Pin-hole free MAPb0.75 Sn0.25(I0.5Br0.5)3 films spin casted without anti-solvent by adding MAAc additive to Perovskite ink

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ABSTRACT

To start the crystallization of the tin (Sn) based perovskite materials, anti-solvent treatment is a useful technique. But the use of anti-solvents increases the complexity of the deposition process thus hinders the applicability in mass production processes. Here we have developed an anti-solvent free $MAPb_{0.75}Sn_{0.25}(I_{0.50}Br_{0.50})_3$ perovskite thin film deposition method based on a one step spin coating process. Addition of 0 - 100 mol% of methylammonium acetate (MAAc) to the precursor ink allows for the deposition of continuous films. A decent crystalline and pin-hole free perovskite thin film can be obtained from 60 or more mol% MAAc additive. These results are confirmed by XRD, AFM and SEM measurements. $MAPb_{0.75}Sn_{0.25}(I_{0.50}Br_{0.50})_3$ has a wide bandgap and is currently being considered for applications in tandem solar cells and under water solar cells.

MOTIVATION

Hybrid perovskite materials

- Have excellent photovoltaic properties such as a high absorption coefficient and carrier mobility, and a long carrier diffusion length
- Have a tunable bandgap to harvest energy from the far UV to near-infrared region
- Are applicable to tandem solar cells or under water energy harvesting
- Can be deposited with low-cost solvent processing methods that are compatible with mass fabrication

CHALLENGES

- Highly efficient perovskite solar cells contains lead (Pb) that is very unlikely to metabolize by organisms
- Tin-based PSCs suffer from low power conversion efficiency (PCE) and have instability issues
- Most Tin-based PSCs require and anti-solvent to start the crystallization for the realization of continuous pin-hole free layers
- Difficult to obtain roll-to-roll compatible fabrication process

SAMPLE PREPARATION

50 mol% MAI, 50 mol% MABr, 37.5 mol% PbI_2, 37.5 mol% $PbBr_2$, 12.5 mol% SnI_2 and 12.5 mol% $SnBr_2$ were dissolved in one ml of DMF solvent and stirred at 500 rpm on a hot plate at 70° C for 1 hour. Different mol% (20-100) of MAAc were added to the ink later on. Inks were filtered using a 0.22 µm PTFE filters before use. Glass microscope slides were cleaned ultrasonically for 20 minutes in 5% Deconex in DI water followed by 20 minutes in DI water. Samples were dried with N_2 gas followed by additional cleaning in an air plasma (300 Watt) for 10 minutes. Spin coating was done at 4000 rpm for 60 sec without the use of antisolvent. Spun samples were annealed in a nitrogen atmosphere at 110°C for 15 min on a hotplate.

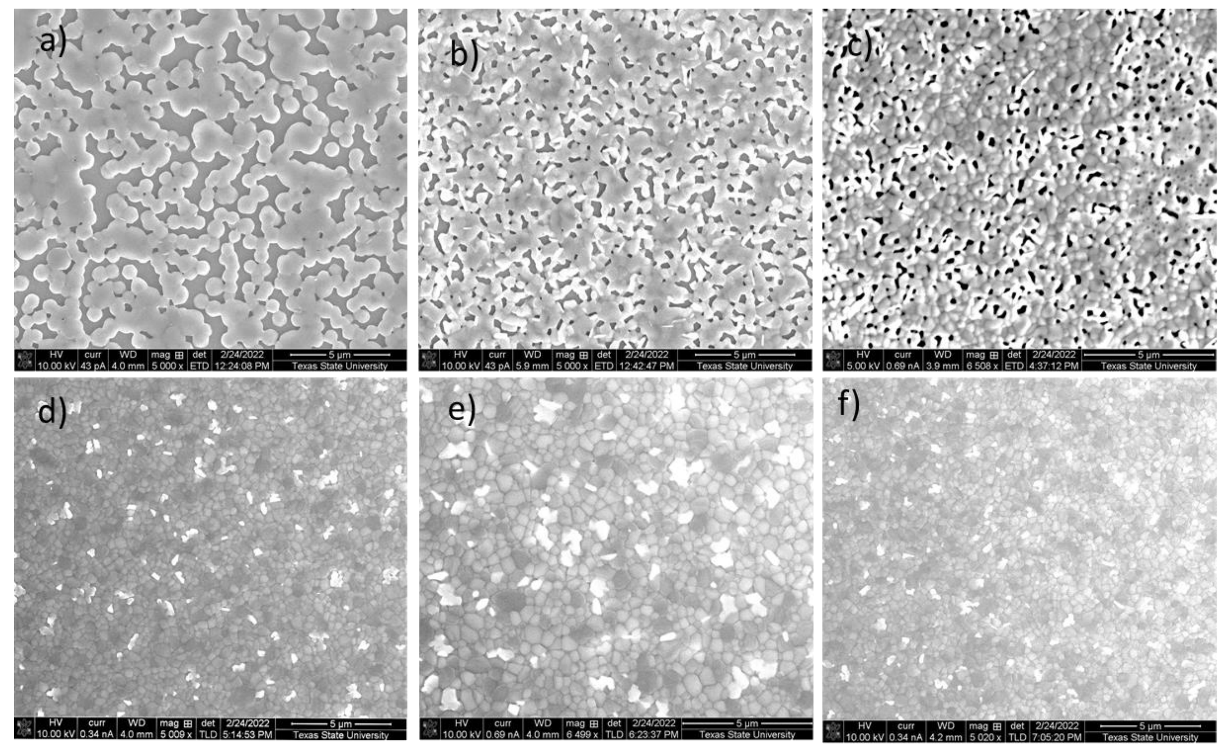

Fig. SEM image of MAPb0.75Sn0.25(I0.50Br0.50)3 with a) 0%, b) 20%, c) 40%, d) 60%, e) 80% and f)100% of MAAc

- Incorporating MAAc in MAPI perovskite ink has shown to impact the nucleation and growth during deposition and result in a pin-hole free layer
- Formation of perovskite is happening through exchange between X- anion of MA+X- and Ac- anion of an intermediate phase
- MAAC does not stay in the film, but is evaporated out during the annealing step
- To get a full coverage perovskite thin film we need to utilize more than 50 mol% of MAAc
- The excess MAAc beyond 60 mol% does not have a reverse effect on the coverage of the perovskite film

- Films spun from an ink containing 0 and 100 mol% MAAc shows a roughness of around ~102 nm and ~12 nm, respectively
- Changing the MAAc concentration from 60 to 100 mol% does not have a significant effect on film roughness
- Film thickness does not depend on the MAAc concentration. Almost they have similar thickness around ~ 237 nm

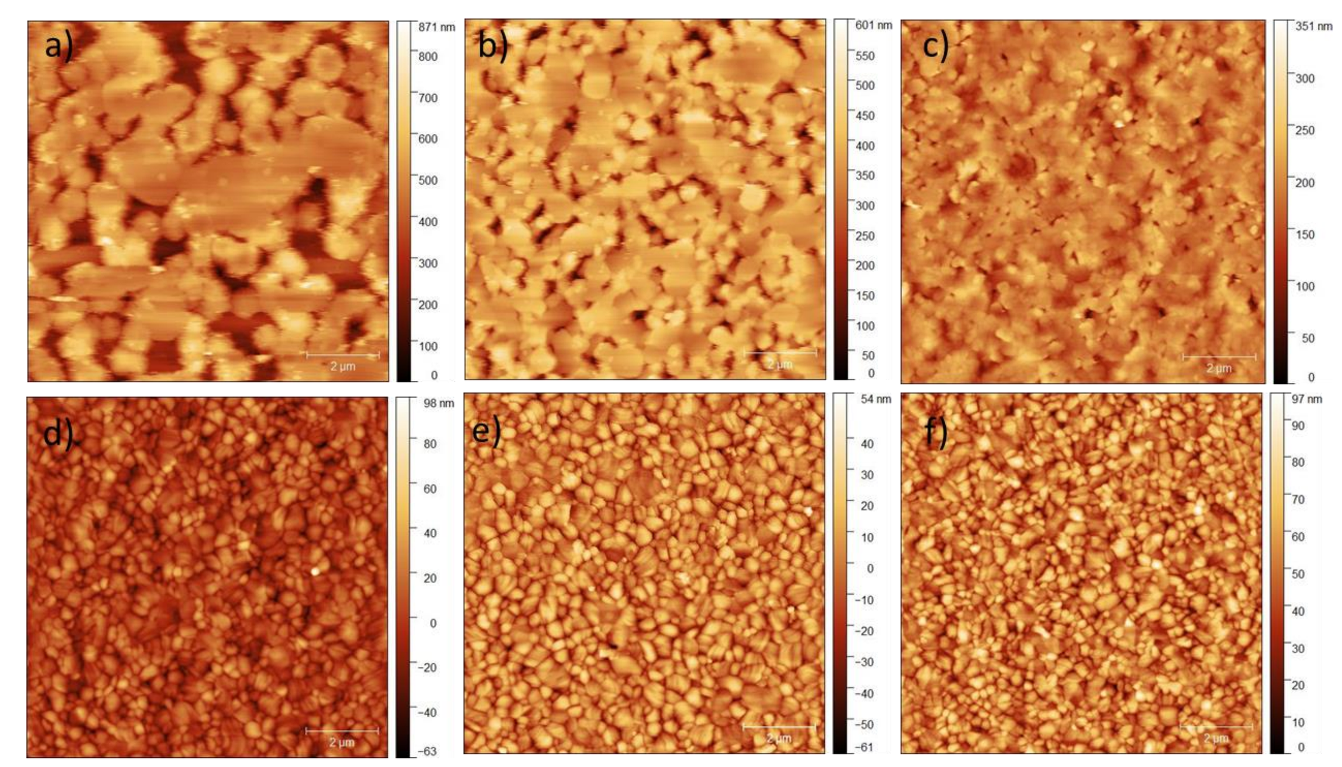

Fig. AFM image of $MAPb_{0.75}Sn_{0.25}(I_{0.50}Br_{0.50})_3$ with a) 0%, b) 20%, c) 40%, d) 60%, e) 80% and f)100% of MAAc

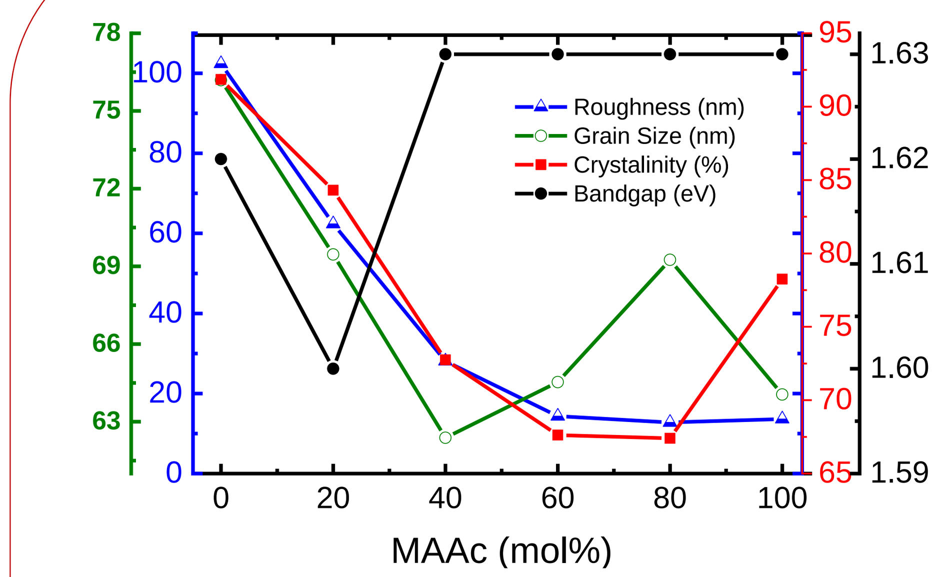

Fig. Properties of $MAPb_{0.75}Sn_{0.25}(I_{0.50}Br_{0.50})_3$ Vs different mol% of MAAc

- Roughness decreases with the increase of MAAC concentration
- Bandgap varies slightly with MAAc concentration (0.03 eV)

Table 1: Properties of $MAPb_{0.75}Sn_{0.25}(I_{0.50}Br_{0.50})_3$ thin film contains 0 mol% to 100 mol5 of MAAc

Sample type	Thickness (nm)	Roughness (nm)	Grain size (nm)	n@632.8 nm	Bandgap (eV)
0 mol%	362.24	102.4	76.19	--	1.62
20 mol%	261.74	62.37	69.46	--	1.60
40 mol%	296.16	28.08	62.38	--	1.63
60 mol%	231.84	14.34	64.53	2.38	1.63
80 mol%	237.19	12.77	69.25	2.34	1.63
100 mol%	237.16	13.61	64.05	2.40	1.63

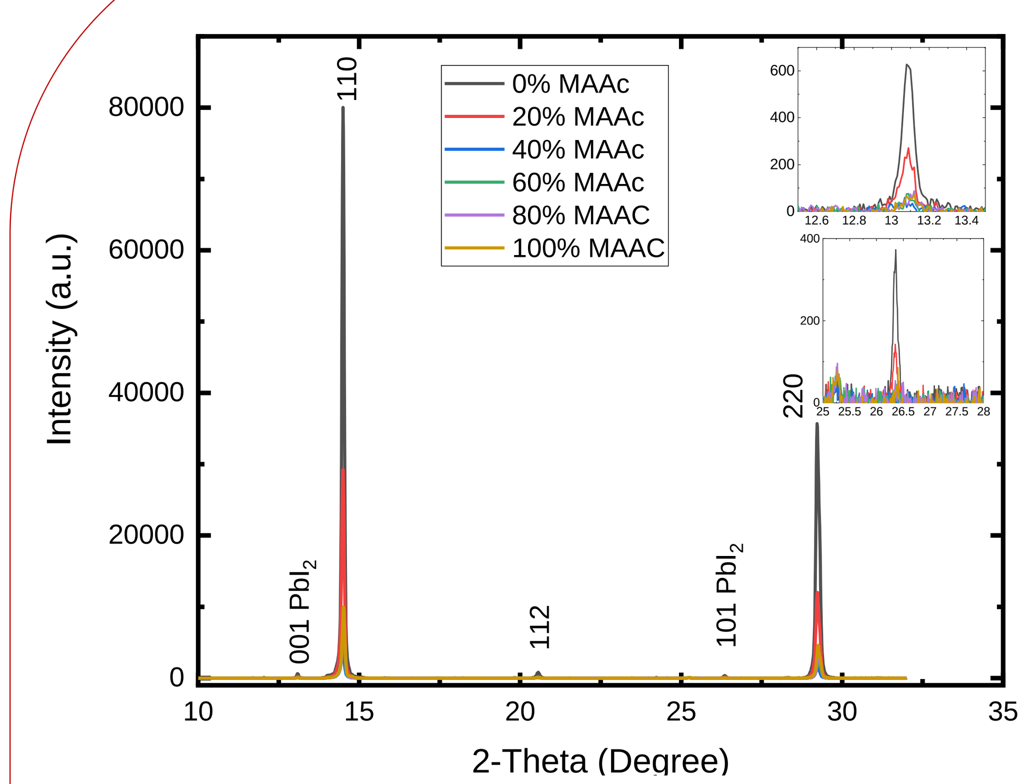

Fig. XRD spectra of $MAPb_{0.75}Sn_{0.25}(I_{0.50}Br_{0.50})_3$ contains different mol% of MAAc

- Determine the phase ID, grain size, and crystallinity using X-ray diffraction
- All of them show very strong perovskite characteristic peaks which match with the spectra reported in literature
- All observed peaks could be assigned to the α – phase of perovskite
- The films have a strong (110) and (220) texture for all MAAc concentrations
- (110) peak intensity decreases with increasing MAAc content.
- Low MAAc concentration have small PbI2 peaks at 13.1 and 26.26 degrees which almost disappear for films spun from ink containing more than 60 mol% MAAc

- The absorption band edges start around 760 nm for films spun from inks of any MAAc concentration
- The absorption profile significantly changes for the shorter wavelength region while adding more MAAc
- Reason could be (1) the low MAAc films were not continuous so UV light can transmit through the pinholes, (2) possibly an intermediate phase is formed in the perovskite thin films spin casted from high MAAc concentration inks
- The steep absorption edge observed around 760 nm confirms the formation of a continuous perovskite layer

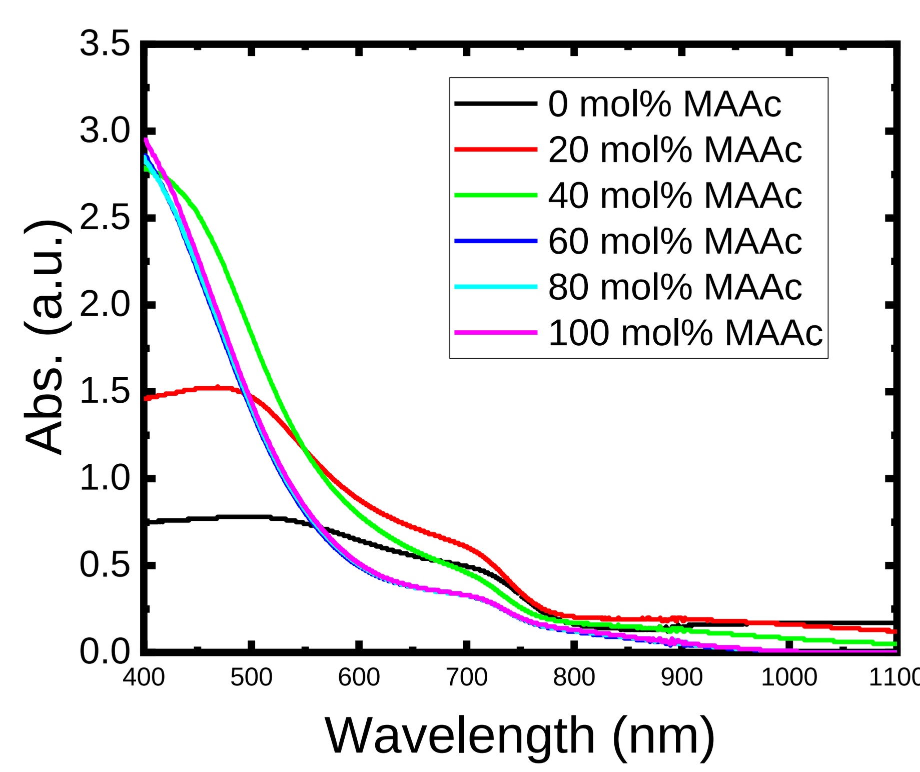

Fig. UV-Vis spectra of $MAPb_{0.75}Sn_{0.25}(I_{0.50}Br_{0.50})_3$ contains different mol% of MAAc

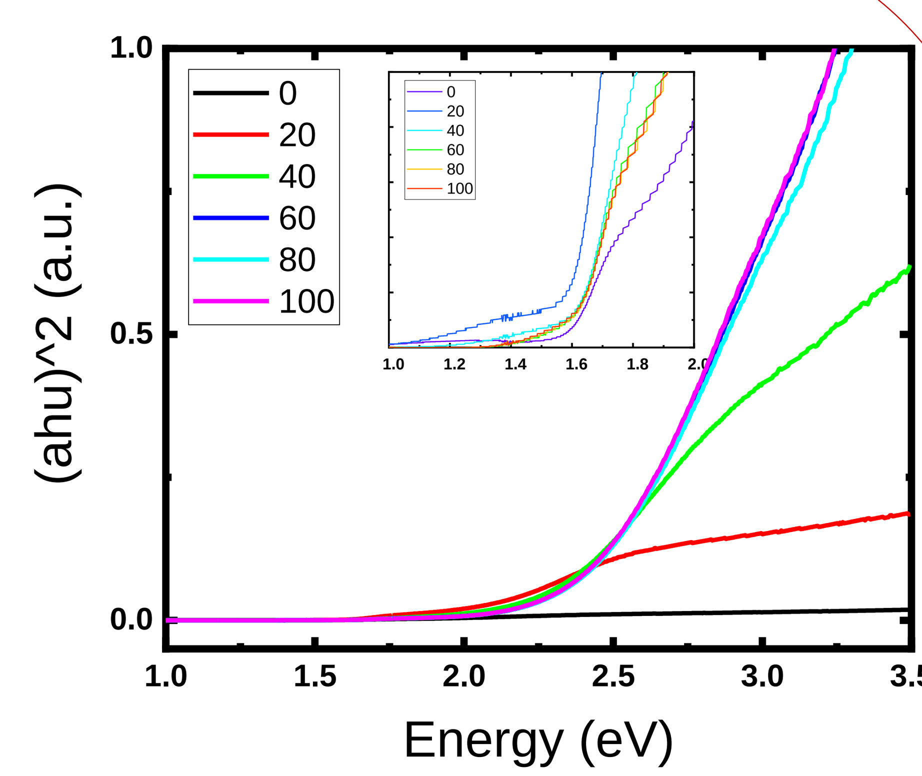

Fig. Tauc plot of $MAPb_{0.75}Sn_{0.25}(I_{0.50}Br_{0.50})_3$ contains different mol% of MAAc

- Bandgaps of the films were obtained from the Tauc plot around ~ 1.63 eV
- These results confirm that the MAAc additive in the ink does not affect the optical properties of these films
- High MAAc concentration inks show a similar absorption profile suggesting that MAAc is not incorporated in the films.

CONCLUSIONS

A one step deposition process of pin hole free Sn-Pb based perovskite films spun from inks containing 50 mol% MAAc additive was demonstrated. The deposition of these inks by spin-casting does not require an anti-solvent step. The MAAc additive does not affect the bandgap and refractive index significantly. The films have full coverage with a roughness of around 13 nm and grain size around 64 nm. The films show a bandgap of around 1.63 eV and a 632.8 nm refractive index of 2.38. The experiments confirm that these results are reproducible.

ACKNOWLEDGEMENT

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