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AMMONIUM-BASED ADDITIVES FOR IMPROVING PEROVSKITE THIN FILM STABILITY

Palavras-Chave: PEROVSKITE, ADDITIVE, STABILITY, AMMONIUM SALTS.

Autores(as):

RAFAELLA MARCOPITO CIANCI, FEQ – UNICAMP

Prof(ª). Dr(ª). ANA FLAVIA NOGUEIRA (orientador(a)), IQ - UNICAMP

INTRODUCTION

The growing impacts of climate change have raised concerns about the current energy matrix, highlighting the need to reduce the global reliance on fossil fuels.[1] Exploring alternative energy sources is essential to ensure a more sustainable and efficient energy future. Among the available options, solar energy stands out due to its high conversion efficiency and widespread availability.[2] This energy source is already well established in the global market, with silicon-based solar panels as the leading technology.[3,4] However, their production involves high costs, significant energy consumption, and the use of high-purity raw materials.[5]

In this context, perovskites have emerged as a class of photoactive materials with promising optoelectronic properties, making them highly attractive for photovoltaic applications. Since their first report in 2009,[6] perovskite solar cells (PSCs) have demonstrated remarkable power conversion efficiencies (PCE), with values increasing from 3.8% to an outstanding 26.1%.[7] This rapid improvement has positioned PSCs as strong competitors to monocrystalline silicon panels, which reached a PCE of 27.6% in 2024.[7]

Beyond high PCE rates, PSCs stand out from a manufacturing standpoint, since they can be fabricated through solution-based methods, which provide cost effectiveness and simplicity.[8,9] In these methods, the photoactive layer is prepared by a precursor solution deposited onto a substrate using various techniques.

Despite these merits, PSCs suffer from limited operational lifespan and poor stability due to an accelerated degradation process triggered by environmental stressors – such as oxygen, moisture, UV radiation, and high temperatures.[10,11] These factors affect the perovskite crystalline structure, inducing phase transition – conversion from the photoactive black phase to the non-photoactive yellow phase[12,13] – and compromising overall device's performance.

Moreover, these environmental stressors affect perovskite materials starting from fabrication. To mitigate these effects, PSCs are traditionally fabricated in controlled environments called gloveboxes, filled by nitrogen gas and reduced pressure, where perovskite can crystallize in an ambience of controlled oxygen and moisture levels. However, reliance on this equipment significantly increases production costs and complexity.

Given the inevitability of exposure to environmental stressors in real-world applications and the necessity to surpass the dependency on gloveboxes – which significantly increase production- is essential. Understanding the crystallization process under real-world conditions is crucial to overcoming or minimizing the adverse effects that compromise PSC operation.[14] One of the most common approaches is additive engineering, a technique that exploits the nature of the precursor solution by deliberately introducing compounds that interact with perovskite precursors.[15,16] These additives modulate crystallization kinetics, thereby improving the quality and performance of perovskite devices.

This research investigated the role of additives in improving perovskite crystallization and enhancing the stability of perovskite layers fabricated under ambient-air conditions. The effects of different additives on optical, structural, and morphological properties of the films were analyzed.

METHODOLOGY

The glass substrates were prepared to receive the perovskite layer by sequential cleaning through sonication in Hellmanex™ solution for 25 minutes, deionized water for 20 minutes, ketone for 10 minutes, and isopropanol for 10 minutes. The cleaned substrates were then treated with UV-ozone for 40 minutes.

Following the two-step perovskite method,[17–19] two precursor solutions were prepared. The lead salt solution was prepared by dissolving 1036.5 mg of PbI_2 in 1.5 mL of DMF:DMSO (9:1 v/v). The organic salt solution consisted of 260 mg of FAI and 36 mg of MACl dissolved in 4 mL of isopropanol (IPA).

The additive tested was an ammonium salt. Specifically, 36 mg of 2,4-dimethoxybenzylammonium iodide (2,4-MBA) were added, matching the mass of MACl used in the control solution.

The deposition was carried out using a two-step spin coating method. First, the lead iodide layer was formed by dripping 50 µL (static method) of the solution onto the substrate, which was then rotated at 2000 rpm for 36 s. The films were then annealed at 70 °C for 1 minute. The second layer was deposited by dynamically dropping 150 µL of the organic salt solution onto the spinning substrate at 1800 rpm for 36 s, followed by annealing at 150 °C for 20 minutes. After deposition, the films were stored in a sealed container with silica gel inside a nitrogen-filled box to minimize exposure to ambient humidity prior to characterization.

All film fabrication steps were conducted under typical ambient-air conditions.

RESULTS AND DISCUSSION

The prepared films (Figure 1a) were characterized by their optical and morphological properties by X-Ray Diffraction (XRD), Steady State Photoluminescence (PL) and Time Resolved Photoluminescence (TRPL).

The XRD technique was employed to evaluate the crystalline structure of the perovskite films,[20] enabling the investigation of the perovskite phase and the presence of secondary phases, such as residual PbI_2. The first observation from the XRD patterns was their overall similarity (Figure 1b), as the main diffractions were preserved with the incorporation of the additive, particularly the perovskite peak, confirming that it formed even in presence of 2,4-MBA.

The characteristic PbI_2 peak, originally located at approximately 12,6º,[21] was slightly shifted to 12,8º (Figure 1c). In comparison, the control film presented a much more intense PbI_2 peak than the modified films. The additives performed similarly in suppressing residual PbI_2. This reduction effect is important for the structural stability of the perovskite, since PbI_2 has been reported to reduce carrier lifetimes, by introducing a major density of defects where non-radiative recombination sites are more likely to occur. Moreover, PbI_2 is a hygroscopic compound, which can accelerate degradation, as moisture is one of the most critical environmental stressors for perovskite stability.

Diffraction corresponding to the (100) plane of the cubic α-$FAPbI_3$ phase was consistently detected at 14° across all samples,[22] confirming the formation of the perovskite phase (Figure 1c). The slight shift in peak positions relative to reference values is attributed to instrumental conditions. Compared to the control, the modified films exhibited more intense peaks, indicating enhanced crystallinity. These results suggest that the additive contributed positively to the perovskite system.

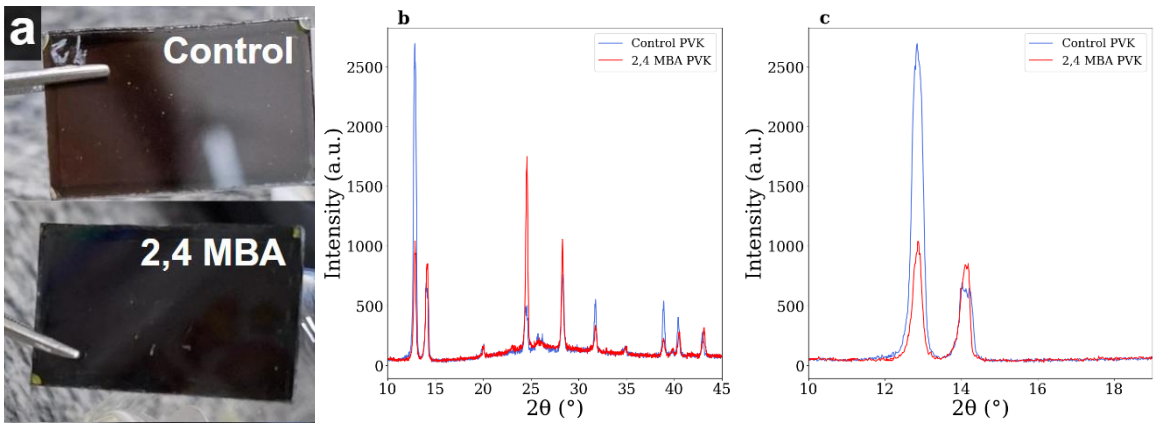

Figure 1. *(a) Films prepared via two-step deposition method, with and without the incorporation of 2,4 MBA. (b) XRD patterns of the prepared perovskite films. (c) Magnified view of the PbI_2 peak region (~12.8°) and the (100) diffraction peak of the α-$FAPbI_3$ phase (~14º).*

Then, TRPL (Figure 2a) was utilized to determine the mean lifetime of charge carriers. Experimental data obtained was adjusted to an exponential decay, typically as $\boldsymbol{f(t) = A_1 e^{(-\lambda_1 t)} + A_2 e^{(-\lambda_2 t)}}$.[23] To extract control carrier lifetime, it was not possible to extract the second decay parameter, suggesting that the control film decay was better described by a single-exponential function. In contrast, the modified film exhibited biexponential behavior, as expected. Based on the fitted curves, it was possible to compare the films by the mean lifetime (Table 1), revealing a 3.07% improvement for the modified film compared to the control.

PL measurements (Figure 2b) were used to investigate the optical properties of the perovskite films,[24] assessing the material quality and the presence of non-radiative recombination pathways within the films. The modified film exhibited a narrower emission peak, and a smaller low-intensity tail compared to the control, which suggests that the 2,4-MBA improved perovskite optoelectronic and structural quality.

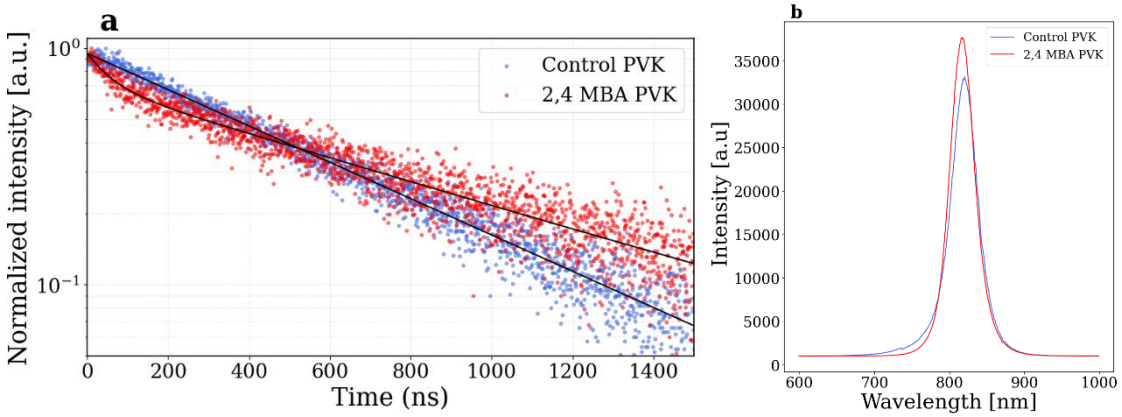

Figure 2. *(a) Time-resolved photoluminescence (TRPL) decay curves for the prepared films. (b) Steady-state photoluminescence (PL) spectra of the samples.*

Sample	Fitted curve	Lifetime (ns)	Improvement (%)
Control	Monoexponential	τ = 552,12	-
2,4 MBA PVK	Biexponential	τ_{avg} = 569,07	3,07%

Table 1. *Fitting results and corresponding improvement in carrier lifetime for all samples.*

CONCLUSIONS

This study demonstrated the effectiveness of additive engineering as a strategy to enhance the stability of perovskite films even under ambient-air conditions. The incorporation of 2,4 MBA improved key film properties such as crystallinity and charge carrier lifetimes, while reducing residual PbI_2. XRD patterns confirmed the formation of the photoactive perovskite phase in the modified films, and optical analyses indicated a decrease in non-radiative recombination. These results highlight the ability of additive engineering to improve film quality and stability under environmental stress, reinforcing its potential for advancing scalable fabrication of perovskite solar cells.

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