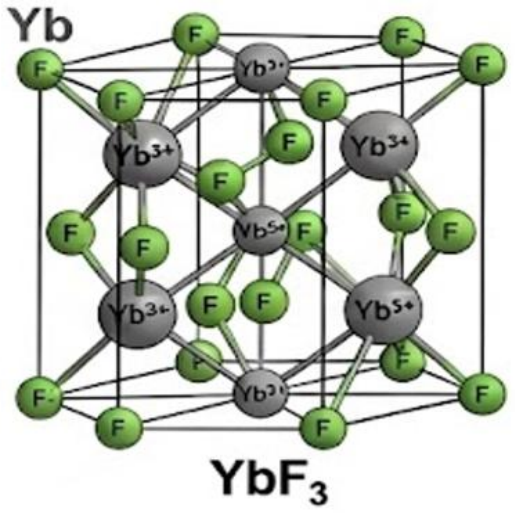


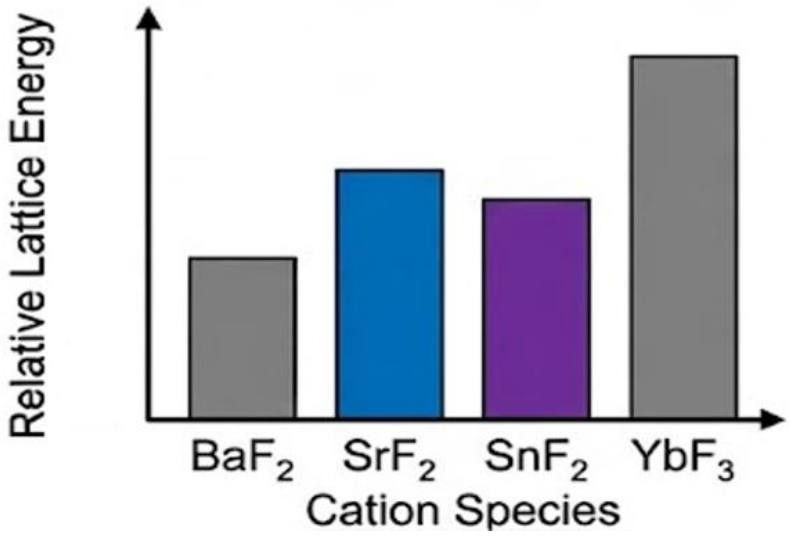
Interaction-Schematic > MF_x-Sn-perovskite lattice

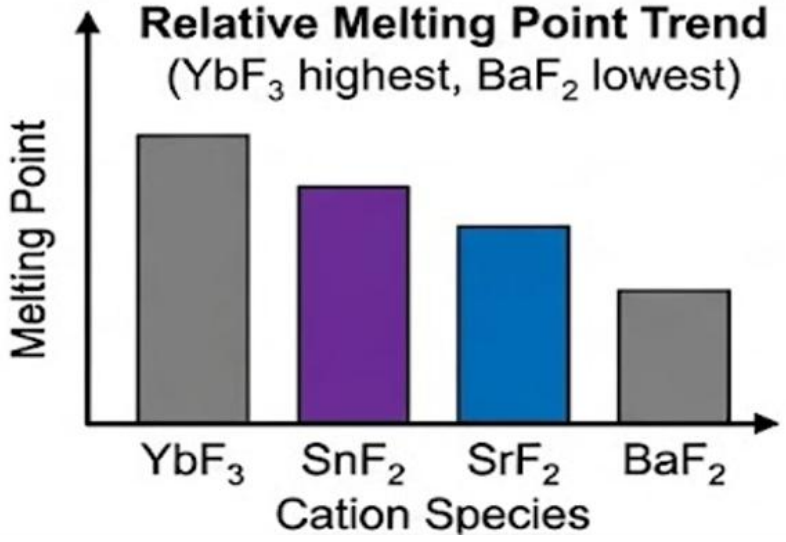


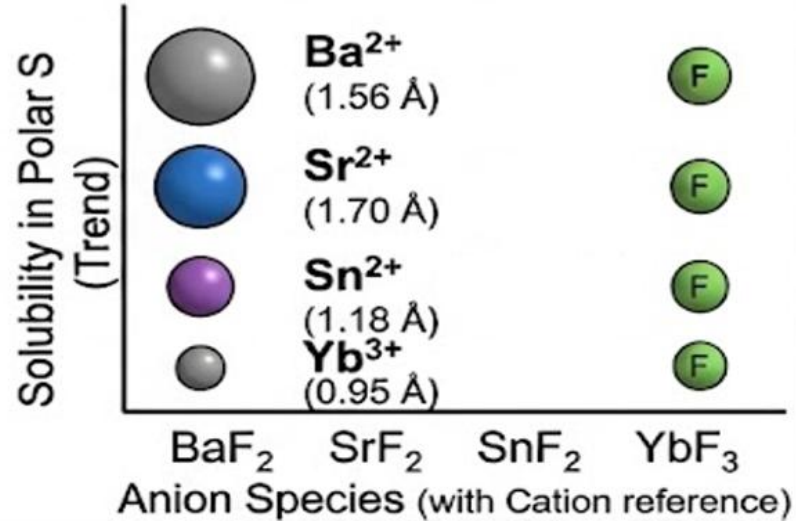






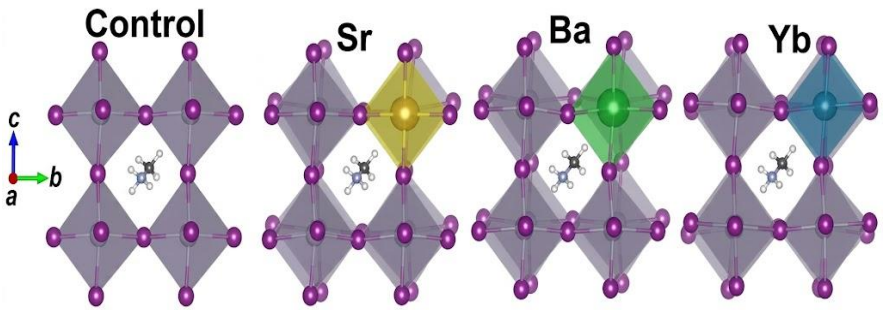




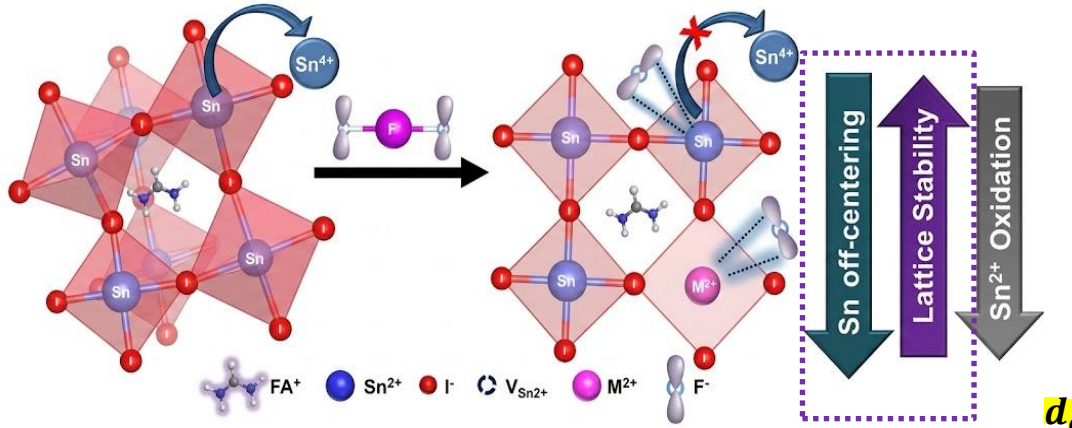


Theoretical Eye: MF_x-Sn-Perovskite

>Optimized crystal structures viewed along the a-axis



$Ba^{2+} > Sr^{2+} > Pb^{2+} > Sn^{2+} > Yb^{3+}$





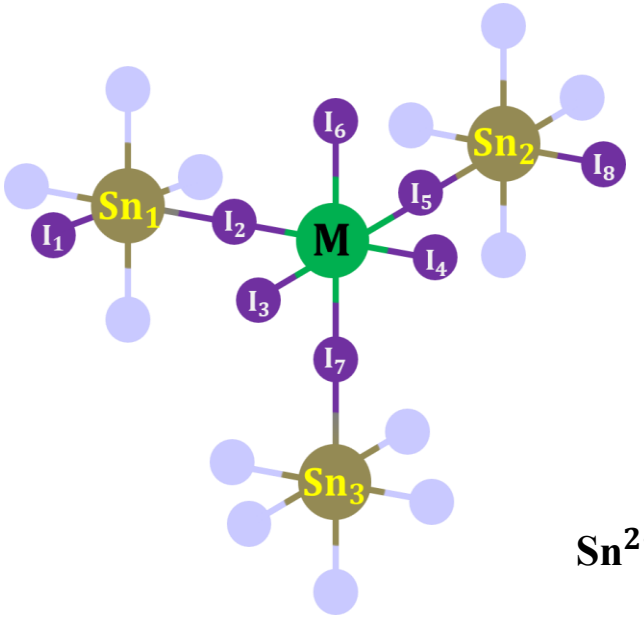
Prof. Azusa Muraoka
Japan Women's University, Tokyo

> Octahedral volume (V_{oct})

System	V_{oct} (Å^3)			
	Central	Neighboring-1	Neighborin-2	Neighboring-3
$FASnI_3$	41.74	41.74	41.74	41.74
Sr-doped	43.90	40.67	41.62	41.62
Ba-doped	46.85	39.85	40.73	40.73
Yb-doped	39.59	42.32	42.59	41.32

Dopant ionic size:

- Dictate local octahedral volume distortion
- Expansion for large Ba^{2+}/Sr^{2+} cations
- Localized contraction for smaller Yb^{3+} cations



d_{off} -geometric displacement of the central M^{2+} wrt its six -iodide atoms:

System	d_{off} (Å)
$FASnI_3$	0.025
Sr-doped	0.014
Ba-doped	0.024
Yb-doped	0.002

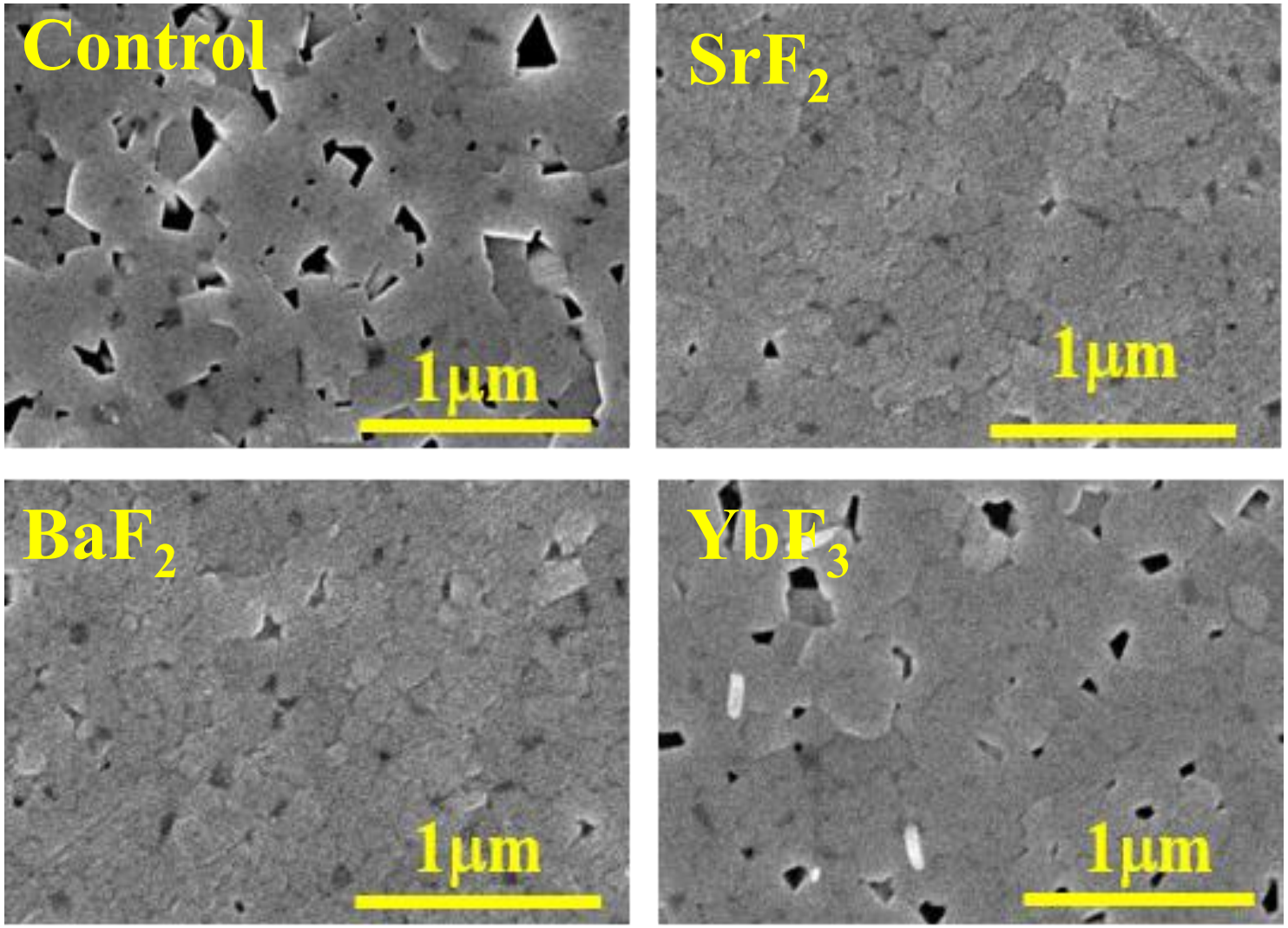
$$d_{off} = |r_M - r_{center}|$$

- Sn/Ba- local asymetry
- Sr/Yb- suppress off-centering

Sn^{2+} > significant off-centering displacement
> stereochemically active $5s^2$ lone pair

Effect of Fullerene-derivatives in Sn-perovskite film growth

Film- morphology



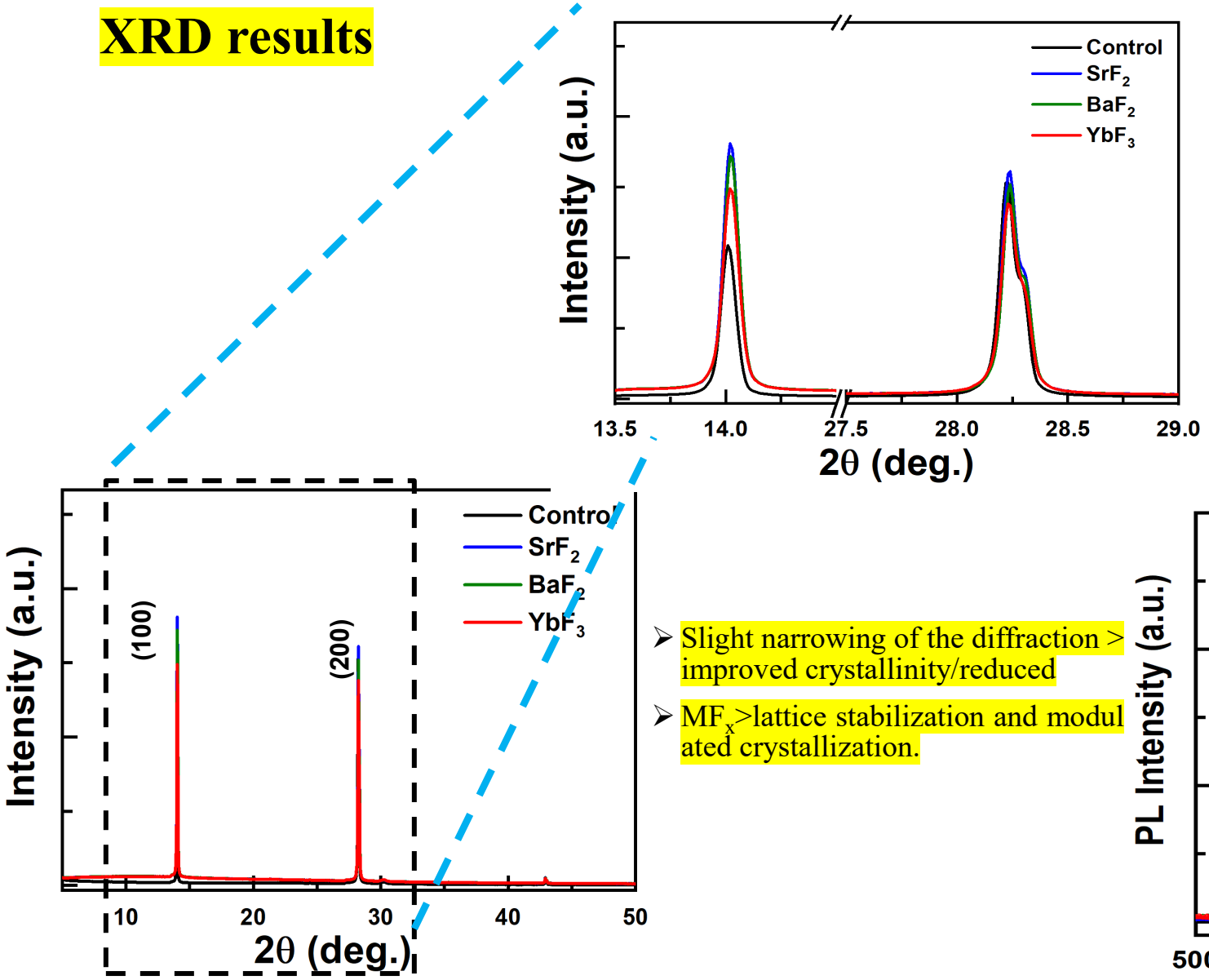
MF_x additive

> Surface coverage and grain uniformity

> Chemically mediated regulation of crystallization and interfacial bonding

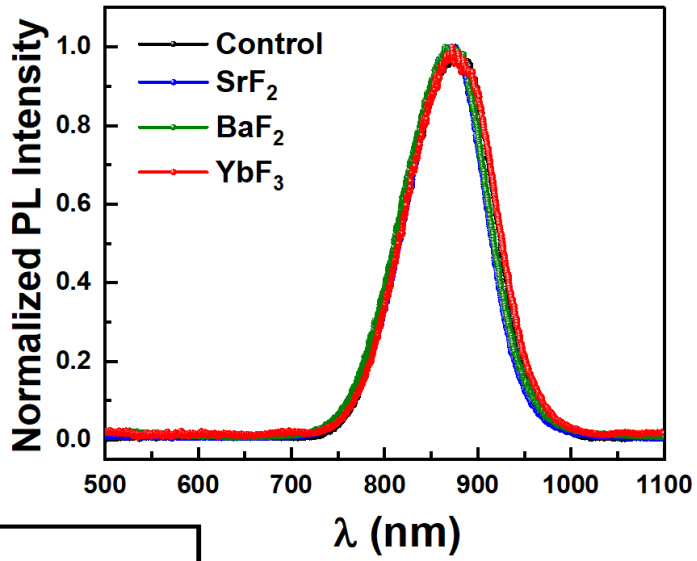
Effect of MF_x-additive in Sn-perovskite

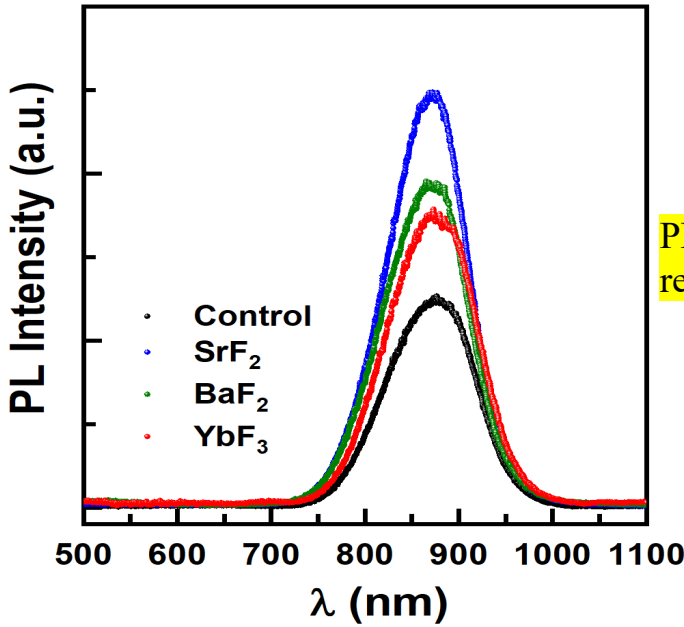
XRD results



- Slight narrowing of the diffraction > improved crystallinity/reduced
- MF_x>lattice stabilization and modulated crystallization.

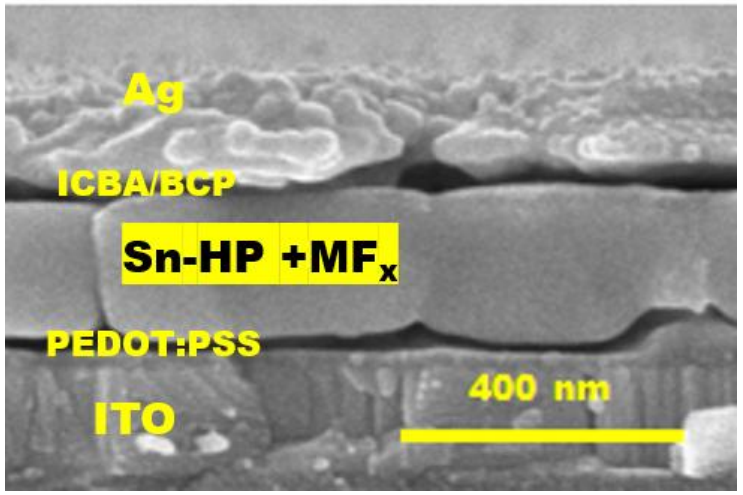
PL spectra

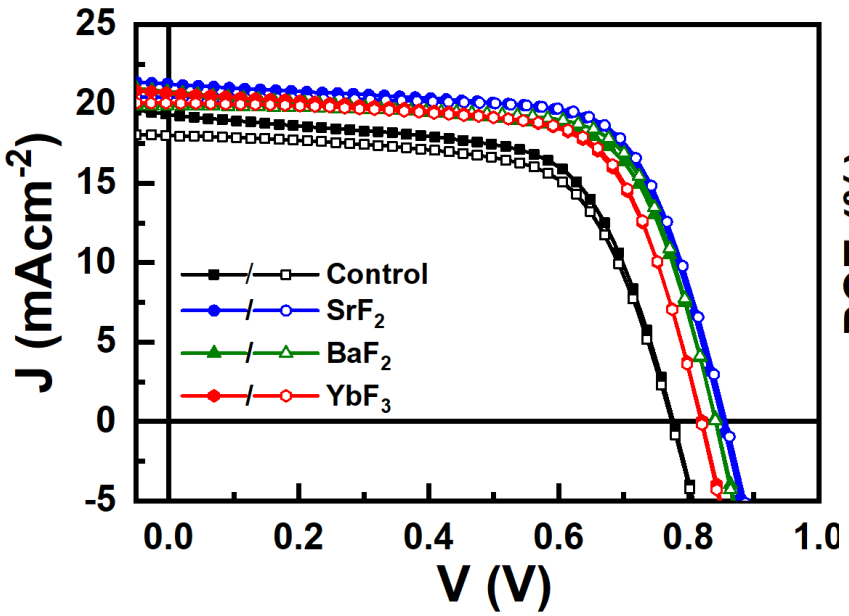


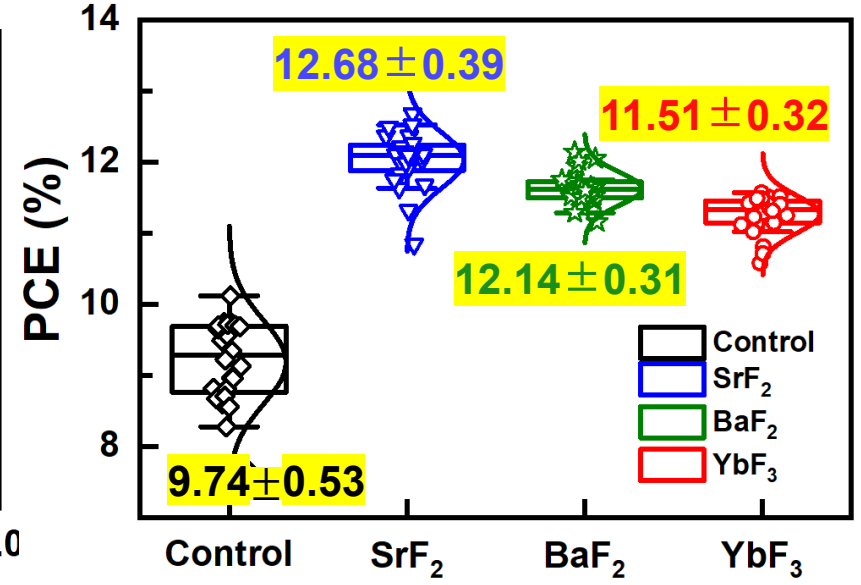


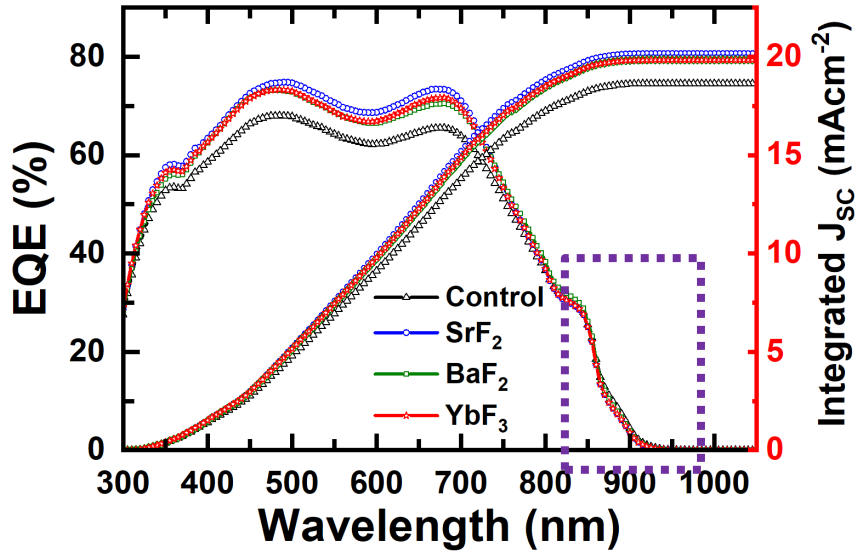
PL- single emission peak centered around 875 nm (1.417 eV)

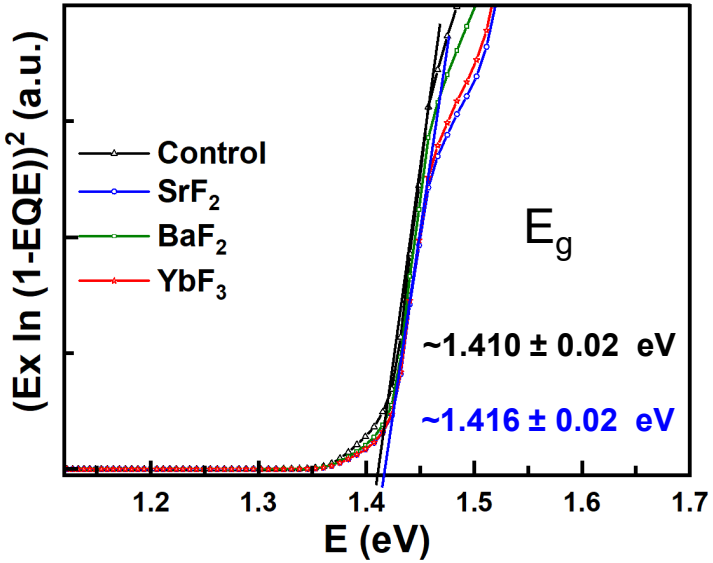
Effect of MF_x : Sn-PSCs







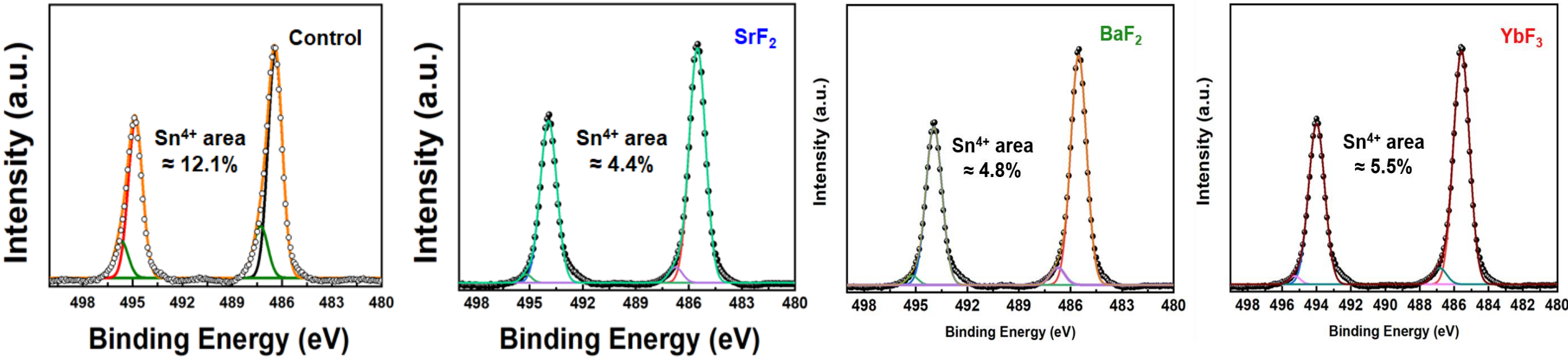




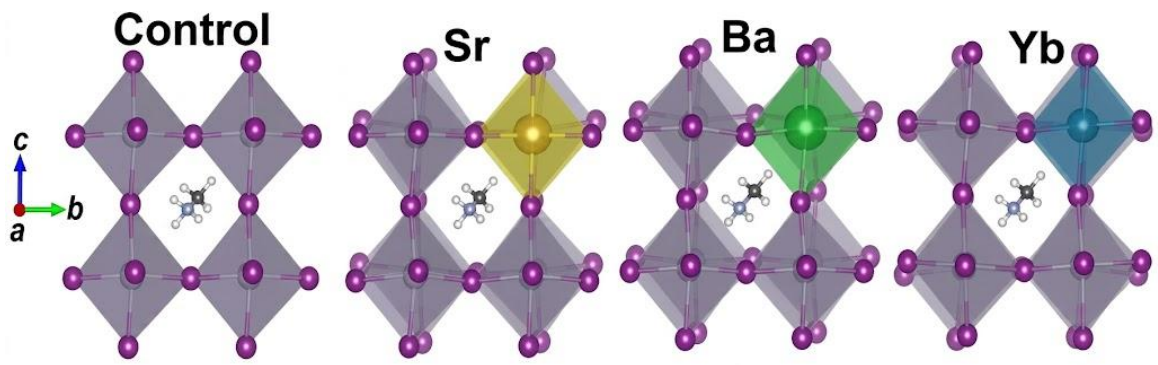
Effect of MF_x –Surface Chemistry

XPS: Suppression of oxidation:

Sn^{4+} from 12 % to 5.5-4.4 % with MF_x additive



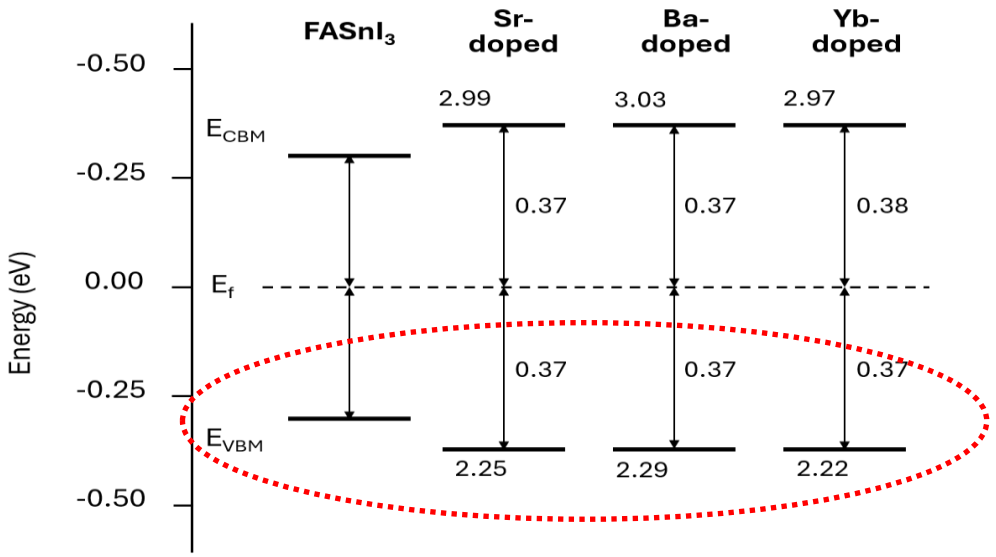
Theoretical Insight:- MF_x-Sn-Perovskite



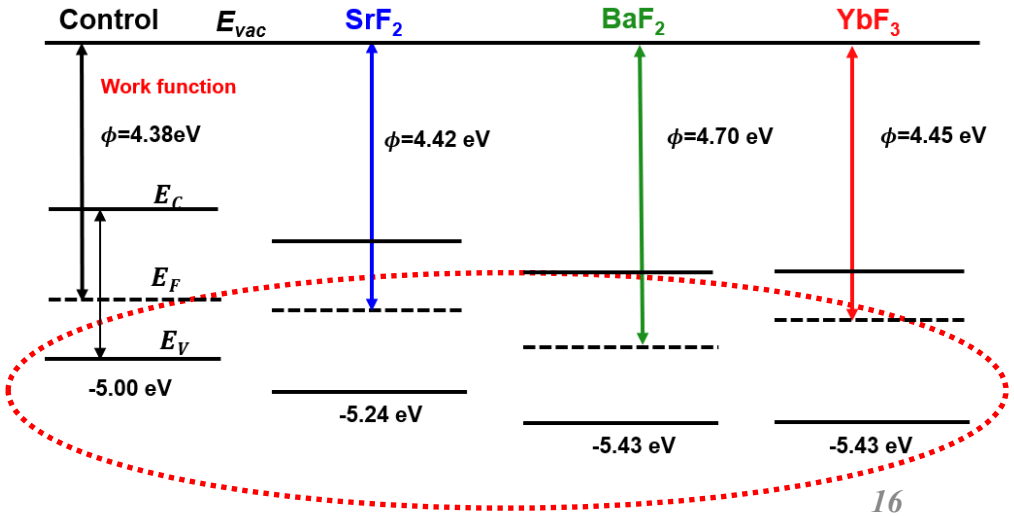
Doped system	Sn/M Anti-site	Defect formation energies (eV)
Sr-doped	Sr_{Sn}	-6.52
Ba-doped	Ba_{Sn}	-7.09
Yb-doped	Yb_{Sn}	-6.33

- -Ve- $E_{Formation}$ - dopant antisites are thermodynamically favorable
- Ba_{Sn} - most energetically favorable substitutional defect

Theoretical calculations



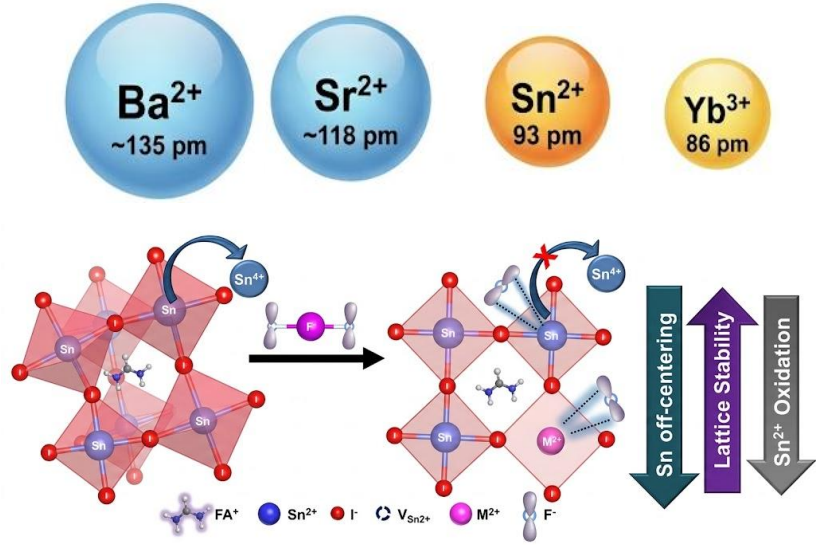
UPS- analysis



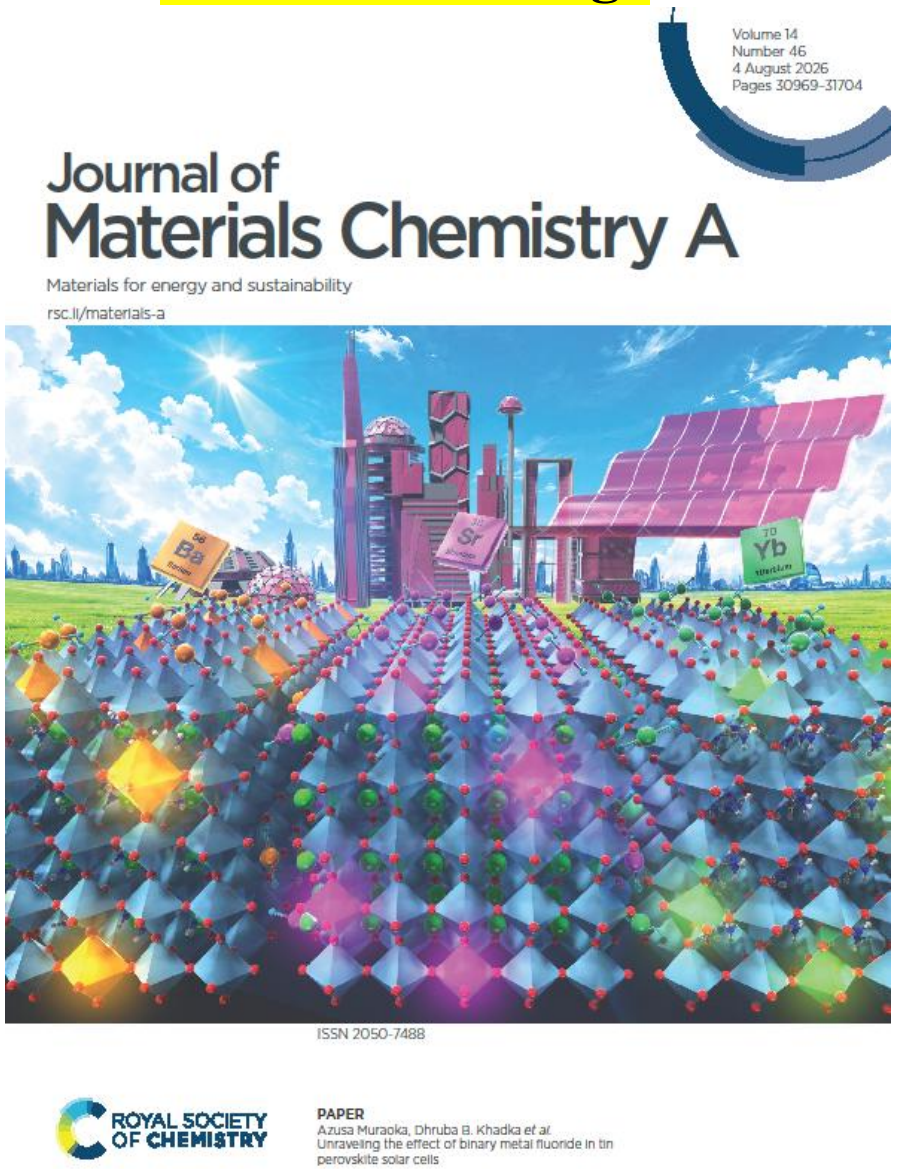
Report Summary

Effect of MFx additive in Sn-perovskite:

- ***MFx- induces Sn-off-centering-lattice modulation- antisite –favorable (M_{Sn})***
- ***Facilitates uniform morphology with better crystal quality***
- ***Control the extent of oxidation of Sn^{2+} /Mitigation of defects***
- ***PCE > improved 9.8 to ~ 12,7 % - better stability***



Front Cover-Page

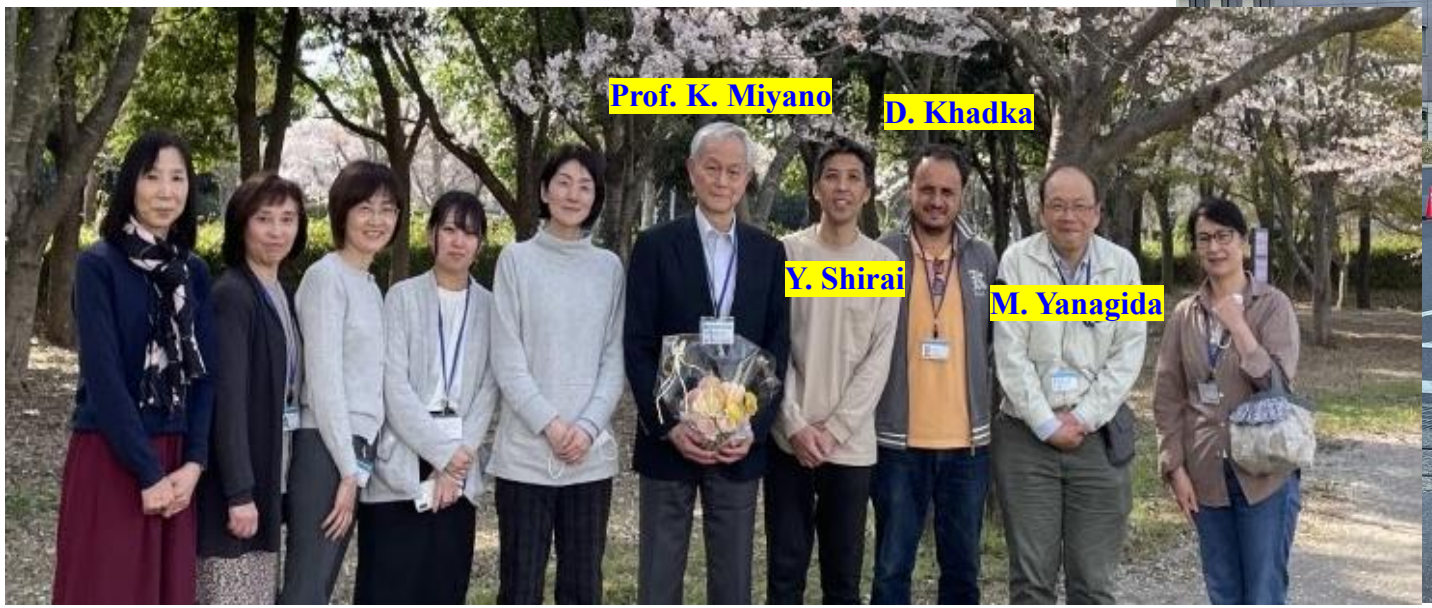


Khadka *and co-workers, J. Mater. Chem. A, 2026, 46, 31131*

Acknowledgement

- Hitachi Global Foundation, Kurata Grant (PI)
- JST-ALCA-Next Program

Our team





Thank you for your attention