Effect of Halide Composition on the Photochemical Stability of Perovskite Photovoltaic Materials

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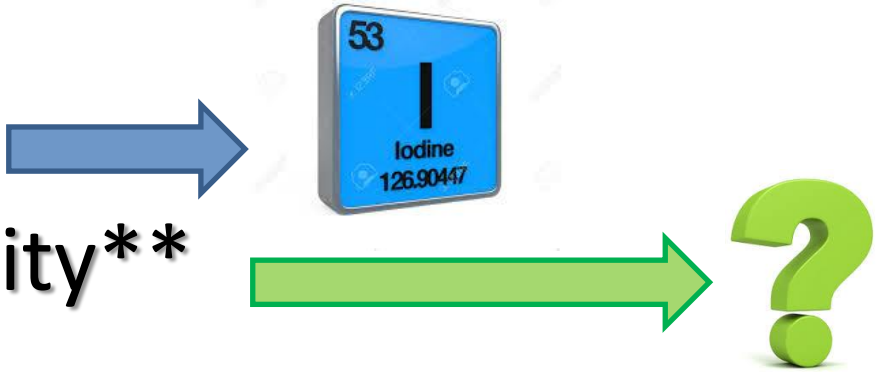
BGU-ENEA WORKSHOP

Motivation:

Development of **Mixed Halide** Perovskite-based PV materials **$MAPbI_nBr_{3-n}$** combining

high efficiency*

operational stability**



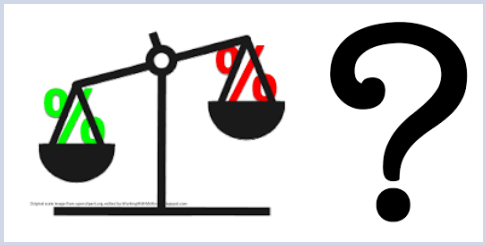
Research question:

How is operational stability dependent on the halide content in $MAPbX_3$?

* Kojima et al., *J. Am. Chem. Soc.*, **2009**, *131* (17), pp 6050–6051

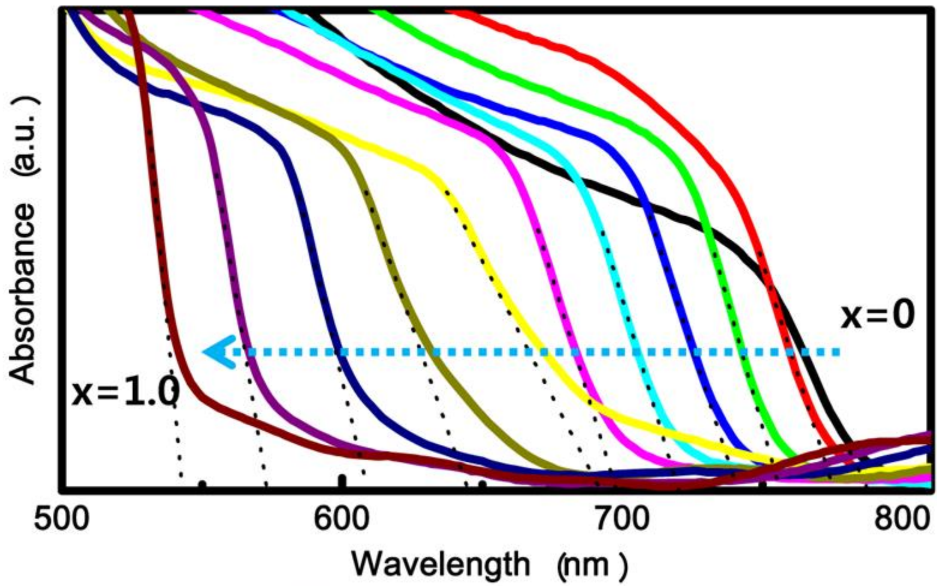
** R. K. Misra, I. Visoly-Fisher, E. A. Katz, et al., *J. Phys. Chem. Lett.*, **2015**, *6* (3), pp 326–330

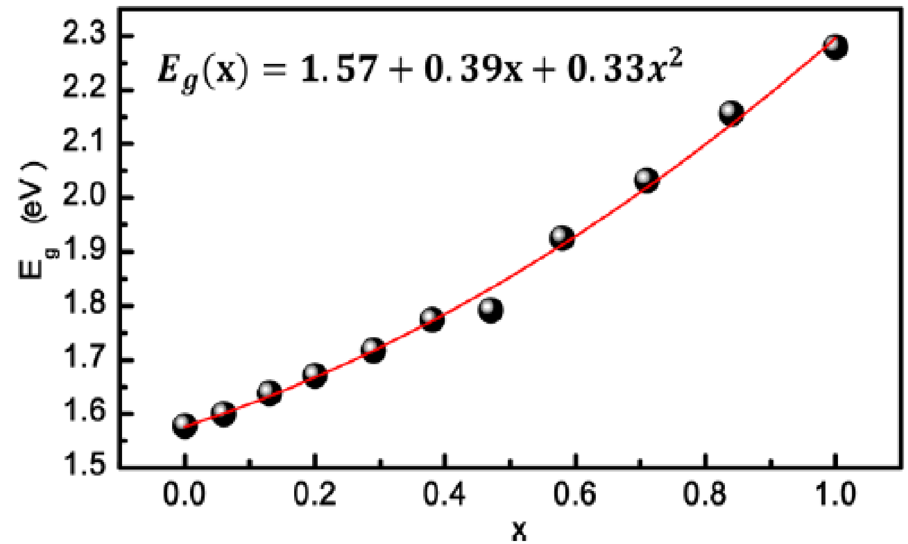
Pure Halide Perovskite PV Materials

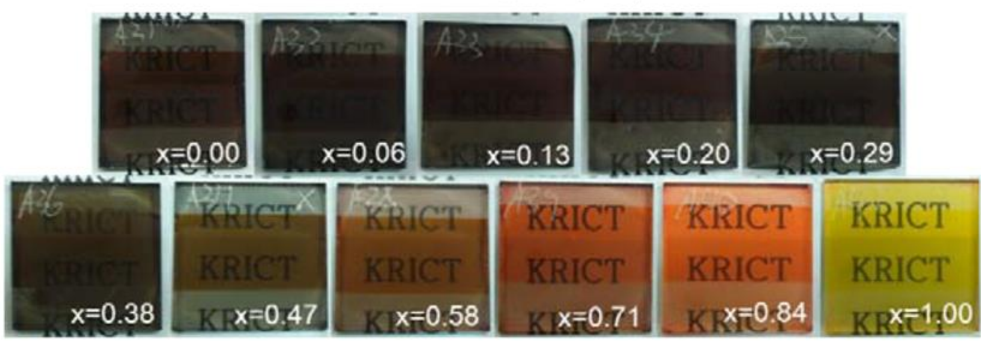
$MAPbX_3$	Solar absorption	Stability* * 100 suns + T ≈ 50°C
X = I	✓ ✓	✓
X = Br	✓	✓ ✓
Mixed Halide $MAPb(I_{1-x}Br_x)_3$		

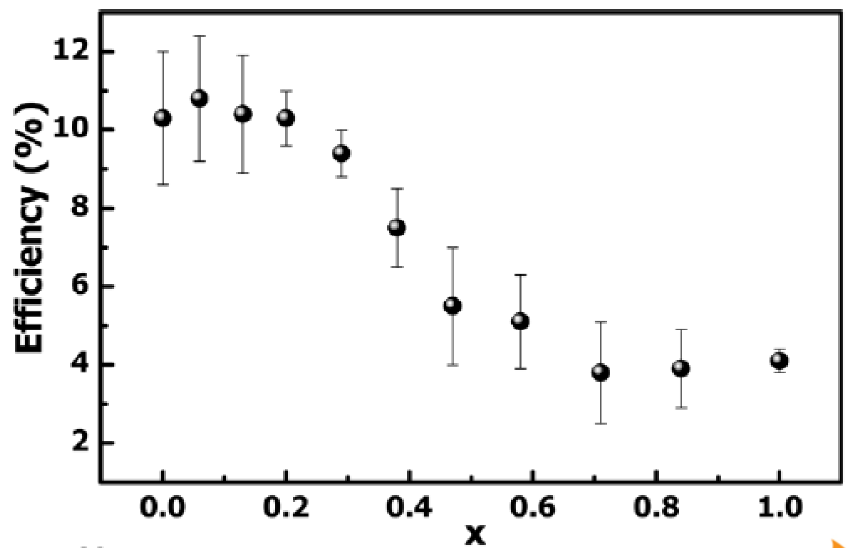
* R. K. Misra, I. Visoly-Fisher, E. A. Katz, et al., *J. Phys. Chem. Lett.*, **2015**, *6* (3), pp 326–330

Mixed halide $MAPb(I_{1-x}Br_x)_3$ Perovskite PV Materials









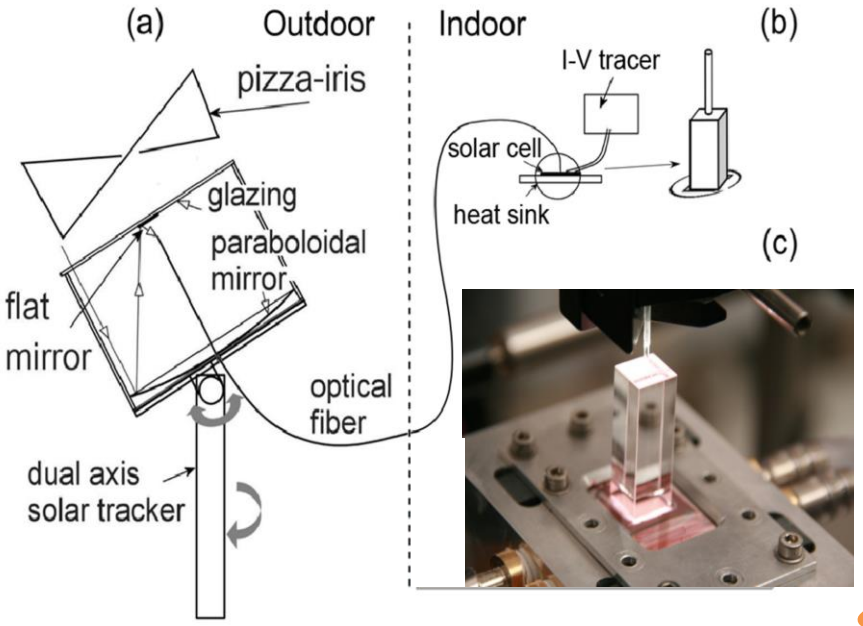
Stability ?

Seok et al., Nano Lett., 2013, 13 (4), pp 1764

Experiment layout

Accelerated testing
100 sun+T≈50°C

Encapsulated Films
MAPb($I_{1-x}Br_x$)$_3$ –
various compositions
Seq. dep. method



OUTCOME

$MAPbI_3$ - $MAPbBr_3$ more stable than mixed halides MAPb($I_{1-x}Br_x$)$_3$

Comparison to degradation under outdoor 1sun exposure (validate acc. testing)

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Assessment – Validation – Usage of Accelerated Stability Tests for PV Materials/Cells

1. Gordon, J. M.; Katz, E. A.; Feuermann, D.; Huleihil, M. Toward Ultra-High-Flux Photovoltaic Concentration. **Appl. Phys. Lett. 2004**, 84, 3642−3644

2. Tromholt, T.; Katz, E. A.; Hirsch, B.; Vossier, A.; Krebs, F. C.
Effects of Concentrated Sunlight on Organic Photovoltaics. **Appl. Phys. Lett. 2010**, 96, 73501-1−73501-3

3. I. Visoly-Fisher, E.A. Katz, et al., **Sol. Ener. Mater. & Sol. Cells 134 (2015)**, 99–107

4. L. Ciammaruchi, F. Brunetti, I. Visoly-Fisher, Solvent effects on the morphology and stability of PTB7:PCBM based solar cells, **Solar Energy 137 (2016)**, 490-499

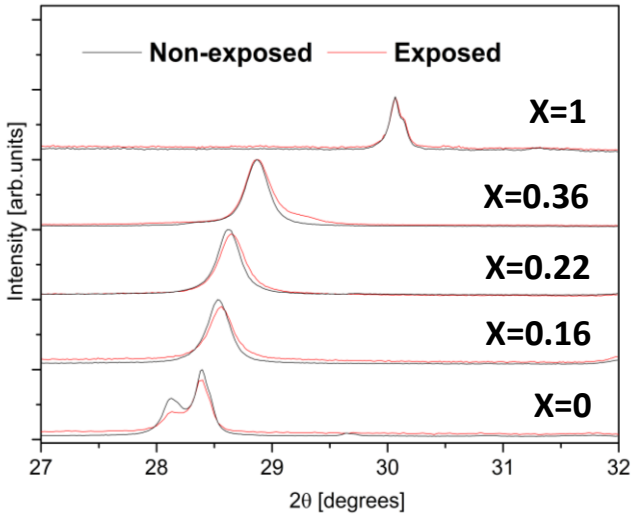
…….

Encapsulated Films MAPb($I_{1-x}Br_x$)$_3$ – various compositions

Characterization: UV/Vis – XRD

Table 1. The halide compositions and structural parameters of MAPb($I_{1-x}Br_x$)$_3$ thin films.

Sample	MAI/MABr [a]	Lattice parameter [Å] [b]	FWHM [°] [b]	Br content, x expected [c]	Br content, x calculated [d]	E_g [eV] [e]
1	1:0	6.312[f]	0.16	0	0	1.55
2	2:1	6.256	0.228	0.11	0.15 ± 0.02	1.65
3	1:1	6.236	0.223	0.16	0.20 ± 0.03	1.69
4	1:2	6.186	0.226	0.22	0.33 ± 0.03	1.78
5	0:1	5.934	0.1	1	1	2.31



[a]: Ratio in the organic precursor solution
[b]: peaks' full width at half maximum (FWHM)
[c]: Br content according to the precursor materials
[d]: Br content calculated from the XRD (Vegard's law)
[e]: optical bandgap determined from UV/Vis spectrum

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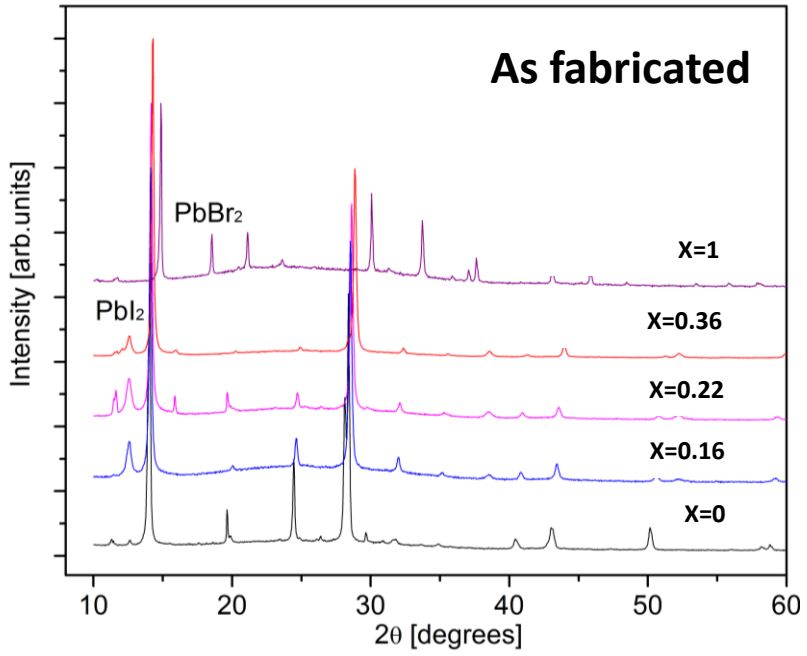
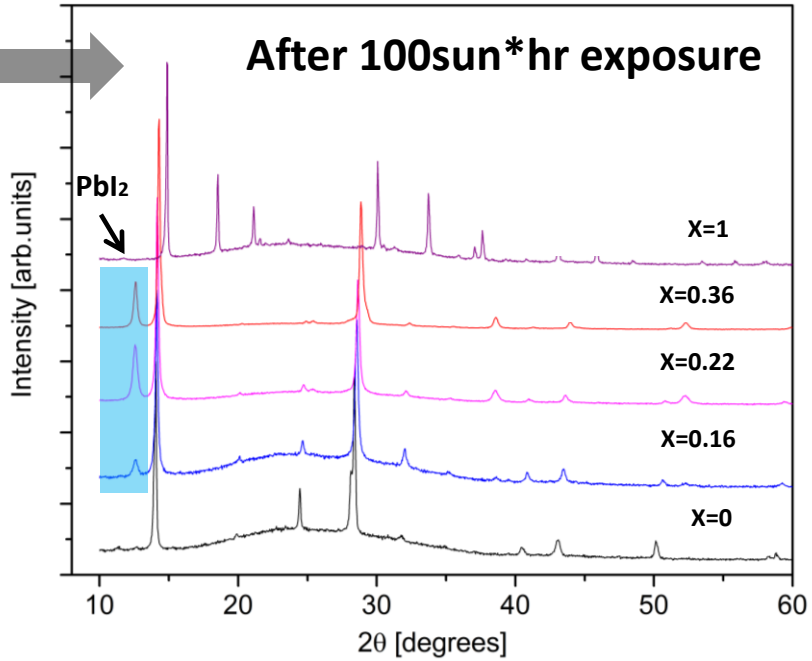
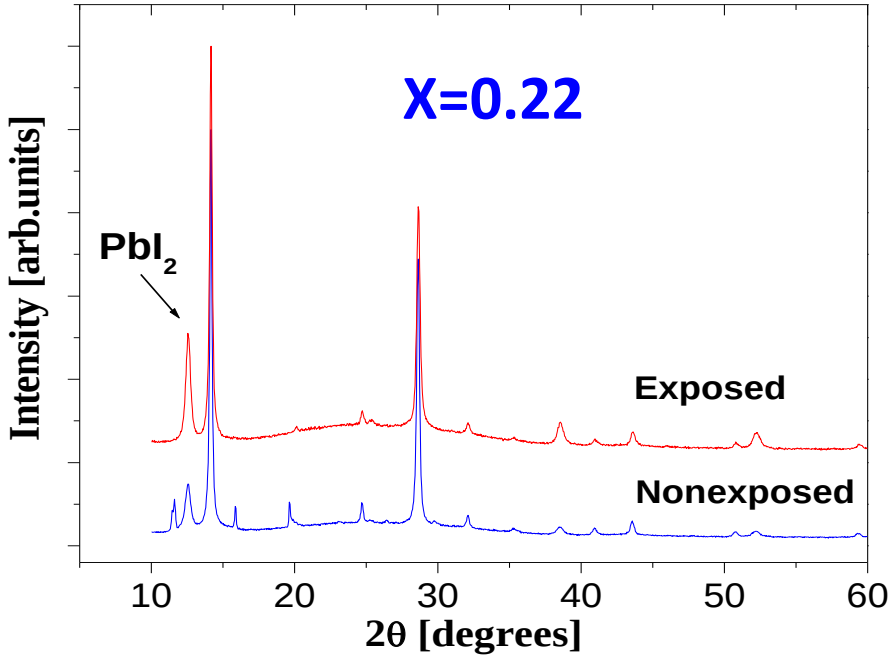
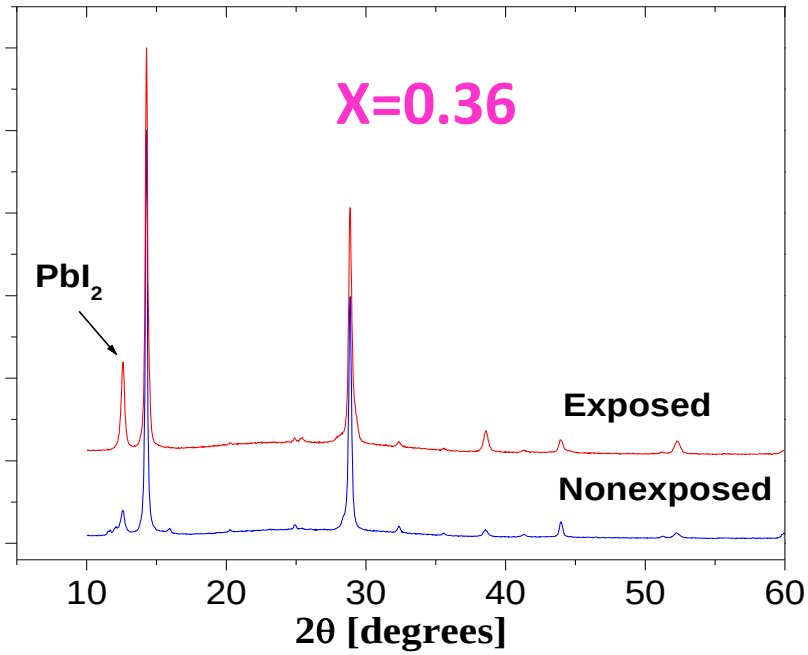
Results - $MAPb(I_{1-x}Br_x)_3$ - XRD

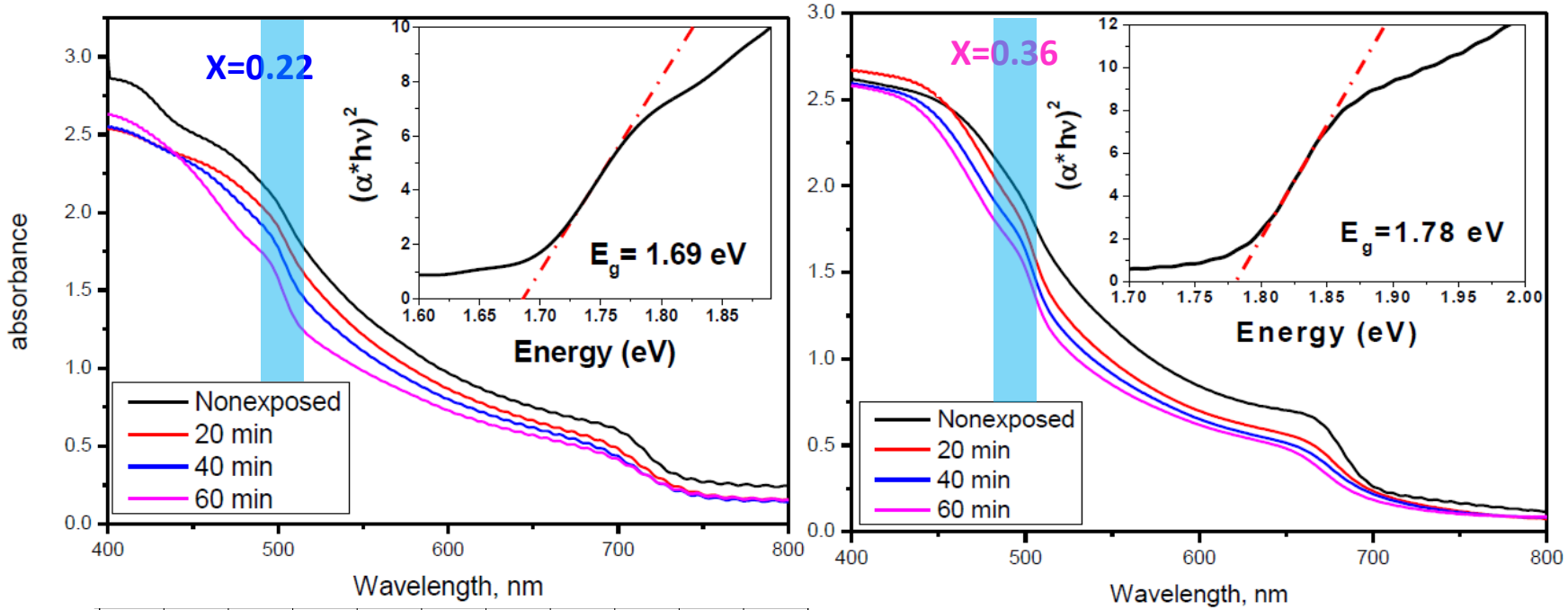


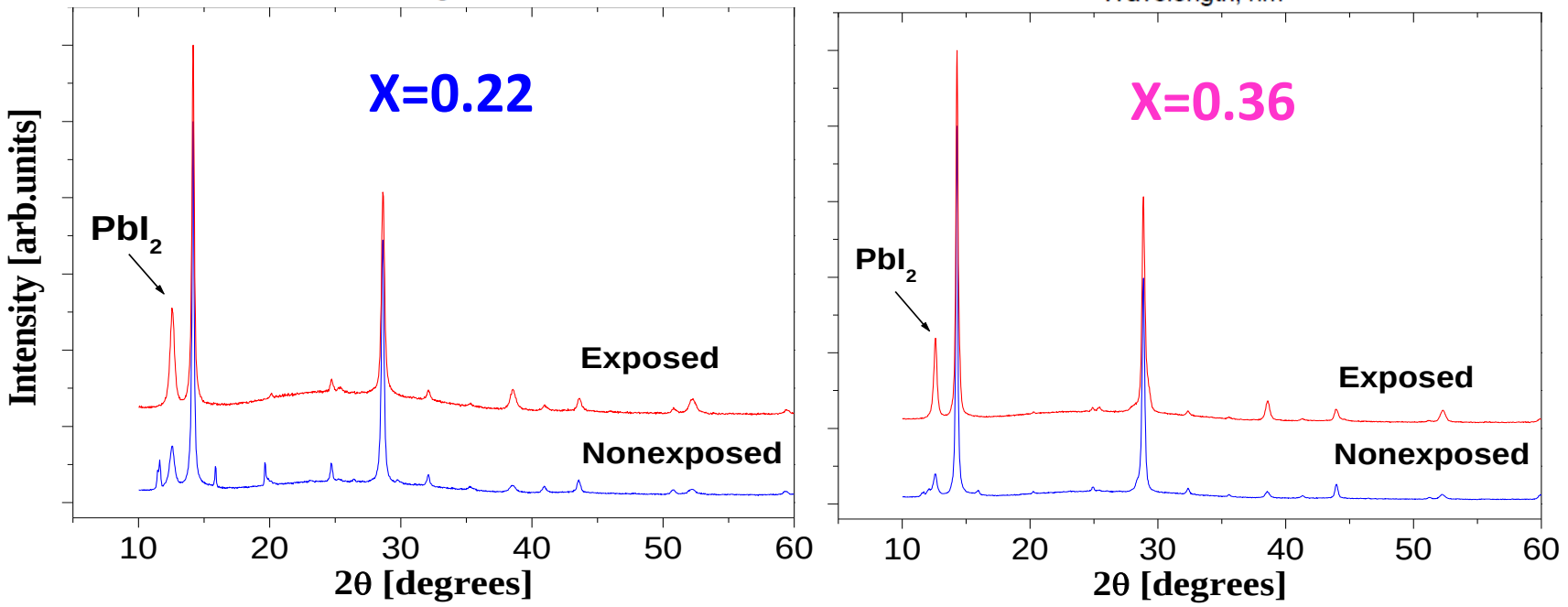






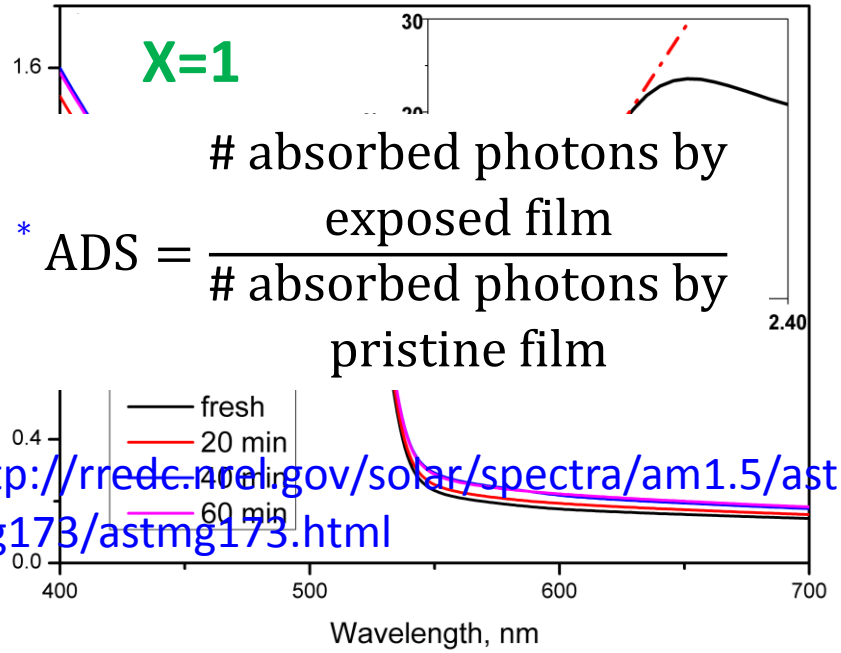
Results - $MAPb(I_{1-x}Br_x)_3$ - XRD + UV/Vis





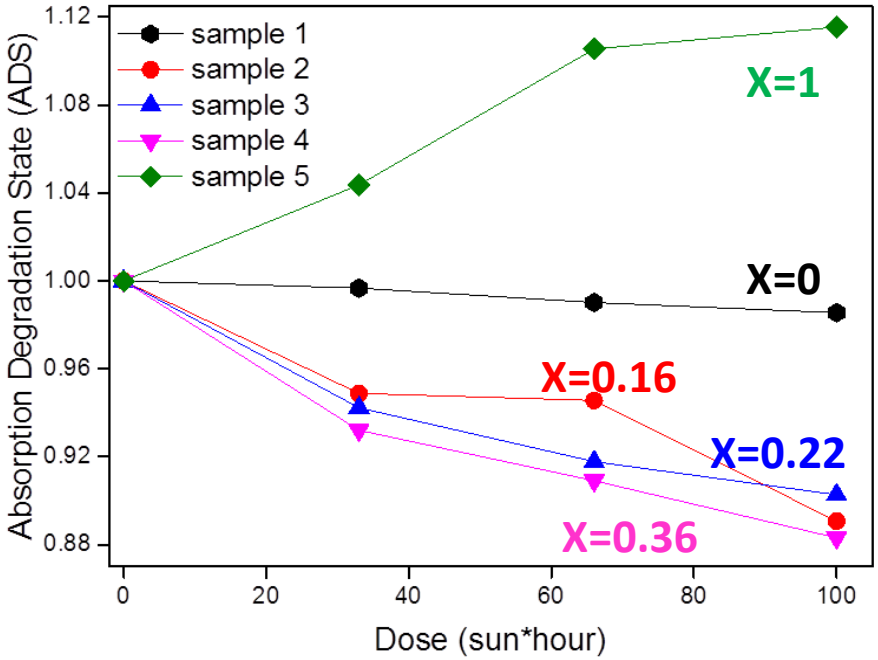
Results - MAPb($I_{1-x}Br_x$)$_3$ - UV/Vis

100 sun exposure

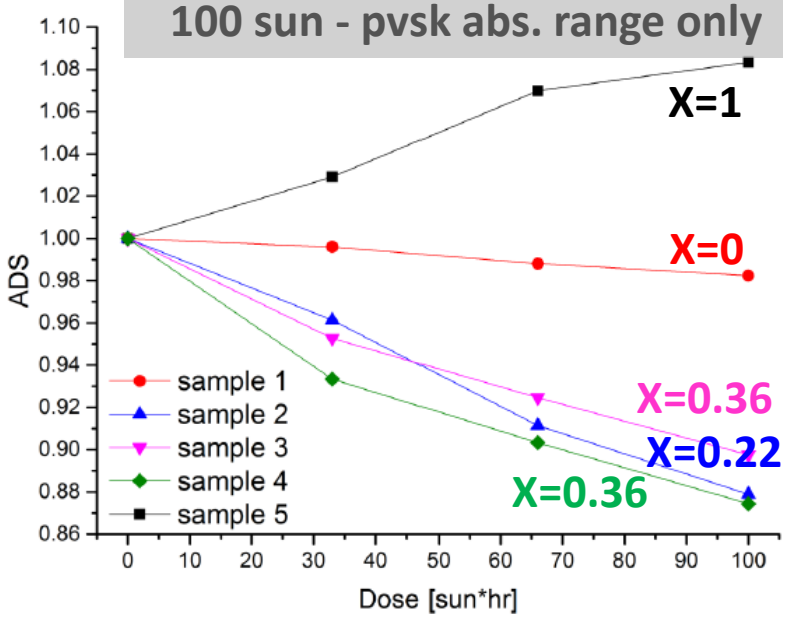


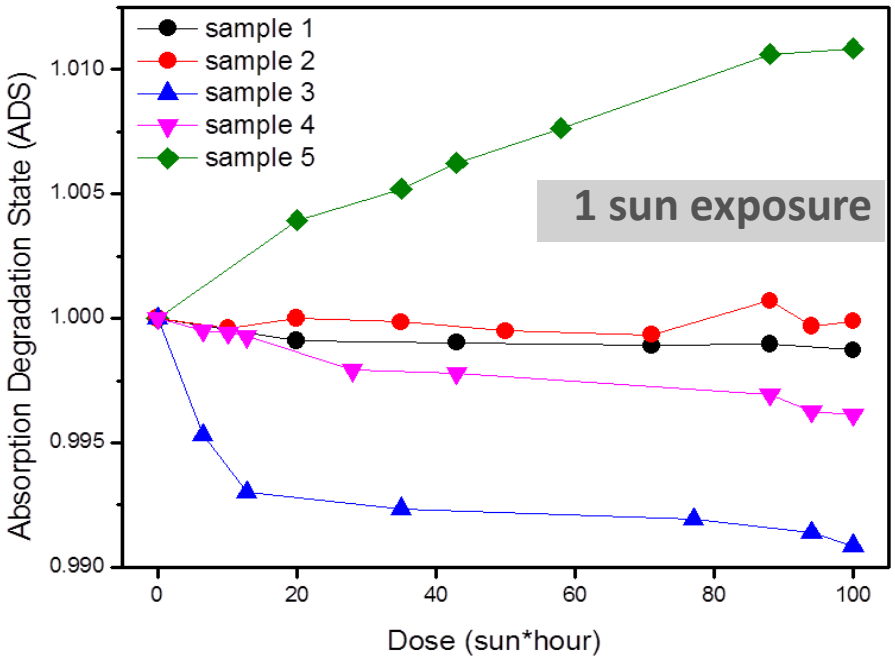
$$^{*}\mathrm{ADS} = \frac{\#\text{ absorbed photons by exposed film}}{\#\text{ absorbed photons by pristine film}}$$

http://rredc.nrel.gov/solar/spectra/am1.5/astmg173/astmg173.html



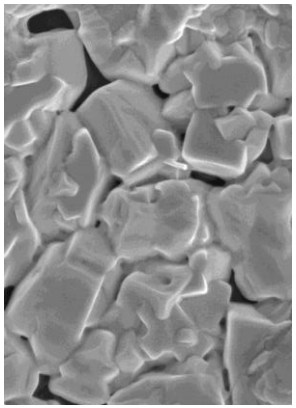
100 sun - pvsk abs. range only

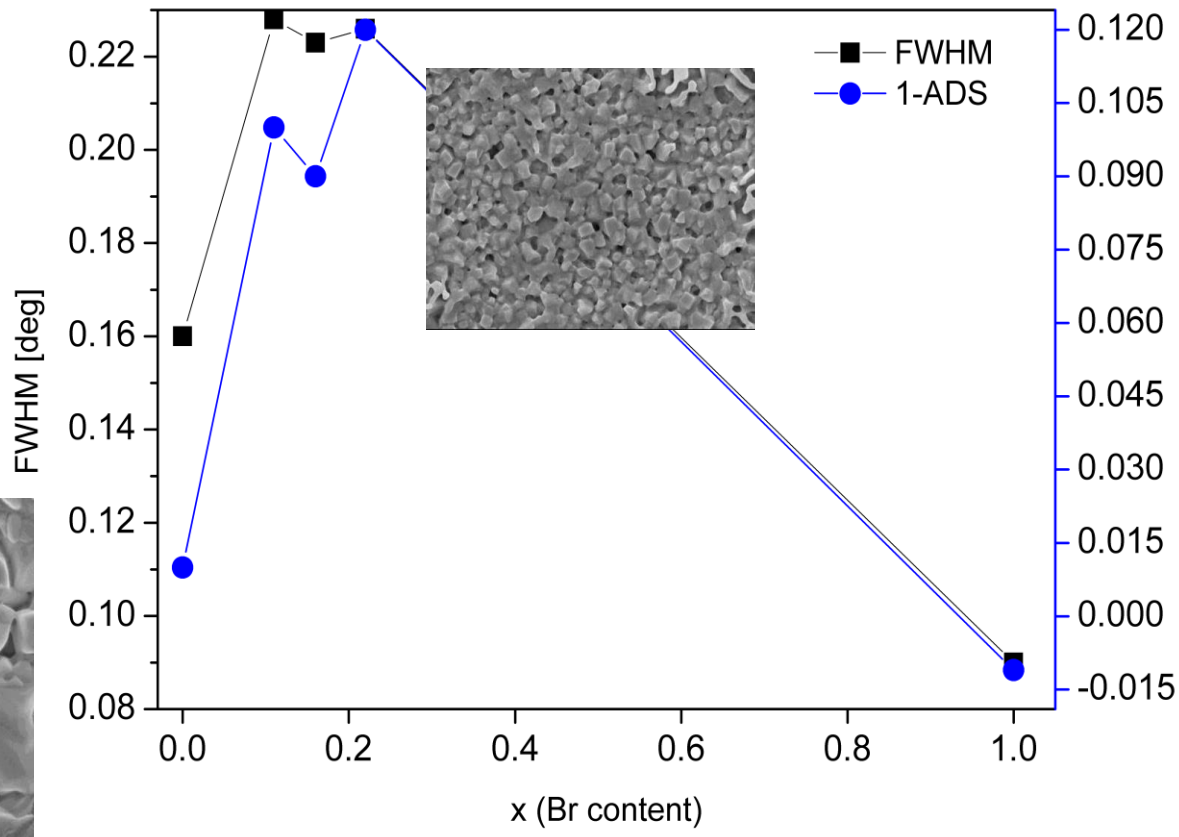


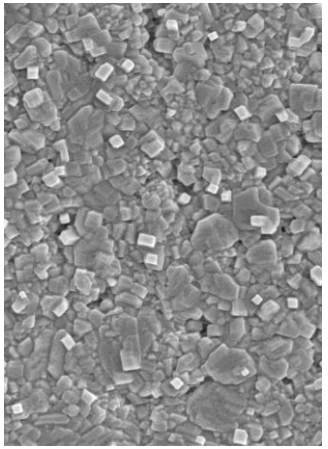


Results - $MAPb(I_{1-x}Br_x)_3$ – XRD + UV/Vis

$$ADS = \frac{\text{\# abs. photons by exposed film}}{\text{\# abs. photons by pristine film}}$$







Correlation between increased FWHM (mixed halide) and enhanced absoption degradation

Suggested degradation mechanisms:

- ✓ Perovskite decomposition proceeding *via* PbI_2 formation and perovskite Br-enrichment
- ✓ Connection between enhanced decomposition rate and smaller crystal coherence length (FWHM). Possible explanation includes:
  - distortion of the skeletal octahedral structure of $[PbI_6]4^-$
  - corresponding perovskite strain amplification
- ✓ Excess Br - grain size - binding energy -traps formation*

* (‘stolen’ from prof. Lanzani yesterday’s talk)

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Conclusions:

- Perovskite stability: $MAPbBr_3$ > $MAPbI_3$ > $MAPb(I_{1-x}Br_x)_3$
- Photolysis induced/accelerated by a *combined* effect of light and heat, resulting in perovskite decomposition (PbI_2 and organics).
- Perovskites with a smaller structural defect concentration more stable to photolysis.
- Crystal coherence length as an indicator for relative photolysis degradation rate.

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Acknowledgments:

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Italian National Agency for New Technologies, Energy and Sustainable Economic Development

Ministry of National Infrastructures, Energy and Water Resources

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EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

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