How do Binary Metal Fluorides Rewire Defect Chemistry and Carrier Transport in Lead-Free Tin Perovskite Solar Cells?

Aman Shukla[1,2], Mai Otake[3] , Masatoshi Yanagida[1], Koichi Yamashita[3], Azusa Muraoka[3], Yasuhiro Shirai[1], Dhruba B. Khadka[1]*

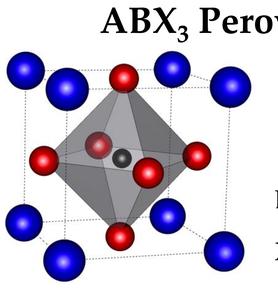
[1]*Center for GREEN Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS), Japan.*
[2]*Department of Materials Science & Engineering, National Centre for Flexible Electronics, Indian Institute of Technology Kanpur, India*
[3]*Graduate School of Science, Japan Women's University, Tokyo, 112-8681, Japan*

**Email: KHADKA.B.Dhruba@nims.go.jp*

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Introduction

ABX_3 Perovskites



A-site: $MA^+: CH_3NH_3^+$, $FA^+: (NH_2)_2CH^+$, Cs^+

B-site: Pb^{2+}, Sn^{2+}…

X-site: I^-, Br^-…

- ❑ Tunable direct bandgap
- ❑ High absorption coefficient
- ❑ Solution-processable at low temperature
- ❑ Low exciton binding energy
- ❑ Defect tolerance
- ❑ Long carrier diffusion lengths

Potential candidate as a light-absorbing material for photovoltaic devices.

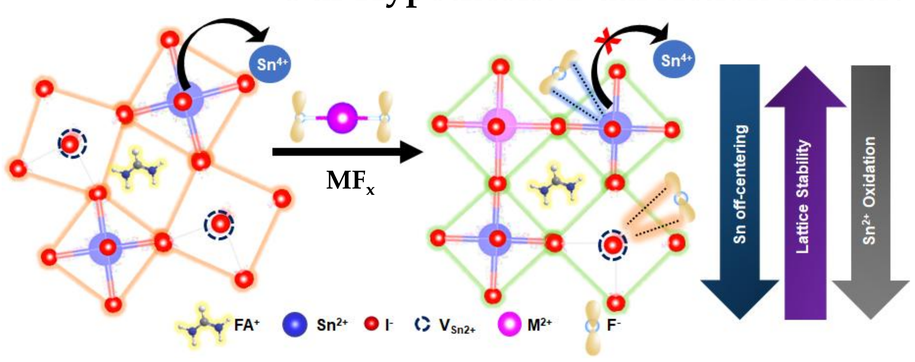
ABX_3 Tin perovskite solar cells

82 **Pb** Lead → Replace → 50 **Sn** Tin

- ✓ Ideal direct bandgap (≈1.5-1.6 eV)
- ✓ Antibonding Pb-6s/I-5p VBM → shallow traps
- ✓ High efficiency (>26%)
- ✓ Excellent stability
- X Highly Toxic
- X Moisture Sensitive

- ✓ Less toxic
- ✓ Ideal narrow bandgap (≈1.2-1.4 eV)
- X **Sn^{2+} oxidizes to Sn^{4+}**
- X Self-p-doping
- X High Defect Density
- X Sn-off-centering
- X Low efficiency
- X Poor Stability

Our Hypothesis: Dual Action Additives



- **F^- coordinates under-coordinated Sn^{2+}/Sn^{4+} and passivates V_{Sn} → suppresses oxidation.**
- **M^{x+} incorporates at the Sn site → heals off-centering & reinforces the lattice.**

Materials & Methodology

Device structure for this work:

Anode | *HTL* | *Absorber Layer* | *Surface Passivation* | *ETL* | *Cathode*

ITO / PEDOT:PSS / Perovskite Precursor / 4F-BHZ / ICBA / BCP / Ag

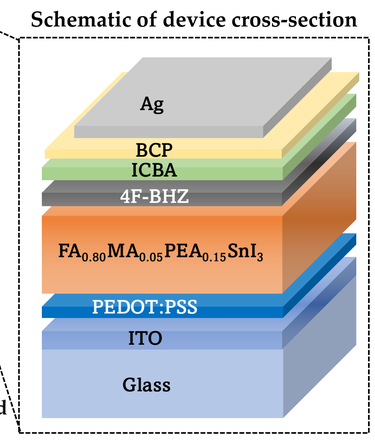
$FA_{0.80}MA_{0.05}PEA_{0.15}SnI_3$ + 0% additive / 0.1 mol% SrF_2/ BaF_2/ YbF_3 additives

Deposition of Perovskite Absorber Layer via spin coating

1M $FA_{0.80}MA_{0.05}PEA_{0.15}SnI_3$ in DMSO (with and without additives)



Fabricated devices with an active area of 0.26 cm^2



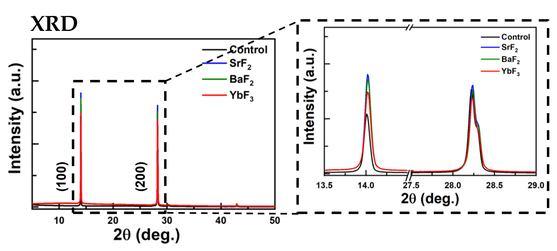
Approach:

Thin Film Characterisation → Device Fabrication & Characterisation → DFT Calculations

Results and Discussion

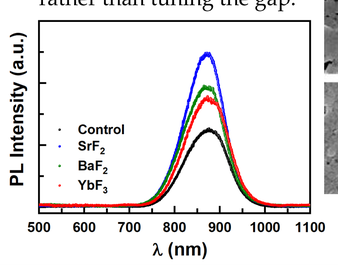
1. Impact on thin-film quality

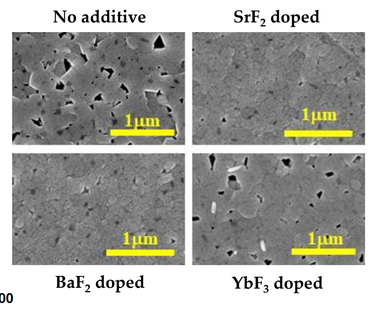
XRD



Additive films show stronger, sharper peaks, indicating **improved crystallinity**, preferred (100) orientation, and **reduced microstrain**.

Brighter PL, same bandgap: additives **passivate defects** rather than tuning the gap.





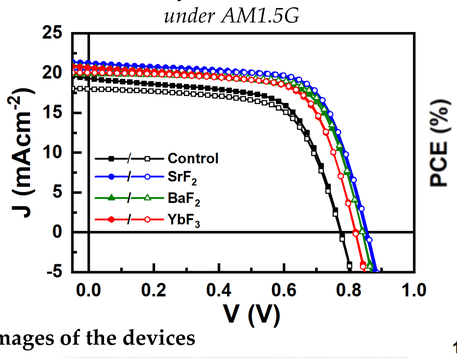
Additives give **smoother films**.

- *Metal fluorides give better-ordered, electronically cleaner films without changing the bandgap. Does it translate to a device?*

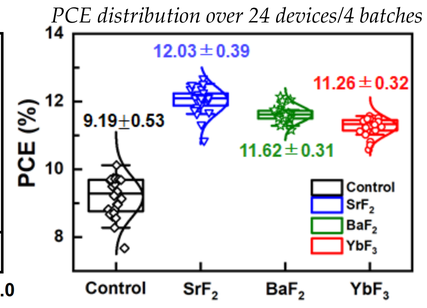
2. Device Performance

- ***J-V* curves** show that all additive devices outperform the control, with SrF_2 best.
- Forward/reverse scans of devices with additive overlap, confirming low hysteresis.
- The reduced spread in device PCE suggests that additives promote more **uniform film formation** and **minimize batch-to-batch variability**.

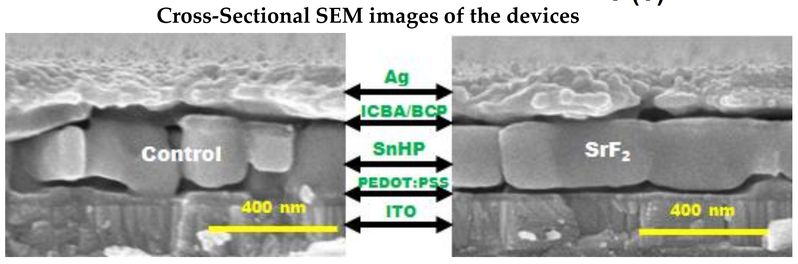
J-V Curves *under AM1.5G*



PCE Statistics *PCE distribution over 24 devices/4 batches*

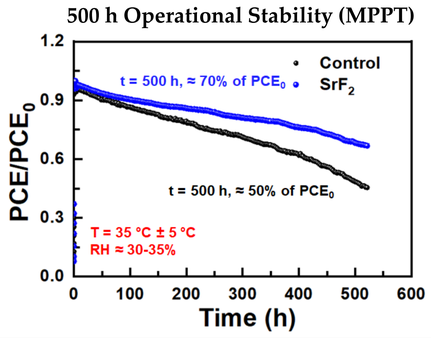


Cross-Sectional SEM images of the devices



SrF_2 gives compact columnar grains and better interfacial contact than the undoped one.

500 h Operational Stability (MPPT)



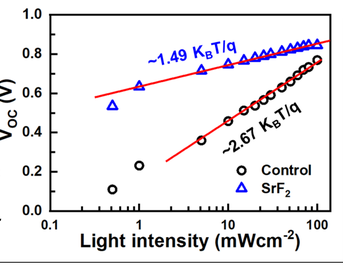
- *Higher device efficiency, reproducibility, and stability all point to suppressed recombination, but which kind of recombination, where, and by how much?*

3. Recombination Mechanism

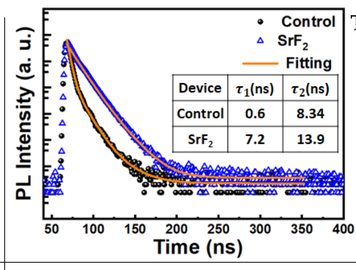
Light Intensity Dependence of V_{OC}

Diode Ideality Factor:
n ≈ 2 for trap-assisted (SRH) recombination
n ≈ 1 for band-to-band recombination

n drop from 2.67 to 1.49 with SrF_2 → **suppression of trap-assisted non-radiative recombination.**



Time-Resolved PL Decay

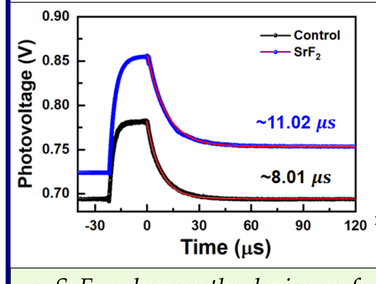


Device	τ_1(ns)	τ_2(ns)
Control	0.6	8.34
SrF_2	7.2	13.9

Bi-exponential fit. Both lifetimes lengthen with SrF_2.

Longer τ_1 → **passivation of surface/grain boundary traps.**

Longer τ_2 → **improved bulk carrier lifetime.**

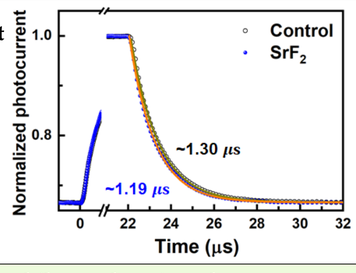


Transient Photovoltage (TPV) Decay

Longer TPV lifetime → **long-lived charge carriers** under operating conditions → **reduced charge recombination rate**

Transient Photocurrent (TPC) Decay

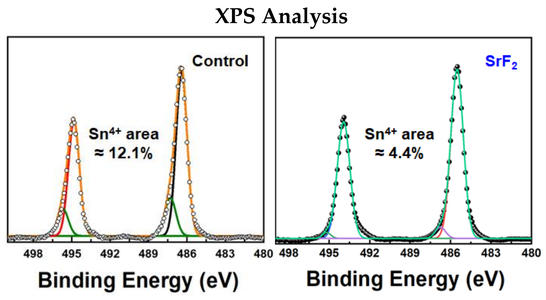
Faster photocurrent decay → more **efficient charge extraction** and **reduced carrier trapping**



- *SrF_2 enhances the device performance by suppressing trap-assisted recombination while accelerating charge extraction. What chemistry drives it?*

4. Modulation of Surface & Bulk Chemistry

XPS Analysis



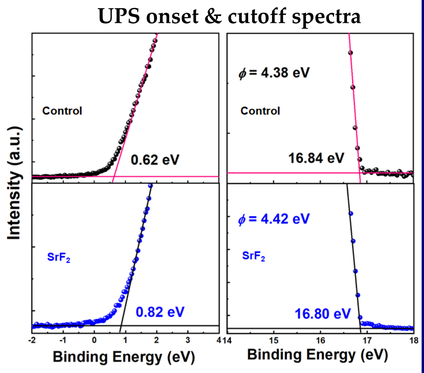
Reduction of Sn^{4+} fraction → SrF_2 suppresses Sn^{2+} oxidation

UPS Analysis

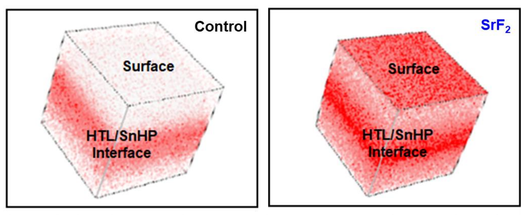
Valence band-to-Fermi level offset increases → SrF_2 shifts E_F toward mid-gap → Self-p-doping suppressed → Higher V_{OC}

Near-ohmic alignment with PEDOT:PSS → efficient hole extraction, less interfacial loss

UPS onset & cutoff spectra

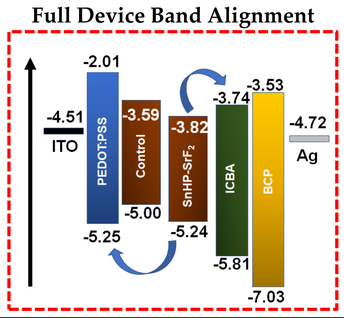


ToF-SIMS: 3D reconstruction of F- distribution

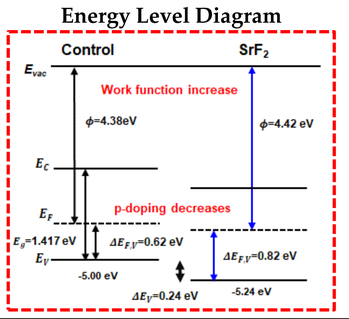


Fluoride localizes at the perovskite/HTL interface and surface → guards the most defect-prone regions.

Full Device Band Alignment



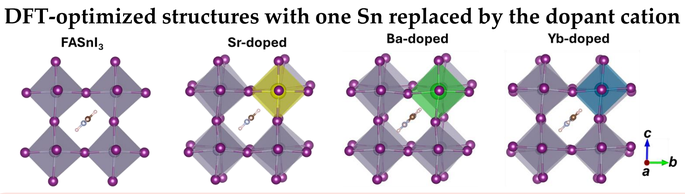
Energy Level Diagram



- *SrF_2 suppresses Sn^{2+} oxidation and self-doping, and improves band alignment. What exactly happens at the atomic and electronic level to deliver these benefits?*

5. DFT Calculations

DFT-optimized structures with one Sn replaced by the dopant cation



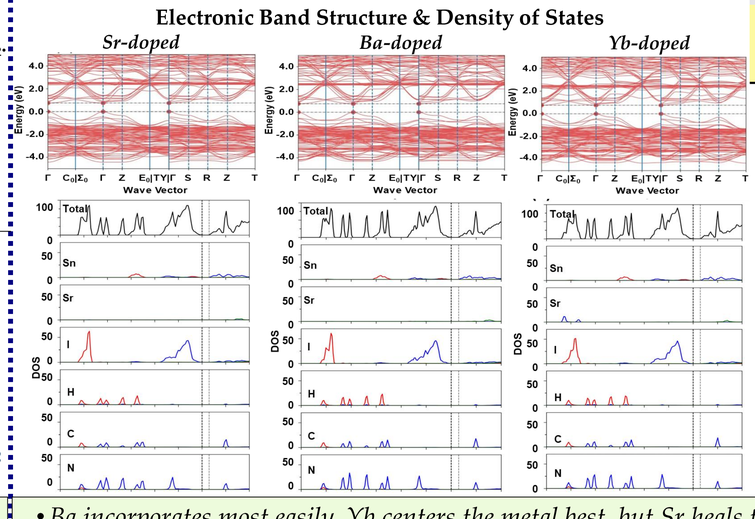
- All three cations reduce Sn off-centering, but each distorts the octahedron differently.
- Ba doping → octahedral expansion and tilting anisotropy
- Yb doping → restoration of metal centering with intra-octahedral distortion.
- **Sr doping → intermediate impact and moderate local structural changes.**
- Ba and Yb flatten the valence band along specific directions, making holes heavy; **Sr preserves valence-band dispersion,** keeping holes light.

m_h^*: Ba > Yb > Sr.

	$FASnI_3$	Sr-doped	Ba-doped	Yb-doped
Octahedral Volume (Å^3)	41.73	43.90	46.85	39.59
Ionic Radii of metal ion (Å)	1.18	1.18	1.35	0.87
Linkage Angle between adjacent octahedra	85.84°	89.31° 88.99°	96.45° 85.26°	87.49° 84.92°
Off-centering displacement (Å)	0.025	0.014	0.024	0.002
Substitutional defect formation energy (eV)	-	-6.52	-7.09	-6.33
Anisotropy# along CB edge	high	low	low	low
Anisotropy# along VB edge	low	medium	high	high
Hole effective mass (m_h^*/m_e) (Γ→Z)	**0.098**	**0.098**	**1.006**	**0.944**

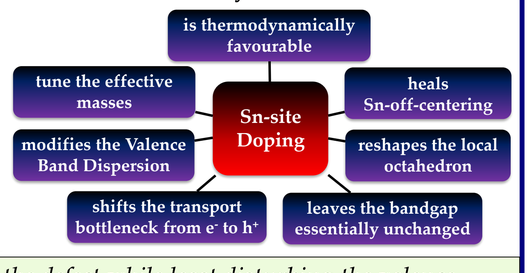
#anisotropy = directional variation of effective mass

Electronic Band Structure & Density of States



- The VBM is Sn-s/I-p hybridized and the CBM is Sn-p. Doping perturbs mainly the VBM, **so the effect falls on hole transport**; the electron band stays robust.

Summary of DFT results



- *Ba incorporates most easily, Yb centers the metal best, but Sr heals the defect while least disturbing the valence band and keeps the holes light. No cation wins on every metric; **Sr wins the balance**.*

Conclusion

- A dual-action mechanism is established in which F^- suppresses Sn^{2+} oxidation; the cation heals the lattice via Sn-site doping.
- SrF_2 incorporation delivers the most favorable outcome, improving PCE from 9.19% to 12.03% with enhanced operational stability.
- Additive selection for tin perovskites should be guided not by fluoride chemistry alone, but by **thermodynamic stability, off-centering suppression, and valence-band preservation.**

Acknowledgements

- Thankful to the NIMS Internship Program for the financial support.
- We sincerely acknowledge the facilities of the Supercomputer Center, the Institute for Solid State Physics, the University of Tokyo, where computations were performed.
- We also acknowledge the technical support provided by Yamaguchi Kazuo-San (XPS), Takahashi Hiromi (XRD), and Nariaki Sato-San (ToF-SIMS)

References