

On the Stability of $Cs_xFA_{(1-x)}PbI_3$ Layers Obtained by a Single Step Spin Coating Process

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Abstract— It was possible to improve the chemical stability of FAPbI₃ perovskite thin films (without altering other important characteristics such as the band gap or morphology) by introducing small amounts of Cesium atoms, when the films are deposited by a single step spin coating deposition process. It is shown that an optimum $x = 0.33$, for the prepared $Cs_xFA_{(1-x)}PbI_3$ thin films, provides a long degradation time (more than one month) as compared to pure FAPbI₃ in the alpha phase, which lasts for only one hour, under ambient conditions, before transforming to the degraded (non-desirable) delta phase. The bandgap variation for $Cs_xFA_{(1-x)}PbI_3$ as a function of x was also evaluated, and it was confirmed that this compound behaves approximately according to Vegard's law.

Keywords— $Cs_xFA_{(1-x)}PbI_3$, bandgap, perovskites, spin-coating.

I. INTRODUCTION

Rapid improvements in power conversion efficiency (PCE) from 3.8% to 25.8% in just over a decade have propelled solution-processed lead halide hybrid perovskites as a promising material for light conversion in photovoltaic devices [1,2].

The term "perovskite" is attributed to the crystal structure of the mineral calcium titanate (CaTiO₃), discovered by the mineralogist Gustav Rose in 1839, and the name is in honor of the Russian mineralogist Count Lev A. Perovskiy [3]. The term perovskite is used to refer to various compounds that conform to the general formula ABX₃, where A and B are cations and X is an anion.

Perovskites based on metal-organic hybrid halides are the subject of analysis, due to their application in solar cells [4]. This class of perovskites generally contains:

A: a monovalent organic cation, which can be methylammonium (MA⁺ = CH₃NH₃⁺), formamidinium (FA⁺ = NH₂CHNH₂⁺). Recent investigations employ a monovalent inorganic cation such as cesium (Cs⁺).

B: a divalent metal cation, such as Pb²⁺, Sn²⁺, or Ge²⁺.

X: a monovalent anion of the halide family: Cl⁻, Br⁻, or I⁻.

Perovskite materials such as Methylammonium Lead Triiodide (MAPbI₃), which has a bandgap of approximately 1.57 eV [5], have allowed high-efficiency solar cell manufacturing in recent years, but they have the problem of

very high thermal and chemical instability. Then, further work has to be done for obtaining more stable materials. One of these materials is Lead Formamidinium Triiodide (FAPbI₃) [6], which has the advantage of being a little more stable, with a better bandgap ~ 1.43 eV in the cubic (alpha) phase and with good morphological characteristics.

Unfortunately, due to the size of the formamidinium FA molecule (NH₂CH=NH₂⁺), the material is not sufficiently stable and tends to degrade by presenting a non-perovskite hexagonal (delta) phase [7], in approximately one hour, when exposed to the environment. This undesirable phase has a bandgap of approximately 2.43 eV, which is not appropriate to be a good solar spectrum absorber [8].

One possible element to be used as a cation in perovskites is cesium (Cs), which is an atom of a smaller dimension than the FA molecule, and so it is expected that their mixture will help stabilize the material. In several experiments, CsPbI₃ layers have been reported with a bandgap of approximately 1.73 eV [9]. Then, the $Cs_xFA_{(1-x)}PbI_3$ perovskite layer (alpha phase) is expected to have a bandgap in the range from 1.43 eV to 1.73 eV, as x changes from 0 to 1.

In the present work, it was decided to combine formamidinium (FA) with cesium atoms in the perovskite compound, obtaining $Cs_xFA_{(1-x)}PbI_3$, through a single-step spin coating process [10], looking for the perovskite material chemical stability improvement. It will be shown that there is an optimum value for x in the compound which assures high chemical stability during long periods (more than one month) under ambient conditions.

II. EXPERIMENTAL DETAILS

A set of experiments was designed using the ratio between the CsI molar concentration to the FAI molar concentration as the control variable $V_c = CsI/FAI$, and this will be related to the degradation time and bandgap of the samples. Table I shows the control variable values (4 levels) in conjunction with the precursor molarities to be used for each experiment.

Using *Design Expert* (commercial software) for the experimental design (single factor with 4 levels), we established that the required number of repetitions needed for each V_c level should be 3 so that it is possible to statistically discriminate the response variables, which in this case were the bandgap and degradation time. Hence, a total of 12 experiments were realized.

TABLE I. MOLARITIES USED FOR EACH LEVEL OF THE CONTROL VARIABLE Vc

Control variable Vc = Cs/FAI	Molarity		
	FAI	CsI	PbI ₂
0	0.8	0	0.8
0.5	0.53	0.27	0.8
1	0.4	0.4	0.8
2	0.27	0.53	0.8

Film Deposition

A corning glass (SiO₂) substrate was cleaned by ultrasonic bath with neutral detergent, deionized (DI) water, and isopropyl alcohol for 15 min. Subsequently, the substrate was transferred to a glove box with N₂ atmosphere with a relative humidity < 20 %.

The precursor solution was prepared (at 65 °C) by dissolving the appropriate amounts of CsI, FAI and PbI₂ in 1 ml of dimethylformamide (DMF)+anhydrous dimethyl sulfoxide (DMSO) solvent in a ratio of 40 %:60 %, respectively.

The perovskite film was deposited on the corning glass substrate by a one-step spin coating process at 2000 rpm for 20 seconds using the above precursor solution, inside a glove box filled with N₂. The substrate was then stored inside the box for 30 min before a heat treatment at 350 °C for 5 sec.

The obtained films were then characterized morphologically, using a JEOL microscope model JSM-6360LV, and optically by diffuse reflectance measurements using a Jasco UV-Vis spectrophotometer model V-670.

III. RESULTS

A. Morphology

Fig. 1 shows the SEM images for the different samples for each Vc level. It can be inferred from the micrographs that the incorporation of Cs reduces cluster (grain) size and pinhole concentration, while inducing a more uniform morphology. Observe that the increase in the ratio of Cs to FA causes the increase of the cluster density in the film.

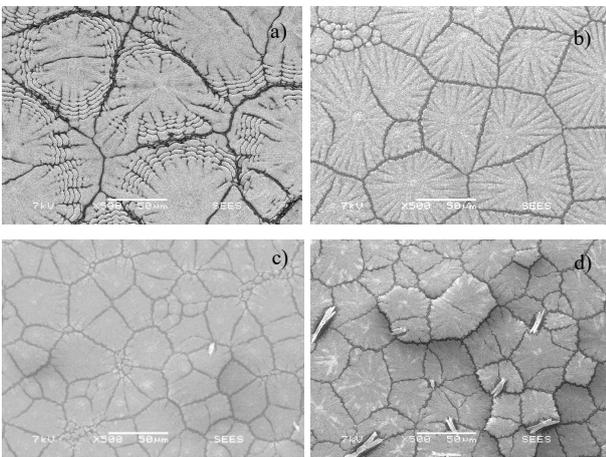


Fig. 1 SEM images of top view of perovskite films a) Vc = 0, b) Vc = 0.5, c) Vc = 1 and d) Vc = 2.

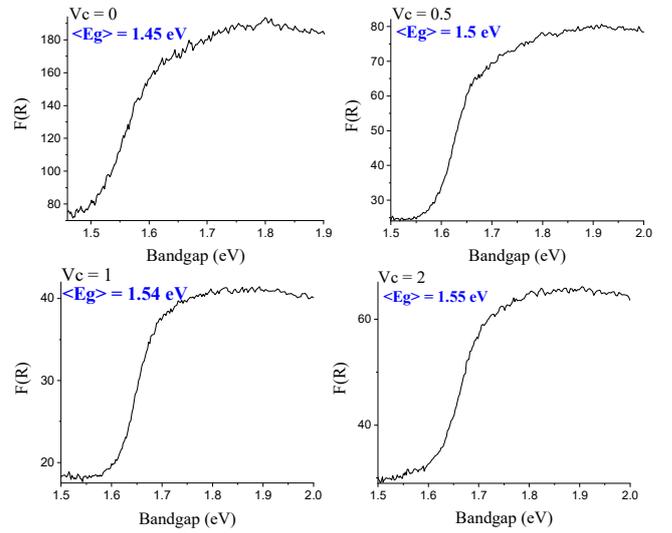


Fig. 2 a) Vc = 0, b) Vc = 0.5, c) Vc = 1 and d) Vc = 2.

B. UV-Visible Optical Spectroscopy

The generated reflectance versus wavelength data were used to estimate the material bandgap by converting the diffuse reflectance data to the Kubelka-Munk function $F(R) = (1 - R)^2/2R$, where R is the reflectance. Then, using Tauc-like plots, the bandgap was determined by fitting the linear region assuming a direct bandgap. In fig. 2, these plots are shown for only one sample at each Vc level. The average bandgap $\langle E_g \rangle$ is also shown. As expected, the bandgap is increased when the Cs concentration is increased. This fact will be quantified below.

C. Film degradation

The degradation time for the films obtained was evaluated. The degradation time was determined by observing how long the dark alpha phase was present in the samples when they are stored (in Petri boxes) under ambient conditions. We considered that the Cs_xFA_(1-x)PbI₃ films were degraded when their dark color (characteristic of the alpha phase) changed to yellow, which is characteristic of the delta phase. This color can also be attributed in part to the presence of PbI₂ in the sample.

Table II shows the final evaluation regarding the approximate degradation time for the different films obtained. We can notice that for the control variable Vc = 0.5 the samples remain more stable (more than one month) in the dark alpha phase, compared to the other Vc values. For Vc = 0, i.e. without Cs, the stability is very short, as has been observed previously for FAPbI₃.

D. Vegard's law conformance

Using the measured average bandgaps shown in table III, the Cs_xFA_(1-x)PbI₃ bandgap energy E_g as a function of x, according to Vegard's law, should be:

$$E_g = 1.45 + 0.23x \quad (1)$$

TABLE II. RESULTS ON DEGRADATION

Vc	Precursors Molarity (M)	Approximate degradation time	Eg (eV)
0	0.8/0/0.8	1 hour	1.47
0	0.8/0/0.8	1 hour	1.45
0	0.8/0/0.8	1 hour	1.44
0.5	0.53/0.27/0.8	For more than a month	1.49
0.5	0.53/0.27/0.8	For more than a month	1.51
0.5	0.53/0.27/0.8	For more than a month	1.51
1	0.4/0.4/0.8	1 week	1.54
1	0.4/0.4/0.8	1 week	1.54
1	0.4/0.4/0.8	1 week	1.54
2	0.27/0.53/0.8	1 week	1.56
2	0.27/0.53/0.8	1 week	1.54
2	0.27/0.53/0.8	1 week	1.56

TABLE III. BANDGAP AS A FUNCTION OF Vc

Vc	Bandgap [eV]
0	1.45 ± 0.02
0.5	1.5 ± 0.02
1	1.54 ± 0.02
2	1.55 ± 0.02

Fig. 3 shows a second order polynomial fit to the plotted average bandgap as a function of x. The fitting equation is:

$$E_g = (1.45 \pm 0.007) + (0.20 \pm 0.04)x - (0.07 \pm 0.07)x^2 \quad (2)$$

Then, the E_g dependence on x deviates only slightly from Vegard's law. A small bowing factor of 0.07 eV is obtained, so that we can say that the prepared $\text{Cs}_x\text{FA}_{(1-x)}\text{PbI}_3$ films behave approximately according to Vegard's law.

IV. CONCLUSIONS

A systematic study of $\text{Cs}_x\text{FA}_{(1-x)}\text{PbI}_3$ thin films obtained by a single step spin-on process was made when the composition x is changed to observe the stability time and bandgap, which are important properties of this material when used in solar cells. In particular, for the optimum $x = 0.33$ the layers achieved the largest degradation times (more than one month) at ambient conditions. This can be compared to the duration of only 1 hour for the FAPbI_3 and CsPbI_3 layers when they are prepared separately. In addition, for $x = 0.33$ a bandgap of about 1.5 eV was determined which makes it suitable for solar cell applications. The sizes of the polycrystalline perovskite clusters are relatively large (50 μm), which are also suitable for solar cell applications. Finally, it was confirmed that the obtained $\text{Cs}_x\text{FA}_{(1-x)}\text{PbI}_3$ films behave according to Vegard's Law, for x in the range between 0 and 0.66.

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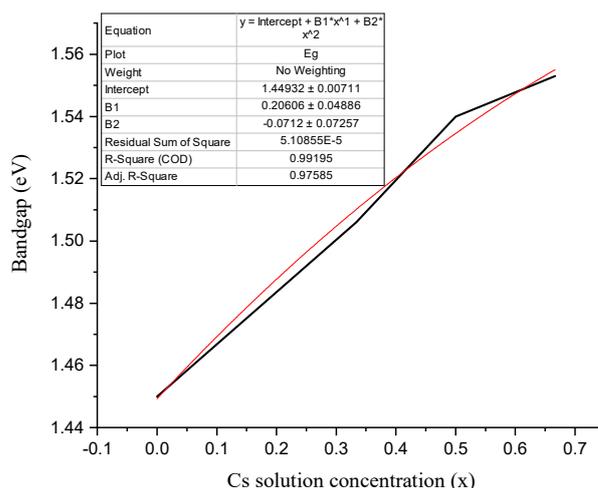


Fig. 3 Values for bandgap about the percentage of atomic cesium.

REFERENCES

- [1] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells", *Journal of the American Chemical Society*, vol. 131, no. 17, pp. 6050–6051 (2009).
- [2] H. Min et al., "Perovskite solar cells with atomically coherent interlayers on SnO_2 electrodes", *Nature*, vol. 598, no. 7881, pp. 444–450 (2021).
- [3] A. R. Chakhmouradian and P. M. Woodward, "Celebrating 175 years of perovskite research: a tribute to Roger H. Mitchell", *Physics and Chemistry of Minerals*, vol. 41, no. 6, pp. 387–391 (2014).
- [4] N. Elumalai, M. Mahmud, D. Wang, and A. Uddin, "Perovskite Solar Cells: Progress and Advancements", *Energies*, vol. 9, no. 11, pp. 861–881 (2016).
- [5] G. E. Eperon, S. D. Stranks, C. Menelaou, M. B. Johnston, L. M. Herz, and H. J. Snaith, "Formamidinium lead trihalide: A broadly tunable perovskite for efficient planar heterojunction solar cells", *Energy & Environmental Science*, vol. 7, no. 3, pp. 982–988, 2014.
- [6] S. Pang et al., " $\text{NH}_2\text{CH}=\text{NH}_2\text{PbI}_3$: An alternative organolead iodide perovskite sensitizer for mesoscopic solar cells", *Chemistry of Materials*, vol. 26, no. 3, pp. 1485–1491 (2014).
- [7] M. P. U. Haris, S. Kazim, and S. Ahmad, "Low-Temperature-Processed Perovskite Solar Cells Fabricated from Presynthesized CsFAPbI_3 Powder", *ACS Applied Energy Materials*, vol. 4, no. 3, pp. 2600–2606, (2021).
- [8] F. Ma, J. Li, W. Li, N. Lin, L. Wang, and J. Qiao, "Stable α/δ phase junction of formamidinium lead iodide perovskites for enhanced near-infrared emission", *Chemical Science*, vol. 8, no. 1, pp. 800–805 (2017).
- [9] T. Ye et al., "Synthesis of Highly-Oriented Black CsPbI_3 Microstructures for High-Performance Solar Cells", *Chemistry of Materials*, vol. 32, no. 7, pp. 3235–3244 (2020).
- [10] P. U. Haris, S. Kazim, and S. Ahmad, "Low-Temperature-Processed Perovskite Solar Cells Fabricated from Presynthesized CsFAPbI_3 Powder", *ACS Applied Energy Materials*, vol. 4, no. 3, pp. 2600–2606 (2021).
- [11] L. Vegard, "Die Konstitution der Mischkristalle und die Raumfüllung der Atome", *Zeitschrift für Physik*, vol. 5, no. 1, pp. 17–26 (1921).