Towards Manufacture Stable Lead Perovskite APbI₃ (A = Cs, MA, FA) Based Solar Cells with Low-Cost Techniques †

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Abstract: Herein, we examine the impact of cations on the structural, morphological, optical properties and degradation of lead perovskite APbI₃ (where A = MA, FA, Cs). Its structure, surface morphology and optical properties have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Visible spectrometer. The structure of perovskite thin films was found to be in the direction of (110) plane. It is seen from the XRD results that this kind of cation assumes a significant part in stabilising and improving the performance of APbI₃ based solar cells. Here, the cesium lead iodide thin films show a smooth and homogenous surface and enormous grain size without pinhole perovskite film. An optical investigation uncovered that the band gap is in a range from 1.4 to 1.8 eV for the different cations. Additionally, in ~60% humidity under dark conditions for two weeks, the structural and optical properties of CsPbI₃ films remained good. Furthermore, the efficiency of FTO/TiO₂/CSPbI₃/Spiro-Ometad/Au solar cells was calculated to be 21.48%.

Keywords: thin films; hybrid perovskite; optical properties; phase stability; efficiency

1. Introduction

Perovskites solar cells have shown a huge improvement in efficiency in recent years; with an increase in power conversion efficiency (PCE) of 3.8% in 2009 to more than 25% in 2019 [1]. Furthermore, due to the flexibility of Perovskites as a result of their incorporation with different elements, there still exists a window for further increase in PCE in the future [2]. In ABX₃ perovskite, A is the cation where A = (MA, FA, or Cs), B is a small cation where B = (Pb or Sn . . . ) and X is the anion where X = (Cl, I or Br). Numerous techniques have been utilized for the manufacture of perovskite solar cells. Among them are the one-step spin coating technique [3] and the two-step spin coating technique, both techniques are easy to control and produce perovskite thin films [4]. Due to their optimal bandgap of about 1.47 eV for photovoltaic applications, Quantum Dot APbI₃ lead iodide materials are considered suitable perovskite materials. However, they do have a problem regarding their stability [5]. Here, we show that cation A affects the morphological and optical properties of APbI₃, and investigate the stability of CsPbI₃, FaPbI₃, and MaPbI₃. Findings show that CsPbI₃ shows a stable structure under a relative humidity of ~60%.

2. Thin Films Preparation

All compounds, lead iodide (PbI₂, 99%), formamidinium iodide (FAI), methylammonium iodide MAI, cesium iodide (CsI), lead iodide (PbI₂, 99%), DMF, DMSO as solvents, and chlorobenzene as anti-solvent was purchased from Sigma Aldrich, St. Louis, MO, USA.
The APbI₃ (a = Cs, Fa, Ma) perovskite thin films were elaborated on clean FTO glasses. The perovskite solutions were made from 1 M FAI, MAI, CsI, (1 M PbI₂) and were dissolved in DMF solution for two hours. The mixed solutions were kept on a hot plate at 60 °C for two hours in a glovebox, then 100 µL was spin-coated at 3000 rpm for 10 s and 1 mL chlorobenzene was dropped onto the wet APbI₃ films at 4000 rpm for 50 s. Consequently, the as-prepared APbI₃ were thermally annealed at 120 °C for 10 min.

Thin films FAPbI₃, MaPbI₃, CsPbI₃ structure were characterized by X-ray diffraction (XRD). Morphology images were taken by scanning electron microscope (SEM). Optical properties were performed using Ocean Optics HR4000 spectrophotometer and the performance was calculated by Scaps.

3. Results

The XRD analysis was examined for FAPbI₃, MaPbI₃, CsPbI₃ fresh and aged samples in Figure 1a–c, respectively. The aged FAPbI₃ shows degradation issues after two weeks and appears the non-perovskite δ-FAPbI₃ phase. This is verified by the augmentation of the peak characteristic of the δ phase, located at 12.6°. In the case of the sample CsPbI₃ aged, no additional peaks were shown, compared to the aged MAPbI₃, which demonstrated a dissociation of film into PbI₂.

Figure 2 displays SEM images of MaPbI₃, FaPbI₃ and CsPbI₃ fresh and aged that display the apparition of numerous pinholes and transformations in surface morphology compared to the Fresh MAPbI₃ and Fresh FAPbI₃, as we can note that for the CsPbI₃ surface,
less pinholes are seen after two weeks in humidity, which is in good agreement with the results of XRD that approve the stability of the CsPbI\textsubscript{3} sample.

**Figure 2.** SEM images of APbI\textsubscript{3} where A = (Ma/ Fa/Cs) (a) Fresh MaPbI\textsubscript{3} Film (b) Fresh FaPbI\textsubscript{3} Film (c) Fresh CsPbI\textsubscript{3} Film (d) Aged MaPbI\textsubscript{3} Film (e) Aged CsPbI\textsubscript{3} Film (f) Aged FaPbI\textsubscript{3} Film.

XRD results correlate with the UV-visible measurements, which show a good bandgap [6] (Figure 3). A slow decrease in the absorption of aged CsPbI\textsubscript{3} intensity demonstrates the slow degradation of CsPbI\textsubscript{3}. Hence, our results suggest that cesium can slow the degradation of the perovskite structure of APbI\textsubscript{3} films.

**Figure 3.** (a) Bandgap of APbI\textsubscript{3} where A = Cs, FA, MA, (b) the absorption of CsPbI\textsubscript{3} aged.

4. Performance of FTO/TiO\textsubscript{2}/APbI\textsubscript{3}/Spiro-Ometad/Au

The performance FTO/TiO\textsubscript{2}/APbI\textsubscript{3}/Spiro-Ometad/Au of solar cells where FTO is the back contact [7] through changes in the bandgap, SCAPS-1D software was used. The simulation parameters of APbI\textsubscript{3} were taken from our previous calculations, where the bandgap varied from 1.7 to 1.8 eV. Figure 4 shows the J-V characteristic curve; the P-V
curve shows that the maximum power is for FaPbI$_3$ and CsPbI$_3$. On the other hand, CsPbI$_3$ demonstrates the stable performance of solar cells (Table 1).

Figure 4. Performance of APbI$_3$ (A = Cs, Fa, Ma) based solar cells.

Table 1. Characteristics of APbI$_3$ (A = Cs, Fa, Ma) based solar cells.

| Solar Cell | Voc (V) | Jsc (mA/cm$^2$) | FF (%) | eta (%) |
|------------|---------|-----------------|--------|---------|
| MAPbI$_3$  | 0.8562  | 25.654019       | 86.09  | 18.91   |
| FAPbI$_3$  | 1.1413  | 22.401144       | 83.79  | 21.42   |
| CsPbI$_3$  | 1.0715  | 21.571401       | 88.63  | 21.48   |

5. Conclusions

In this work, APbI$_3$ perovskite thin films were determined using the spin-coating technique and the impact of cations on their stability and performance was investigated.

According to the results reported above, cesium may be the best option for the better performance of the cell, as it shows greater crystallinity and stability in humid conditions.

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