



BOISE STATE UNIVERSITY

Hybrid Perovskite Solar Cells

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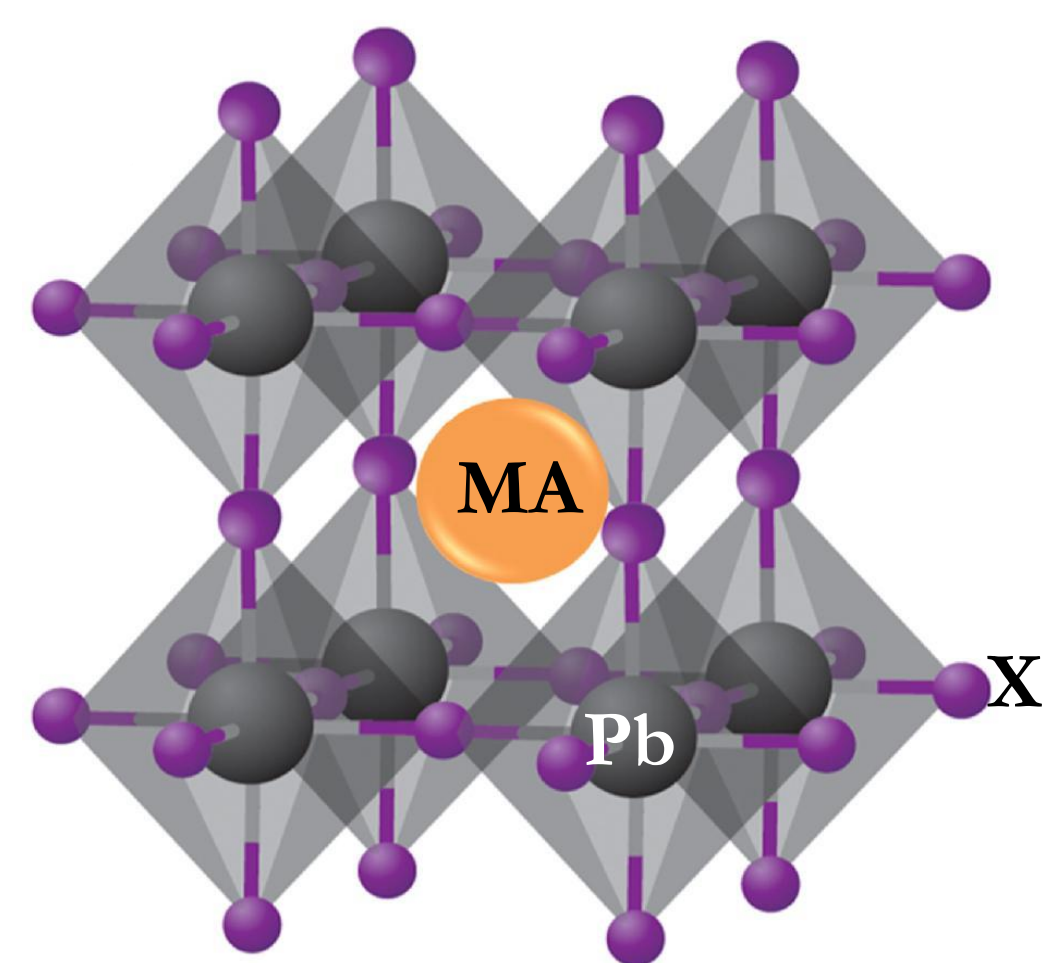
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Abstract

Recent advances in the efficiency of hybrid perovskite solar cells have motivated extensive research aimed at increasing stability with respect to humidity and light.^{[3],[1]} It is known that altering the chemistry of the perovskite crystal can alter the lattice structure, and in turn, stability.^{[2],[1]} In order to fabricate more stable methylammonium lead (II) iodide (MAPbI₃) cells, a series of precursor solutions was created by substituting increasing amounts of thiocyanate (SCN) for iodide following the stoichiometric form MAPbI_(3-x)(SCN)_x. While no working devices were fabricated due to the suspected decomposition of the p-type layer, X-ray diffractometry was ultimately used to characterize the changes in the crystal lattices.



MAPbI₃ Crystal Structure^[4]
Substitution at the X-site, I⁻ and SCN⁻ have similar effective ionic radii^[1]



Methods

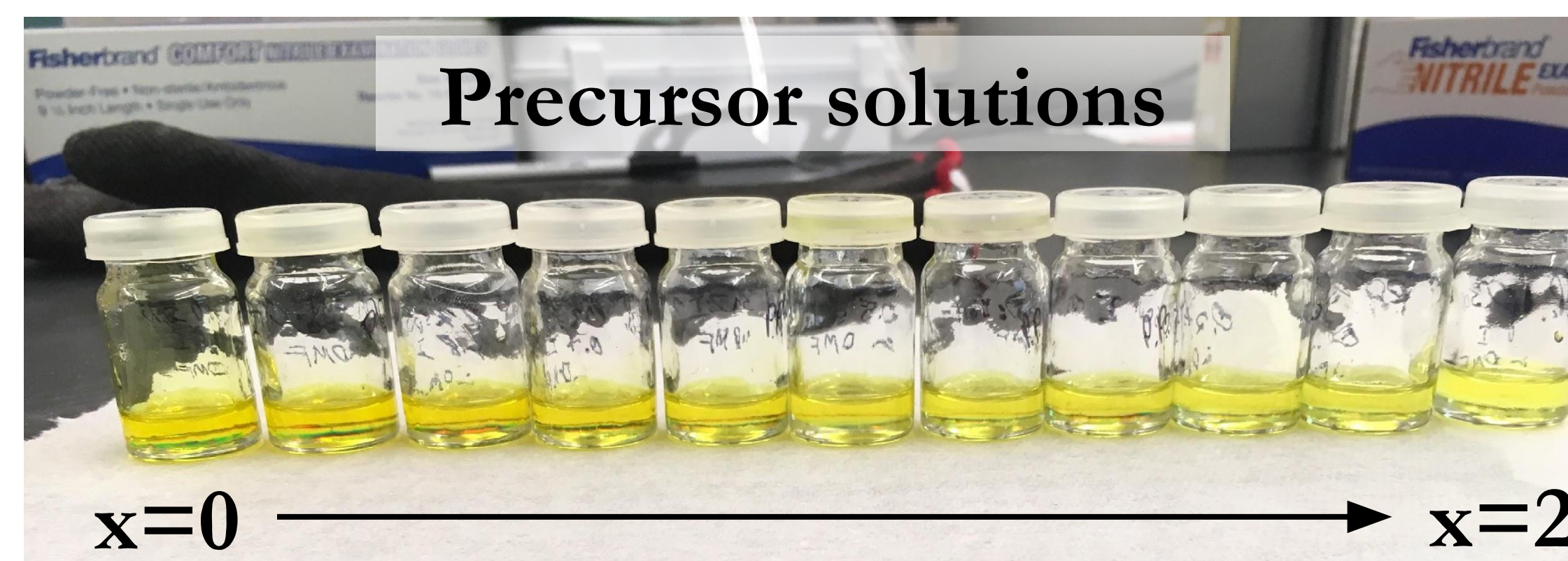
Fabrication:

- Ambient humidity conditions
- Substrate cleaning:
 - sonicated in acetone
 - ozone/UV (improve coverage)
- Spin-coating:
 - p-type: nickel oxide
 - MAPbI_(3-x)(SCN)_x
 - Solvent: dimethylformamide
 - chlorobenzene quench^[5]
 - n-type: PCBM (phenyl C₆₁ butyric acid methyl ester)

- Sputter-coated Al electrodes
 - Instrument: AJA Orion 5
- Characterization:
 - SEM
 - Instrument: FEI Teneo
 - XRD
 - Instrument: Rigaku Miniflex 600
 - Software: GSAS-II^[6]

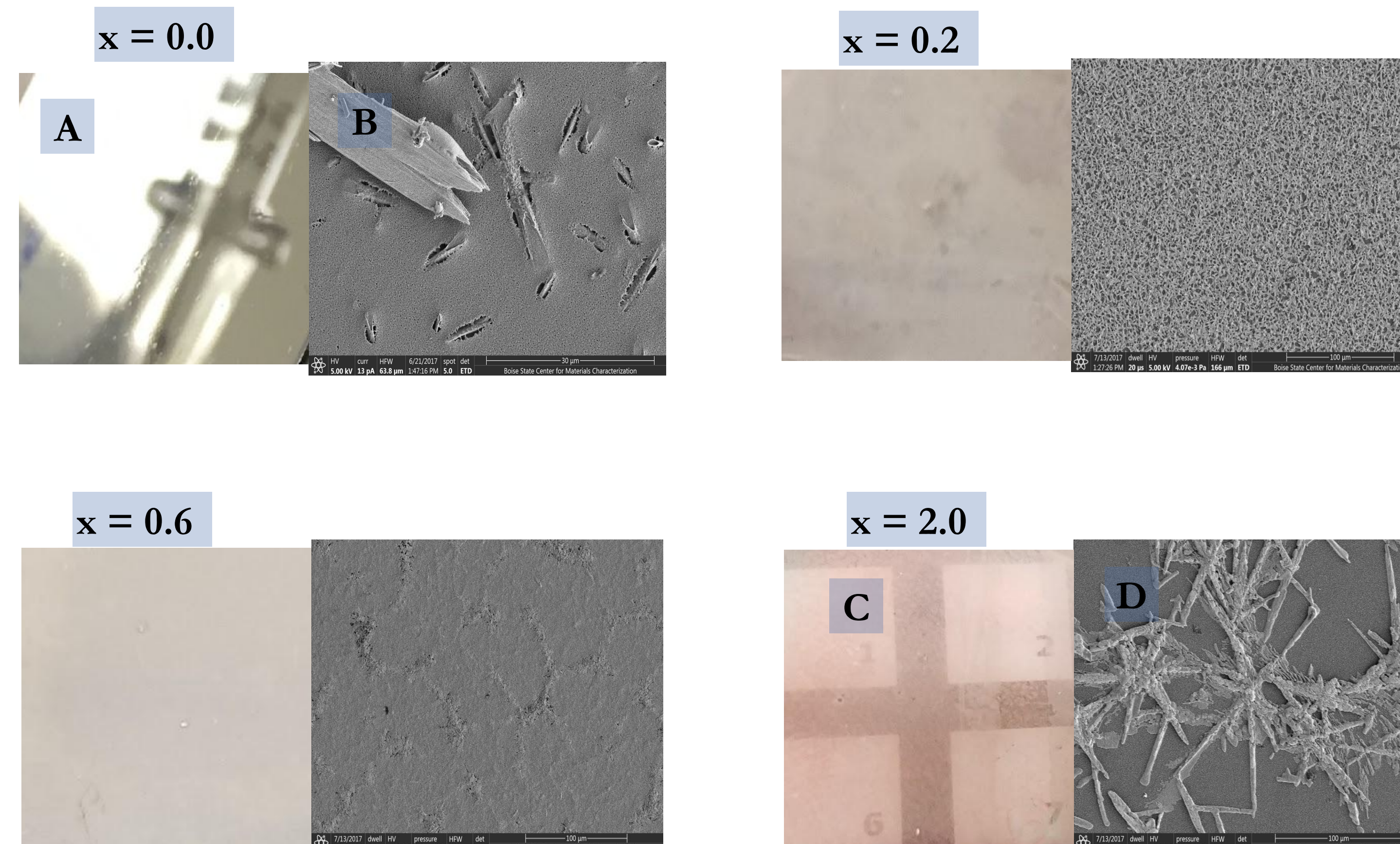
References

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- [6] B.H. Toby & R.B. Von Dreele, *J. Appl. Cryst.* 46, 544-549 (2013)
- [7] Ben Mills, Public Domain, Structure calculated using HF/6-31G* in Spartan '04 Student Edition. Image generated in Accelrys DS Visualizer.



Results

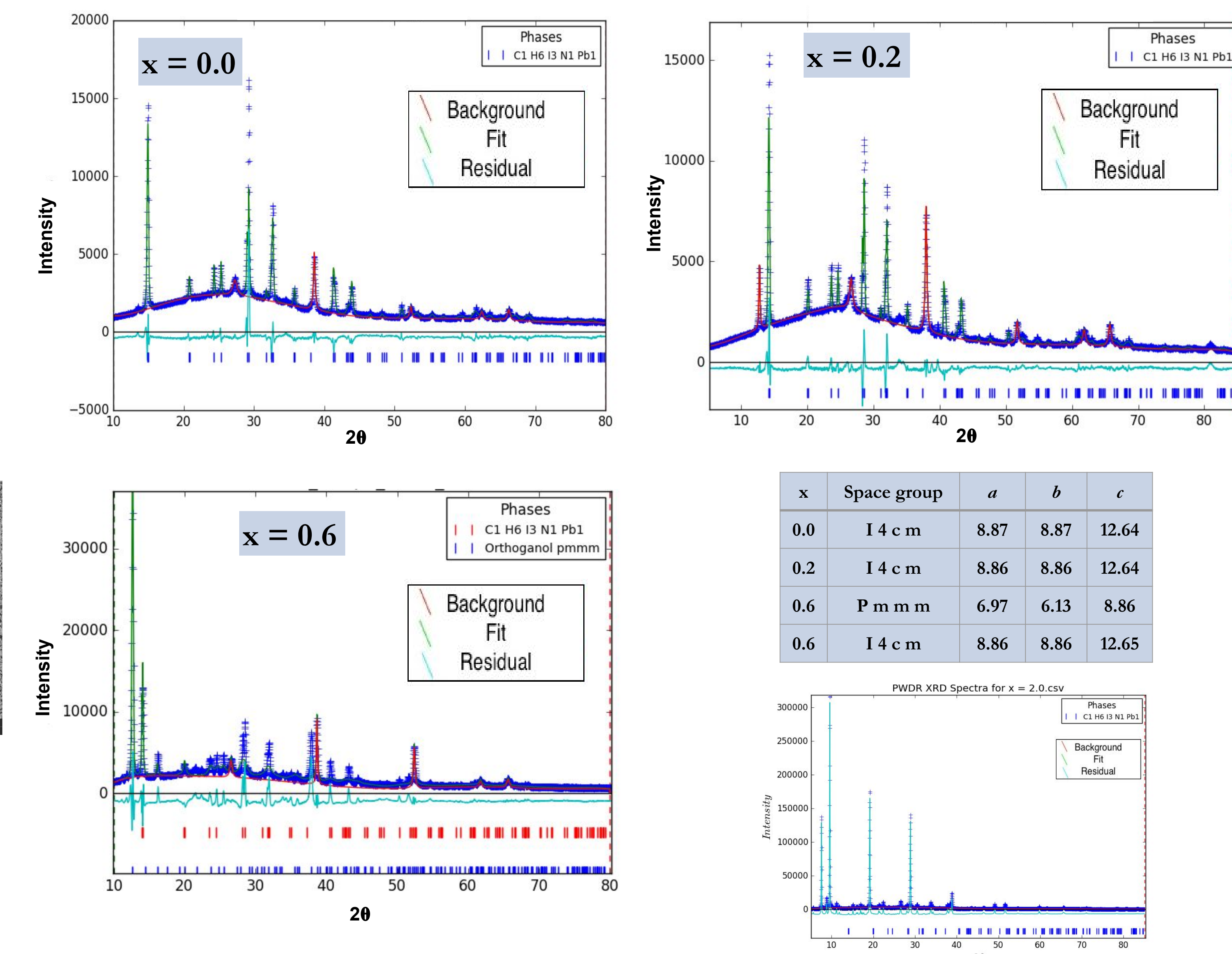
Cells were fabricated with the perovskite layer then characterized initially with scanning electron microscopy (SEM). Changes in the uniformity of coverage as the amount of SCN increased are shown below. It is clear that for $x > 0.8$, a different crystal structure forms. The figures below are paired as unmagnified optical pictures and SEM images.



Notes:

- A: highly reflective surface, pure PbI₂ precursor
- B: apart from impurities, the surface appears very uniform
- C: very thin layer of a new phase (red)
- D: evidence of different crystal structure and poor coverage

The XRD spectra were refined using GSAS-II^[6] and fitted to published MAPbI₃ data. All three lattice parameters remain relatively constant for the tetragonal phase while $0.0 < x < 0.8$. This could indicate that SCN is not altering the lattice size, or that it is not being incorporated at all. As the amount of SCN increased, a new orthorhombic phase emerged, shown in the $x = 0.6$ figure. Perovskite was not formed at the higher concentrations ($x > 1.0$), and these spectra were not analyzed further.



x	Space group	a	b	c
0.0	I 4 c m	8.87	8.87	12.64
0.2	I 4 c m	8.86	8.86	12.64
0.6	P m m m	6.97	6.13	8.86
0.6	I 4 c m	8.86	8.86	12.65

Conclusion

For lower concentrations of SCN in precursor solutions, the resulting perovskite phases seem to be mostly tetragonal, as in the base case of $x = 0.0$ where pure MAPbI₃ formed. Future work should aim to relate the SCN concentration to the stability of working devices, which could seed a model used to predict the effects of other anion substitutions. Furthermore, comparisons of the stability of devices made in controlled humidity should be made.

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