The 86th JSAP Autumn Meeting 2025

September 7 (Sun.) - 10 (Wed.) 2025
Tempaku Campus, Meijo University & Online

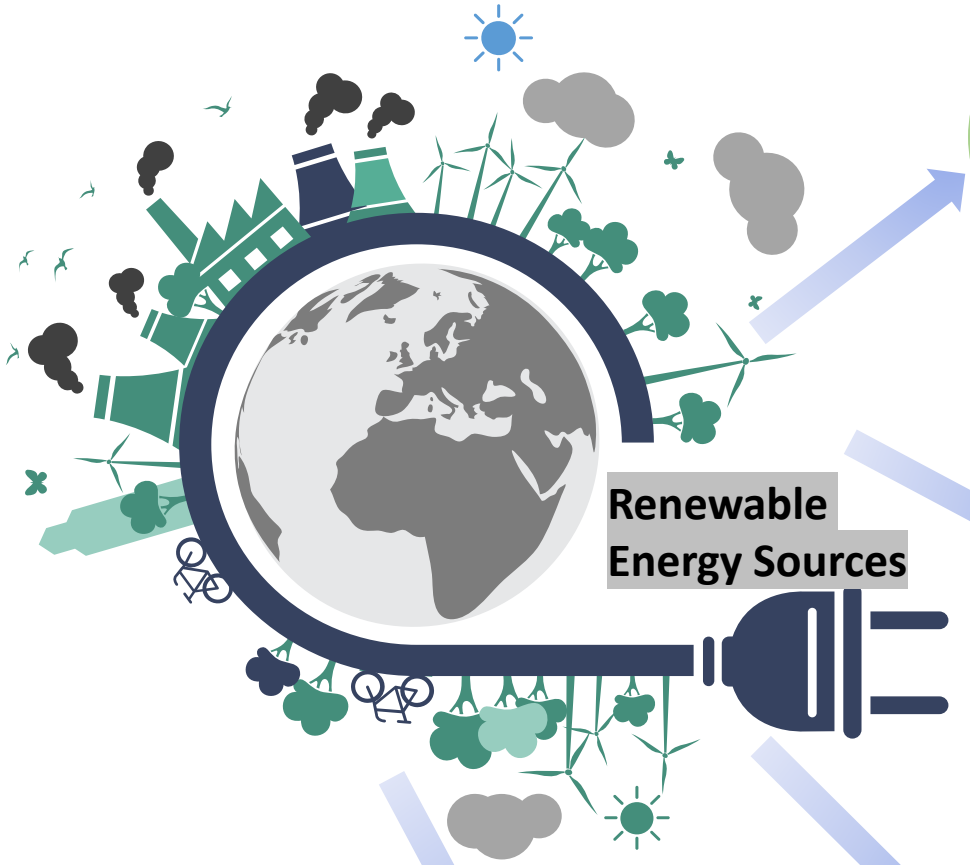


Tailoring $AgBiI_4$ Lead-Free Solar Cells Using Alkali Halide Additive

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Global Research for Environment and Energy-based Nanomaterials (GREEN)
National Institute for Materials Science (NIMS), Japan



Solar

Wind

Bio-mass

Water

Wafer based

- ✓ Mono/polycrystalline Si-Solar cells
- ✓ Multijunction cells

Thin film based

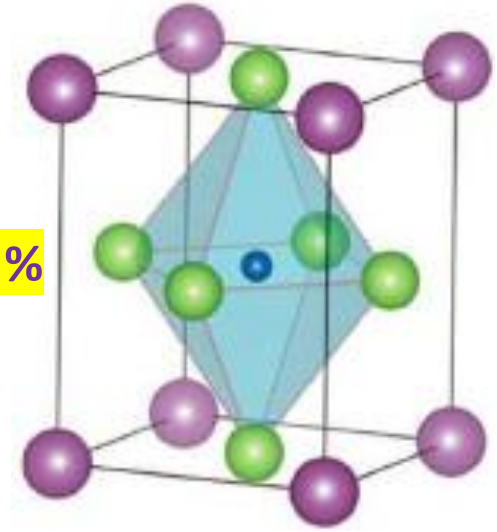
- ✓ Amorphous thin film Si-Solar cells
- ✓ CdTe (Cadmium Telluride)
- ✓ CIGS (Copper Indium Gallium Selenium)

Emerging Technologies

- ✓ DSS (Dye Sensitised solar cells)
- ✓ OPV (Organic Photovoltaics)
- ✓ Perovskite Solar cells
  - ➢ Pb-Based
  - ➢ Pb-Free

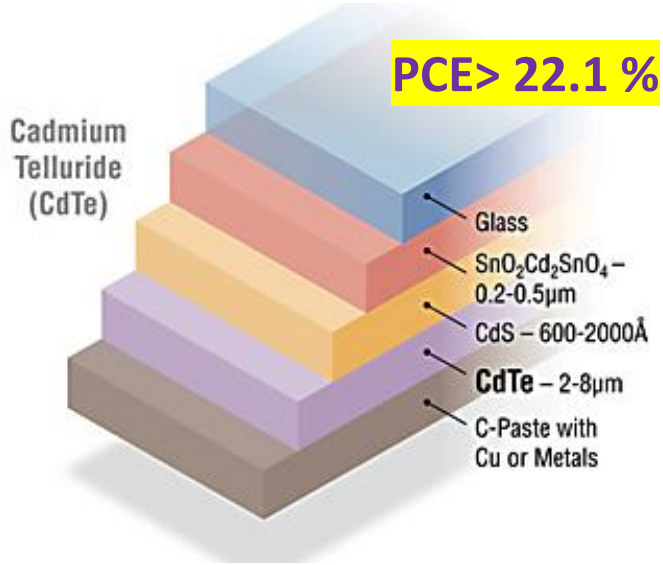
$APbX_3$

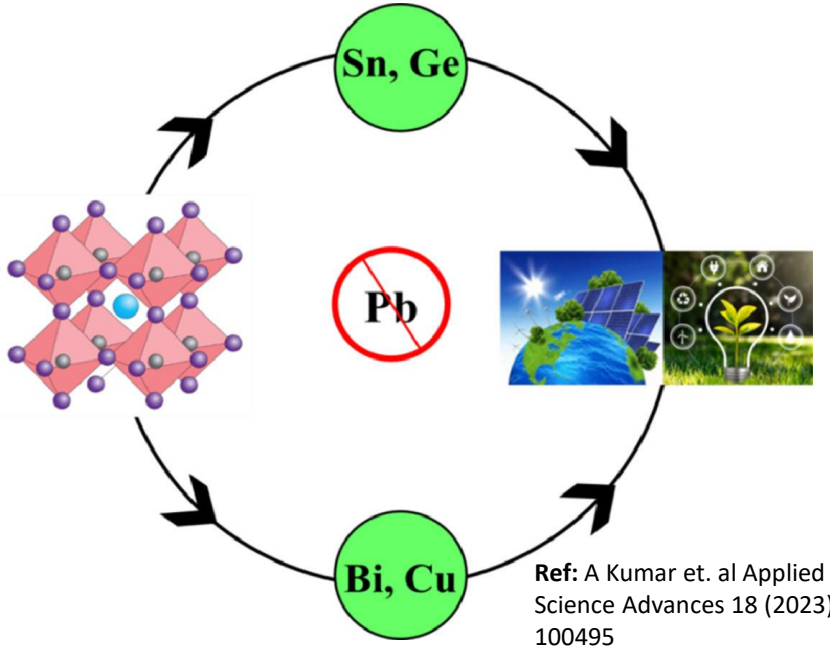
PCE~ 26 %



CdTe

PCE> 22.1 %





Ref: A Kumar et. al Applied Surface Science Advances 18 (2023) 100495

Cd and Pb are listed in the top 6 deadliest/toxic elements known

Solubility product constant

Ksp≈1 × 10^{-22} of Cd^{2+} - being recycled

Ksp ≈ 1× 10^{-8} of Pb^{2+}

Once polluted, the harm to the earth and human beings is almost eternal

- **Standard Pb^{2+} content level:**
  (US, Environmental Protection Agency
- **1.5 μg/m^3 in air**
- **15 μg /L in water**

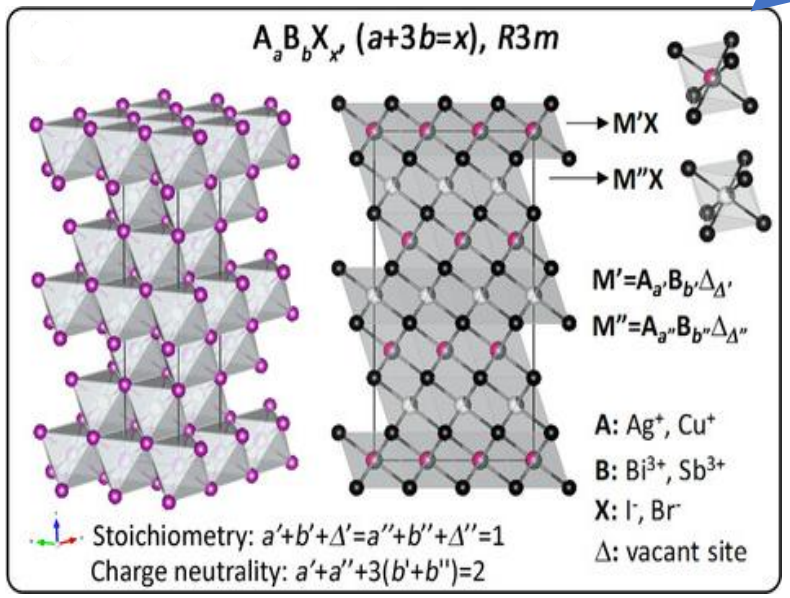
Bi-based absorber material for photovoltaic application

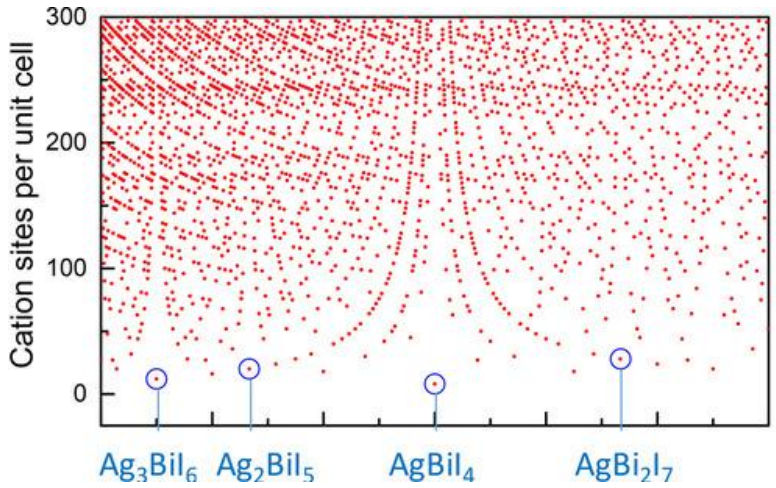
Bi based compounds

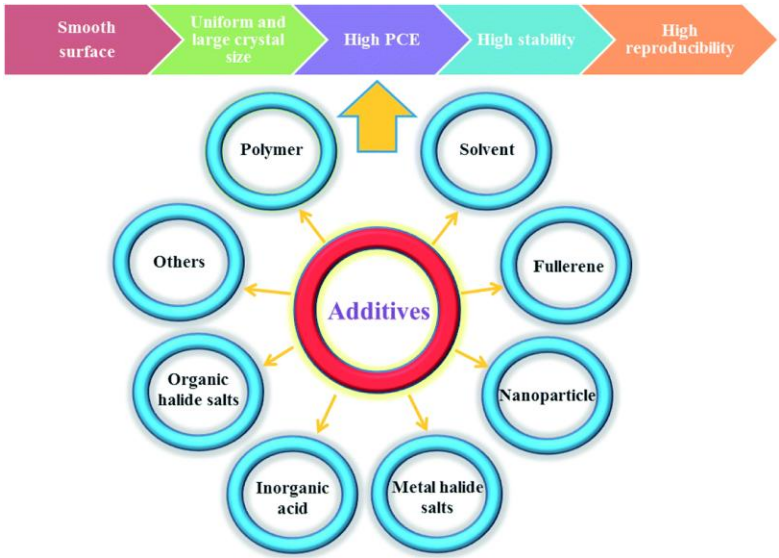
- $A_3Bi_2I_9$
  - Indirect bandgap
  - Low electronic and structural dimensionality
- A_2BBiX_6
- $A_aB_bX_x$

A_2BBiX_6
- Wide and indirect bandgap
- Low charge carrier mobility

Rudorffite Crystal Structure



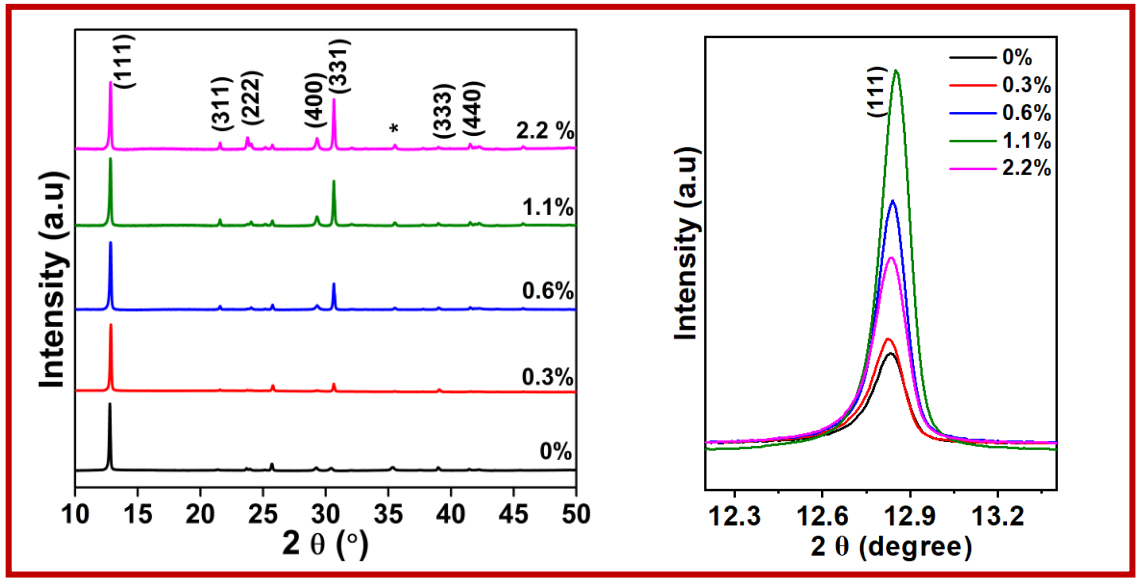




Ref: Turkevychb et.al *ChemSusChem* 2017, *10*, 3754

AgBiI4 as the absorber material

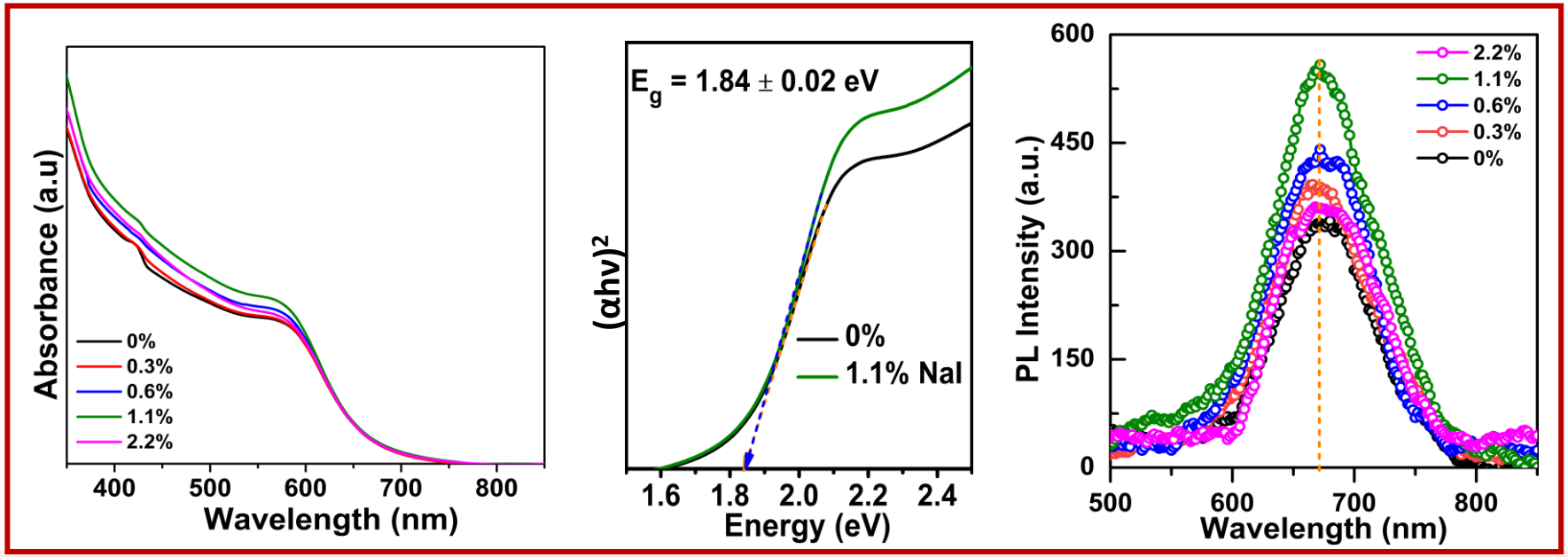
XRD Pattern



- **cubic defect spinel** structure
- **enhanced intensity** of the dominant XRD peak
- **decrease** in the **full width at half-maxima**
- notable **absorption** in the **360–750nm**
- **Optical Bandgap** of **1.84 ± 0.02 eV**

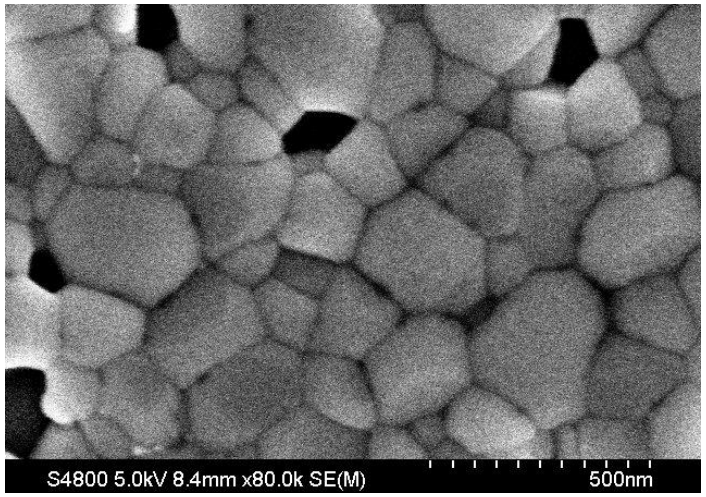
Ref: Fatima et al. ACS Appl. Energy Mater. 2025, 8, 7, 4601

Absorption/emission

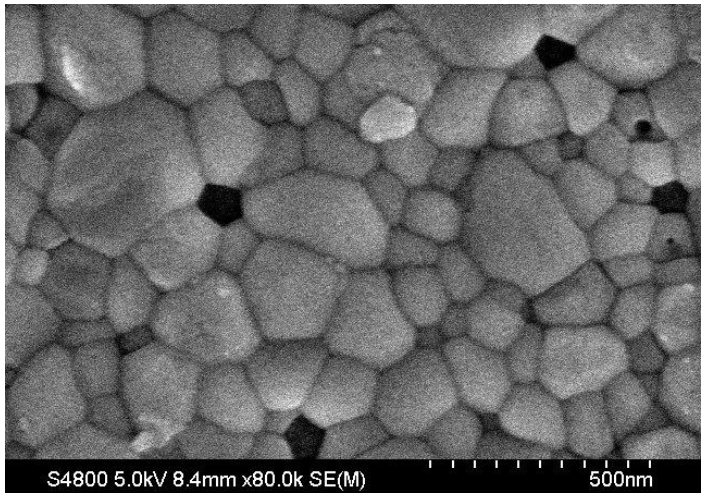


- slight **increase** in **PL intensity**
- **Defect passivation** & decrement in **non-radiative recombination**

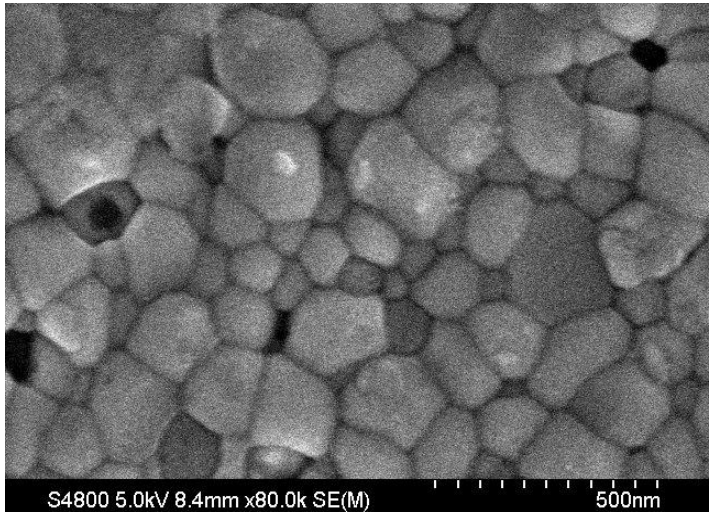
Effect of NaI on the microstructure of thin films



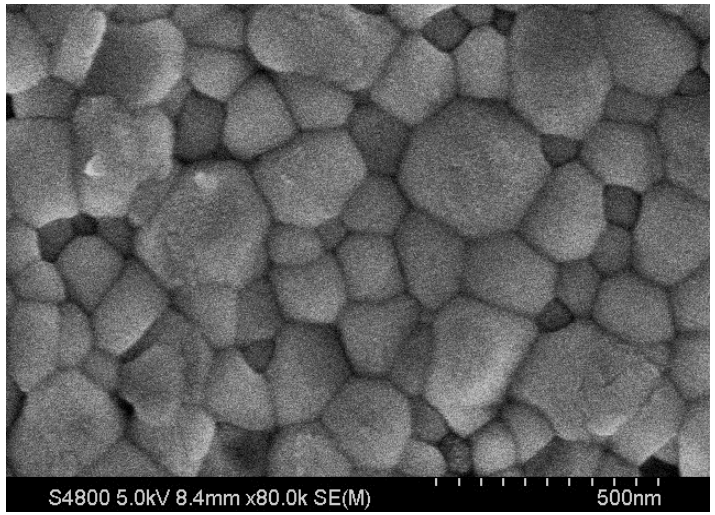
Control



0.3% NaI



0.6 % NaI



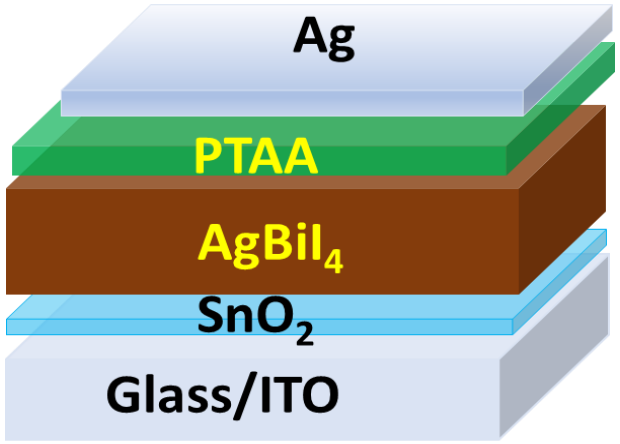
1.1 % NaI

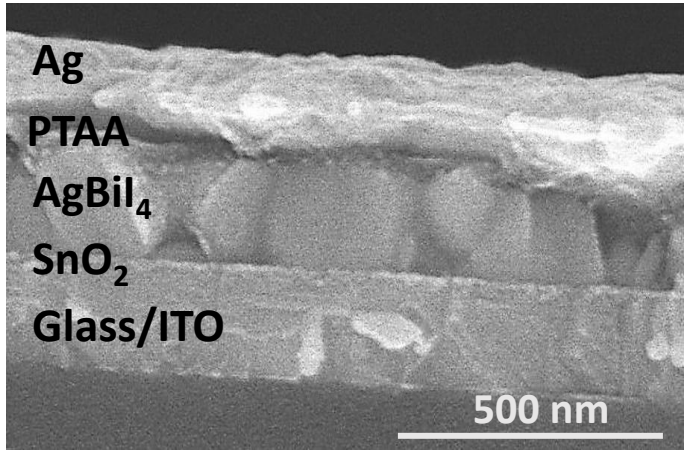
- Without Na: **multiple pinholes, less compact microstructure.**
- With Na: **compact film, significantly fewer pinholes**

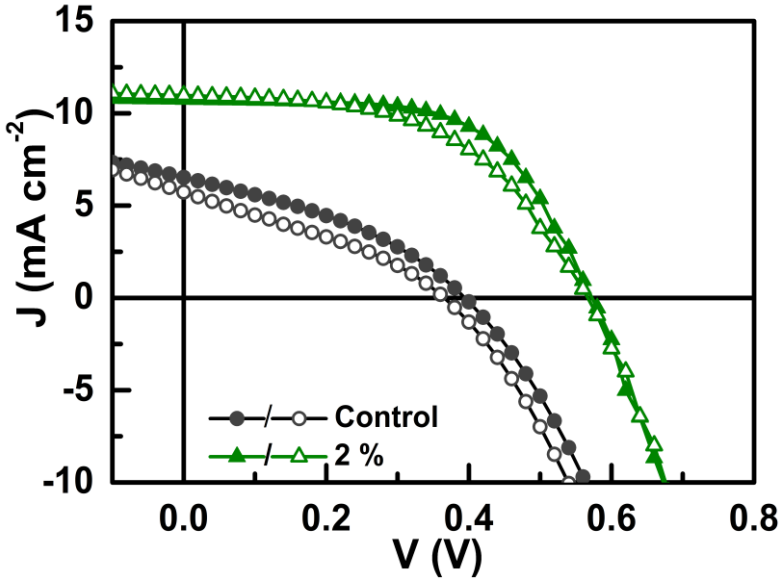
- influences **crystallization process** of the absorber layer
- **more** cohesive microstructure
- **Better device properties**

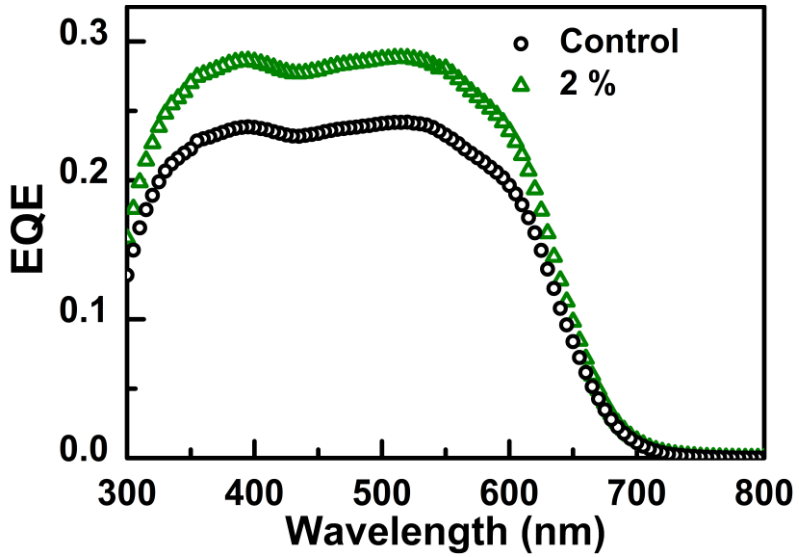
Ref: Fatima et al. ACS Appl. Energy Mater. 2025, 8, 7, 4601

Photovoltaic Characteristics of NaI added AgBiI4 Solar Cells

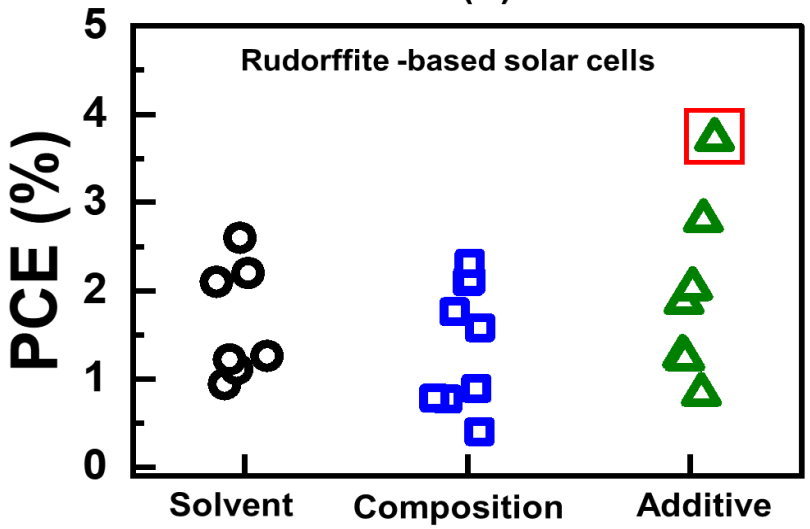






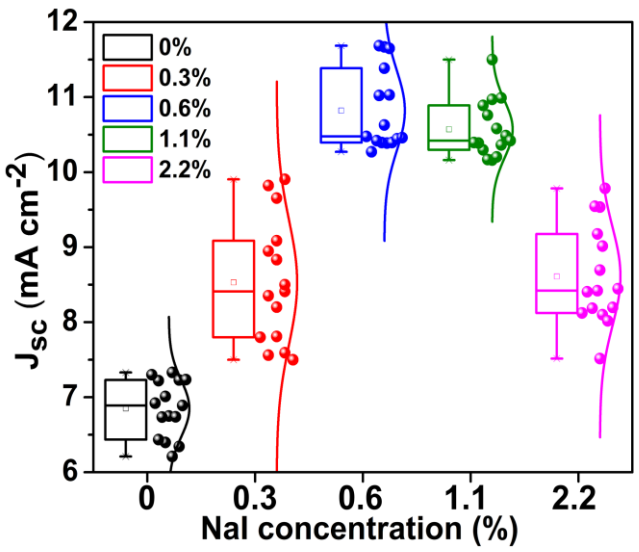


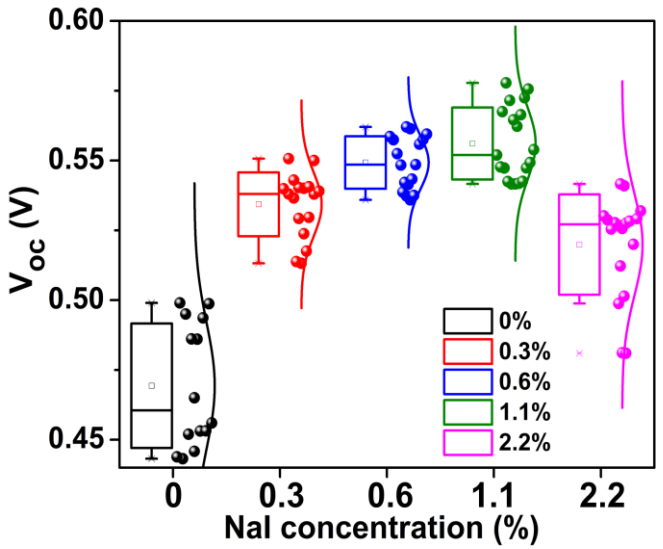
- Less Hyteresis
- Average PCE=3.7%
- Better EQE
- enhancement in spectral response
- improvement in both the bulk & interface quality with NaI additive

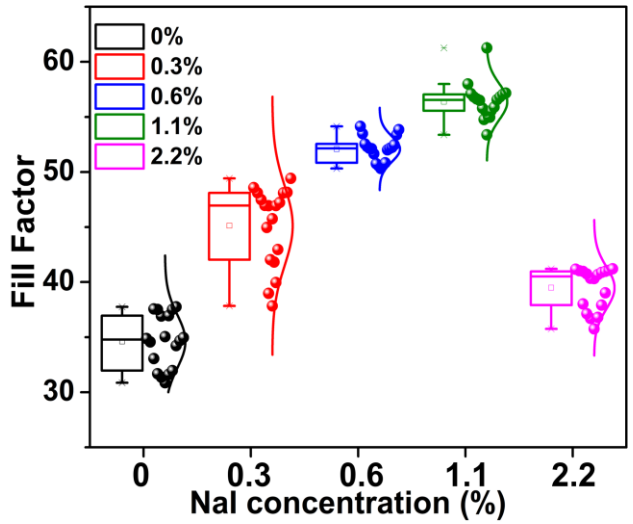


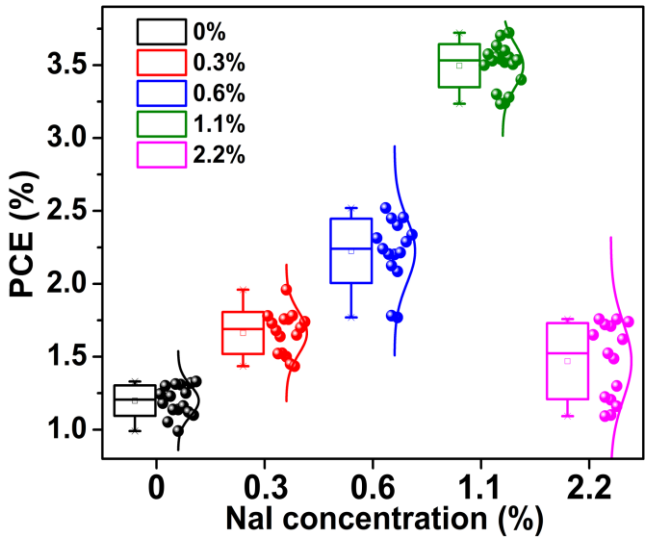
Ref: Fatima et al. ACS Appl. Energy Mater. 2025, 8, 7, 4601

Statistics of the Device Parameters







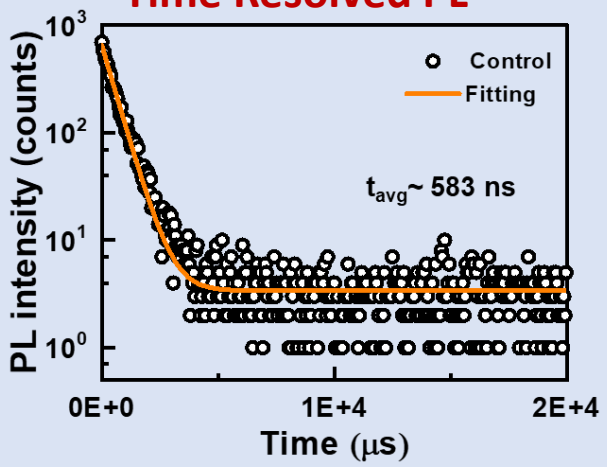


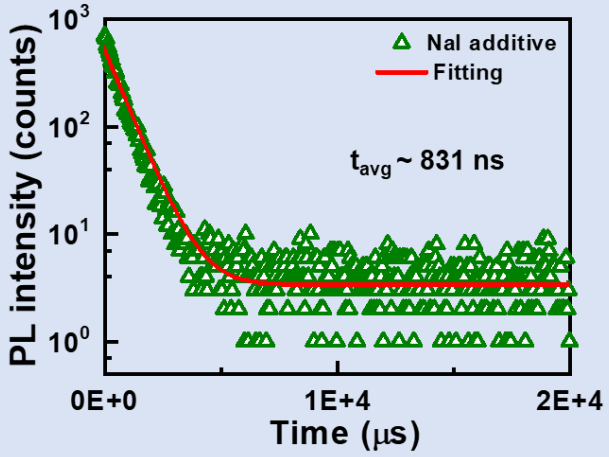
Device (mol % NaI)	J_{sc} (mA cm^{-2}) F/R	V_{oc}(V) F/R	FF (%) F/R	PCE (%) F/R
$AgBiI_4$	7.33/6.94 (6.84 ± 0.27)	0.49/0.46 (0.43 ± 0.02)	37.07/30.84 (34.61 ± 2.40)	1.33/0.99 (1.19 ± 0.10)
0.3	7.81/9.24 (8.53 ± 0.82)	0.55/0.56 (0.53 ± 0.01)	34.86/37.90 (45.12 ± 3.60)	1.52/1.96 (1.66 ± 0.14)
0.6	11.7/11.3 (10.82 ± 0.53)	0.50/0.49 (0.54 ± 0.01)	42.9/31.36 (52.38 ± 1.15)	2.52/1.77 (2.22 ± 0.20)
1.1	10.75/10.97 (10.57 ± 0.37)	0.58/0.56 (0.55 ± 0.01)	60.5/53 (56.38 ± 1.64)	3.72/3.25 (3.49 ± 0.14)
2.2	8.01/7.57 (8.61 ± 0.65)	0.53/0.49 (0.51 ± 0.01)	40.6/24.78 (39.48 ± 1.89)	1.74/0.92 (1.46 ± 0.26)

Ref: Fatima et al. ACS Appl. Energy Mater. 2025, 8, 7, 4601

Effect of Additive on Transient Photo Characteristics

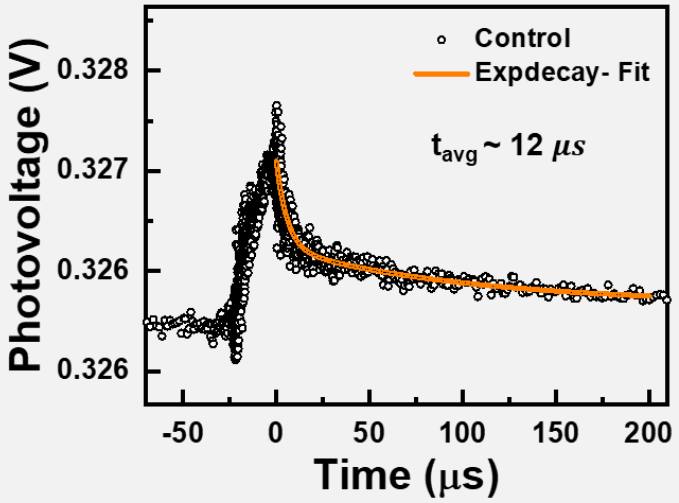
Time Resolved PL

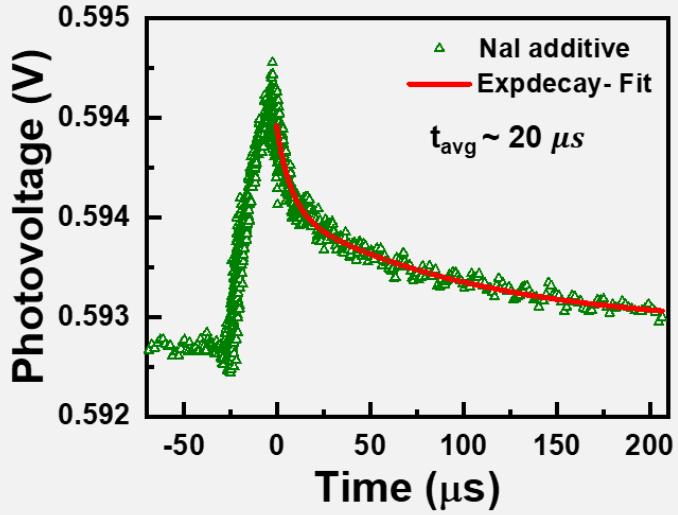




- **longer PL lifetime**
- indicating **mitigation** of **non-radiative recombination** with NaI additive.

Transient photovoltaic results

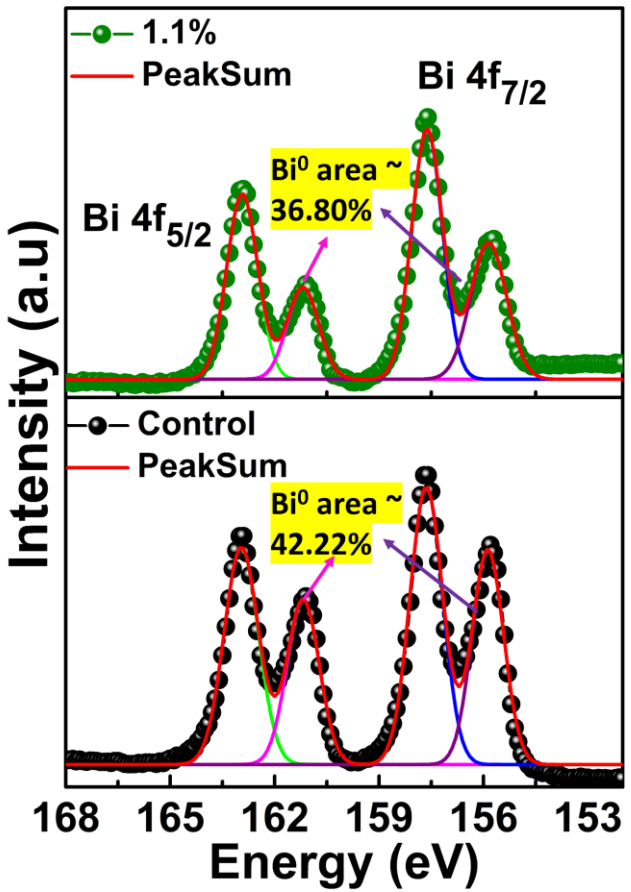




- **Longer carrier lifetime**
- **reduction** in **trap-assisted recombination**

Ref: Fatima et al. ACS Appl. Energy Mater. 2025, 8, 7, 4601

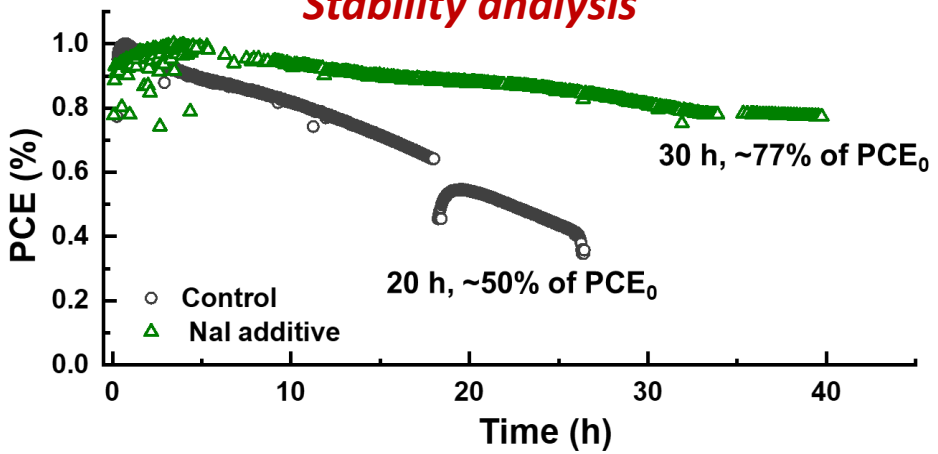
Impact on the surface chemistry and stability

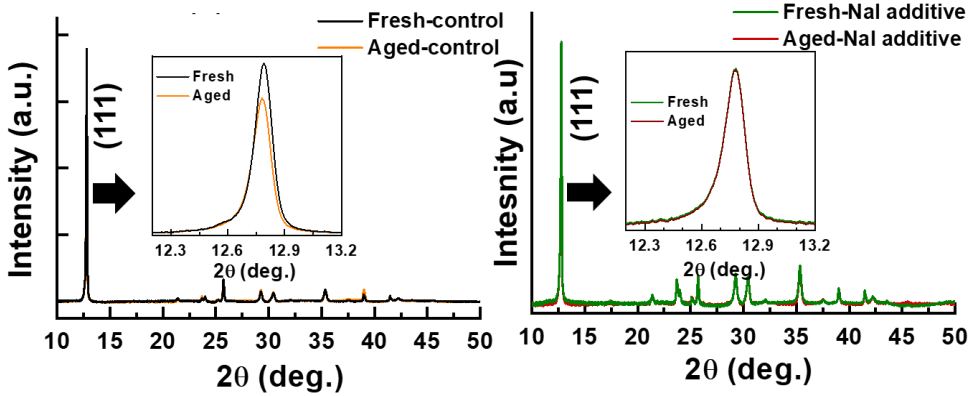


XPS curve of Bi for control and NaI-based thin films

- **XPS** shoulder peaks at **162eV (4f5/2)** and **156eV (4f7/2)** align with the binding energies of **metallic Bi⁰**
- Bi^0 is **deleterious** for **film quality**
- **Suppressed** by **6%** in **NaI additive** films
- modulates **film growth** & ameliorates the **surface chemistry**
- NaI based devices show **better stability**

Stability analysis



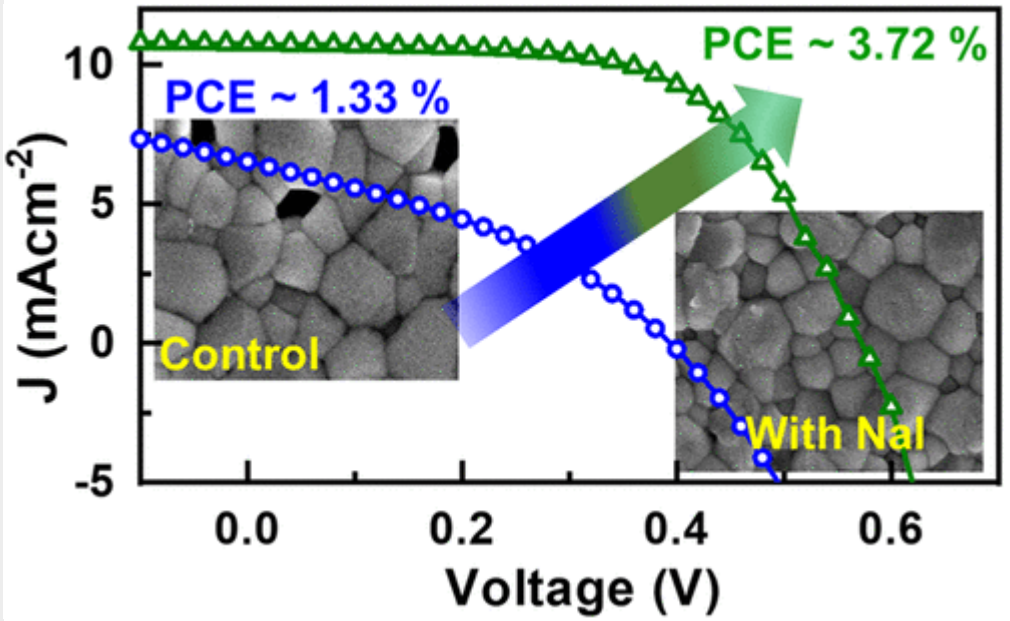


XRD pattern of fresh and aged thin films

Ref: Fatima et al. ACS Appl. Energy Mater. 2025, 8, 7, 4601

Conclusion

- **NaI additive improved crystallisation**, yielding compact, pinhole-free $AgBiI_4$ films.
- **Surface chemistry was modulated**, with Bi^0 ions suppressed as confirmed by XPS.
- **Film quality enhancements** led to higher PCE, rising from **1.33% to 3.72%**.
- **Carrier dynamics improved**, with lifetime increasing from **583 ns to 831 ns**, reducing recombination, making charge transfer more efficient.
- **Additive engineering proved crucial** for boosting both **efficiency and stability** of Rudorffite $AgBiI_4$ solar cells.



Ref: Fatima et al. ACS Appl. Energy Mater. 2025, 8, 7, 4601

Acknowledgement



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LMDD team, IIT(BHU)



IIT(BHU), Varanasi

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