Insights into $(Cs_{0.22}FA_{0.78})Pb(I_{0.85}Br_{0.15})_3$ Triple Halide Perovskite films: Stability Investigations via Angle-Resolved XPS Analysis

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Introduction

Perovskite materials have attracted the scientific community's attention due to their photovoltaic properties and their low manufacturing cost. Films can be deposited with near-room temperature (RT) solvent-based techniques including spin-casting, blade-coating, slot-die printing, and inkjet printing. Triple halide perovskites exhibit an adjustable wide bandgap, offering potential applications in tandem solar cells when combined with silicon bottom cells. Despite such improvement in efficiencies and lower manufacturing costs, perovskite solar cells could not be a marketable product without improving device stability.

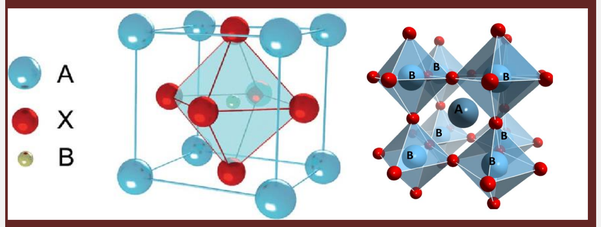
Experimental Procedure

Here, we studied angle-resolved X-ray photoelectron spectroscopy (XPS) of spin-coated $(Cs_{0.22}FA_{0.78})Pb(I_{0.85}Br_{0.15})_3$ + 3 mol % $MAPbCl_3$ absorber layer, where FA ($[CH_5N_2]^+$) stands for formamidinium. This triple halide is also denoted by $Cs_{22}Br_{15}$. Recently, wide bandgap triple halide perovskite absorber, such as $(Cs_{0.22}FA_{0.78})Pb(I_{0.85}Br_{0.15})_3$ + 3 mol % $MAPbCl_3$ have been intensively studied for tandem application as well as single junction solar cell application. DMF-based inks were prepared in a glovebox and spin casted on plasma cleaned glass substrates [1]. The wet films were annealed for 30 minutes at 100°C. The phase of the annealed, unannealed and heated perovskite samples were analyzed by XRD measurement. The chemical composition of the surface of the perovskite films was studied by angle-resolved XPS (ARXPS). ARXPS is a good technique to study the photochemical and thermal decomposition of perovskite solar cell. Samples were cleaned with an ion/cluster beam prior to XPS measurements. A low energy beam was used to avoid damaging the perovskite layer. The survey spectrum and elemental XPS spectra of freshly made glass/perovskite sample were taken using ARXPS.

Motivation

- This wide bandgap (E_g> 1.6) perovskite has the potential to surpass the Shockley-Queisser efficiency limit when it is used as top cell, working in tandem with Si. [2]
- To study the effect of heat and moisture on perovskite absorber layer
- To understand the degradation mechanism

Perovskite structure



Chemical formula = ABX_3

Figure 1: Perovskite crystal structure in (a) unit cell (b) 3D view [3]

Ink Preparation

To prepare as $(Cs_{0.22}FA_{0.78})Pb(I_{0.85}Br_{0.15})_3$ + 3 mol % $MAPbCl_3$ triple halide perovskite ink we took

- 0.22 M mass of CsI
- 0.78 M mass of FAI
- 0.225 M mass of $PbBr_2$
- 0.775 M mass of PbI_2

We dissolved these chemicals into DMF and DMSO (4:1 ratio), i.e. for 1ml solution we use 800 µl of DMF and 200 of DMSO and stirred at 450 rpm on a hot plate at 70° C until all chemicals are dissolved.

For 3 mol% $MAPbCl_3$ we took

- 1 M mass of MACl
- 1 M mass of PbI_2

In DMF and DMSO (1:3 ratio). Then we add 3% $MAPbCl_3$ of into the first solution. After that 1 µm filter was used to filter this solution.

Spin Coating

We used anti-solvent quenching method to initiate crystallization. The perovskite solution is spin-cast at 4000 rpm (ramp time 2s) for 60 s. Methyl acetate (185 μl) is dropped on the film at 25~30 s from the start of the spin. Post-annealing is done at 100 °C for 30mins.

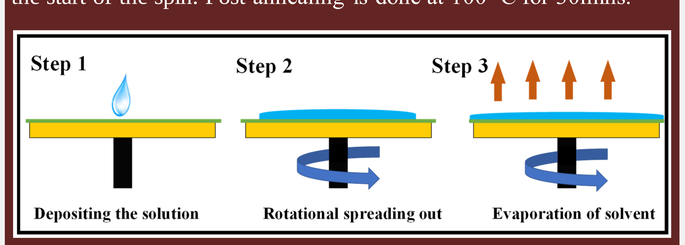


Figure 2: Different steps of spin-coating of a thin film on substrate [4]

Results & Discussion

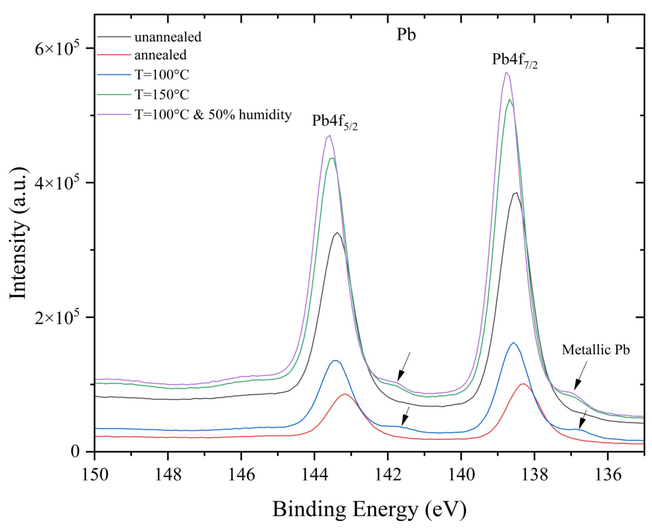


Figure 3: Angle resolved XPS spectra of Pb at 30º upon exposure to different degree of heat and moisture

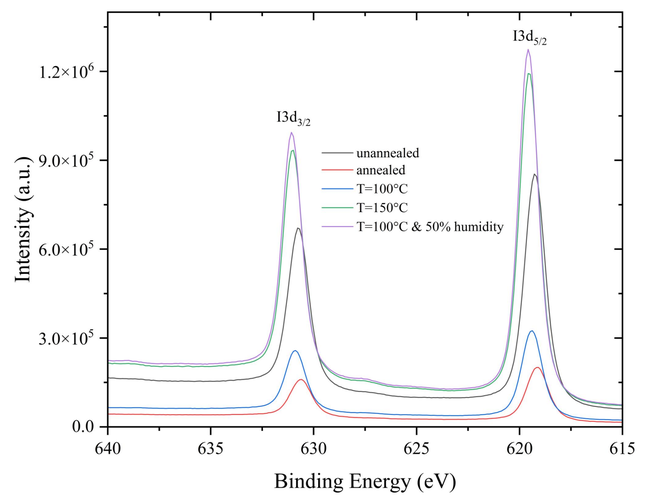


Figure 4: Angle resolved XPS spectra of I at 30º upon exposure to different degree of heat and moisture

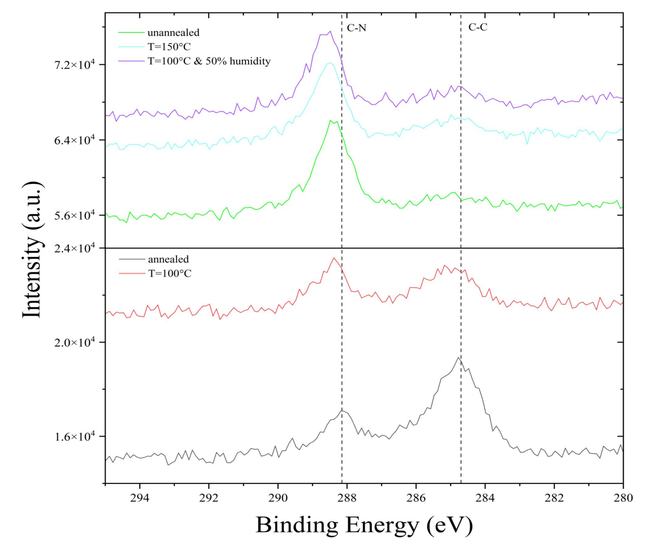


Figure 5: Angle resolved XPS spectra of C at 30º upon exposure to different degree of heat and moisture

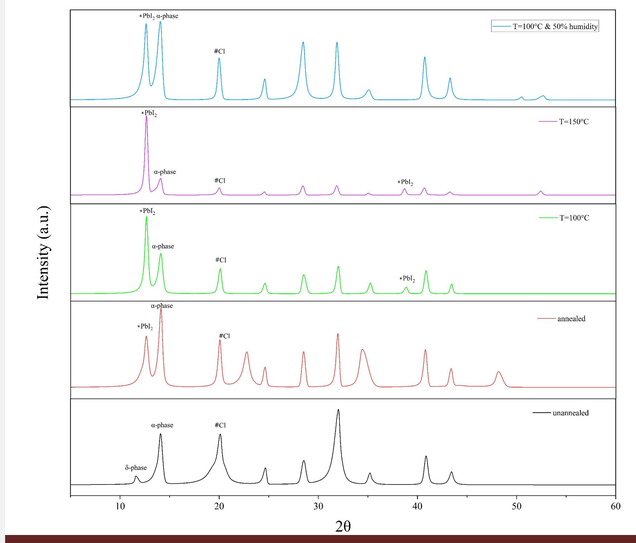


Figure 6: X-ray diffraction patterns of triple halide perovskite samples exposed at different temperature and humidity

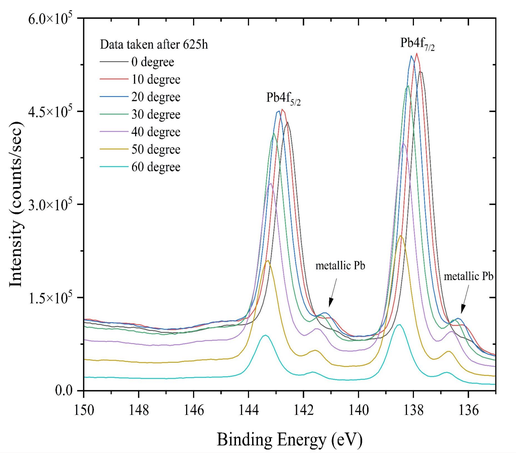


Figure 7: Angle resolved XPS spectra of Pb upon exposure to heat (sample was kept in glovebox about 625h after exposed to heat)

Key-notes

1. At higher temperature and with moisture triple halide perovskite starts to degrade
2. The XPS spectra of Pb suggests that the samples which are exposed to higher temperature and more moisture exhibit a small peak towards lower binding energy, indicating that metallic lead (Pb^0) was formed
3. The C-C peaks in the annealed samples (T=150°C) and the samples exposed to a humid environment decrease with respect to the unannealed sample
4. The Pb XPS spectra that were taken 625 hours later of sample preparation and sample treatment show larger Pb^o peaks. So degradation does not stop upon removing the heat and humidity stresses and storing the sample in a nitrogen filled glovebox
5. The XRD scans show that a lot of intermediate phase are created when the specimens is annealed at elevated temperature and exposed to a high humidity

References

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Acknowledgement

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