

Study of the Long-Term Ambient Stability of Perovskite Alloys $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$: Identification of the Optimal Halide Ratio

Peyena Yacouba Dao¹, Julia Marí-Guaita¹, Fofana Alhassane², Donafologo Soro^{3*}, Bernabé Marí Soucase¹

¹Departament de Física Aplicada-IDF, Universitat Politècnica de València, València, Spain

²Unité de Formation et de Recherche en Sciences des Structures de la Matière et de Technologie, Université Félix houphouët Boigny, Abidjan, Côte d'Ivoire

³Département des Sciences et Technologie, Ecole Normale Supérieure (ENS) d'Abidjan, Abidjan, Côte d'Ivoire
Email: *donafologosoro@yahoo.fr

How to cite this paper: Dao, P.Y., Marí-Guaita, J., Alhassane, F., Soro, D. and Soucase, B.M. (2026) Study of the Long-Term Ambient Stability of Perovskite Alloys $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$: Identification of the Optimal Halide Ratio. *Modeling and Numerical Simulation of Material Science*, **16**, 81-93.
<https://doi.org/10.4236/mnsms.2026.164005>

Received: July 5, 2026

Accepted: October 20, 2026

Published: October 23, 2026

Copyright © 2026 by author(s) and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).
<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

Hybrid halogenated perovskites $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ are attracting increasing interest due to their remarkable optoelectronic performance, particularly in solar cells. However, their instability under ambient conditions remains a major obstacle to their commercialization. This work presents a systematic study of the structural, morphological, and optical properties of perovskite thin films $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ ($x = 0$ to 0.15) as well as their stability under ambient conditions. The main objective is to identify the optimal I/Br ratio that maximizes structural and optical stability without compromising electronic properties. The films were prepared by centrifugation with toluene as an antisolvent, followed by controlled thermal annealing. Degradation was monitored over several weeks using characterization techniques such as X-ray diffraction (XRD), UV-Visible spectroscopy, and photoluminescence. X-ray diffraction (XRD) and UV-Visible spectroscopy analyses confirm the efficient incorporation of bromine, resulting in lattice contraction and a controlled band gap widening from 1.60 eV to 1.68 eV. The degradation evolution over 28 days shows that while the MAPbI_3 pure form amorphizes in less than a week, the addition of bromine significantly delays this process. The sample with 10% Br is identified as the optimum, exhibiting exceptional electronic resilience with a fourfold increase in photoluminescence intensity during aging.

Keywords

Hybrid Perovskite, Halide Engineering, Band Gap Tuning, Environmental Stability, Photoluminescence

1. Introduction

Methylammonium lead iodide MAPbI₃ have revolutionized the field of photovoltaics with efficiencies now exceeding 25% [1]. However, their extreme sensitivity to humidity and oxygen remains the main obstacle to their commercialization [2]. Under ambient conditions, they MAPbI₃ undergo rapid decomposition, often attributed to the infiltration of water molecules into the crystal lattice, causing the breaking of hydrogen bonds between the organic cations and the inorganic cage [3] [4].

To overcome this instability, halide engineering, particularly the partial substitution of iodine (I⁻) by bromine (Br⁻), has become a standard strategy [5]. Bromine, with its smaller ionic radius, induces a contraction of the crystal lattice, which strengthens the cohesive energy of the network and limits the diffusion of reactive species [6]. Furthermore, the ease of tuning the band gap by varying the ratio of bromide, iodide, and chloride halides in, for example, perovskites MAPb(I_{1-x}Br_x)₃ [7], makes these materials attractive for tandem solar cells [8] or LEDs across the entire visible spectrum [9] [10].

Despite a wealth of literature, determining an optimal bromine ratio that guarantees both high crystal quality and maximum durability in humid environments remains an active area of research. Recent studies suggest that while a high bromine content improves structure, it can also induce phase segregation under illumination [11]-[13]. This study focuses on a range of 0% to 15% Br to identify the optimal stability threshold. We correlate structural, optical, and morphological evolution over a 28-day period to demonstrate the superiority of the 10% Br composition.

2. Experimental Section

2.1. Materials and Reagents

Lead iodide (PbI₂, purity ≥ 99.99%), lead bromide (PbBr₂, ≥98%), methylammonium iodide (MAI), and methylammonium bromide (MABr) were used as precursors without further purification. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solvents were used to prepare the solutions, while toluene was used as an anti-solvent during deposition.

2.2. Preparation of Precursor Solutions

The precursor solutions MAPb(I_{1-x}Br_x)₃ ($x = 0, 0.05, 0.1, 0.15$) were prepared by precisely adjusting the molar proportions of PbI₂ and PbBr₂ to obtain the desired halogenated composition, while maintaining an overall 1:1 stoichiometric ratio between total lead and the MA⁺ cation. The total concentration was set at 1.3 M. The salts were dissolved in a DMF/DMSO mixture (4:1, V:V) under magnetic stirring at 65 °C at 600 rpm for 1 h to obtain homogeneous and transparent solutions. The solutions were then filtered using PTFE filters (0.45 μm) before deposition.

2.3. Thin Film Deposition

Fluorine-doped tin oxide (FTO) coated glass substrates were selected and succes-

sively cleaned by ultrasound in distilled water, acetone, and isopropanol, then dried under a nitrogen stream. Film deposition was performed by spin coating. The deposition was performed by applying **100 μL** of precursor solution to the substrate. This was followed by a first rotation at 1000 rpm for 6 seconds, then a second rotation at 4000 rpm for 30 seconds. During the rotation, precisely **20 seconds after the start of the second rotation, 200 μL of toluene** was deposited in the center of the forming film to induce rapid crystallization. The samples were then thermally annealed at 110°C for 30 minutes to promote complete formation of the crystalline phase.

The exact conditions were not recorded by a continuous sensor, but the samples were stored in the dark in a closed cabinet within a temperature-controlled laboratory at the Polytechnic University of Valencia (Spain) in May 2025. During this period, the standard internal temperature was maintained at $22^\circ\text{C} \pm 2^\circ\text{C}$ and the estimated ambient relative humidity within the cabinet was between 45% and 55% RH.

2.4. Characterization Techniques

The crystalline structure of the thin films was studied by X-ray diffraction (XRD) using the RIGAKU-Ultima IV diffractometer, with a Cu K α source ($\lambda = 1.5406 \text{ \AA}$). Angular scans were performed between 10° and 60° . The optical properties were studied by UV-Visible spectroscopy using the Ocean spectrometer. Optics HR4000 was used in the visible and near-ultraviolet spectral range to analyze the absorption behavior of the films and estimate the optical band gap width as a function of halogen composition. Photoluminescence measurements were performed at room temperature to analyze radiative recombination processes. Surface morphology and grain size were examined by scanning electron microscopy (SEM).

3. Results and Discussion

3.1. Structural Analysis by X-Ray Diffraction (XRD)

The XRD diffractograms obtained for the thin films $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ show intense and well-resolved peaks, attributed to the crystallographic planes typical of the perovskite structure [14]. These results confirm the formation of the perovskite crystalline phase for all the compositions studied.

Furthermore, no secondary peaks related to the presence of parasitic phases, such as PbI_2 or PbBr_2 , were detected on the diffractograms (**Figure 1**). This suggests efficient conversion of precursors and good crystallization quality of the deposited films [14] [15].

The progressive increase in bromide content is accompanied by a systematic shift of the diffraction peaks towards higher Bragg angles (2θ) (**Figure 2**). This shift is attributed to the decrease in the crystal lattice parameter resulting from the substitution of iodide ions (I^-) by bromide ions (Br^-), which have a smaller ionic radius. This behavior is consistent with Vegard's law and has been widely reported in the literature for mixed I/Br hybrid perovskites [14].

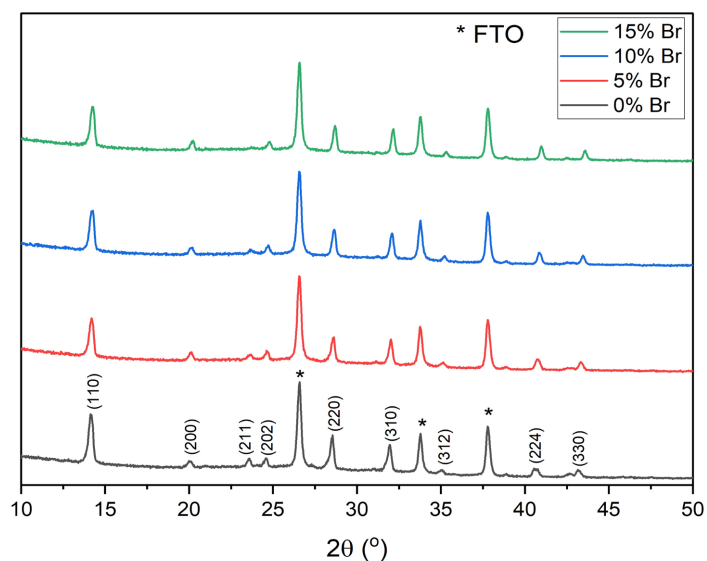


Figure 1. XRD patterns obtained for different mixed halide perovskite films.

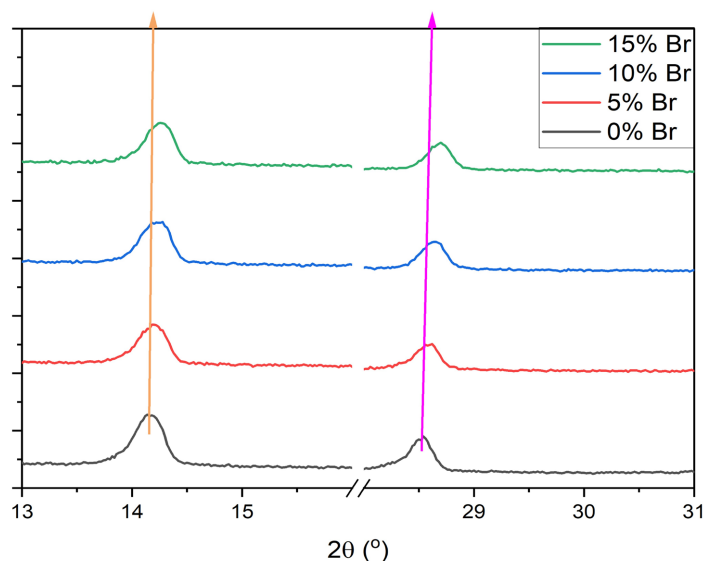


Figure 2. Diffractograms at $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ approximately 14° and 28° .

Furthermore, a decrease in the full width at half maximum (FWHM) of the diffraction peaks is observed overall, which suggests an improvement in the crystallinity of the films as well as an increase in the average size of the crystallites [16].

However, for compositions containing 5% and 10% bromide, a slight increase in full width at half maximum (FWHM) is observed at positions $2\theta = 28.618^\circ$ and 14.25° , respectively (Table 1). This change can be attributed to the appearance of local crystal stresses or to a degree of structural disorder induced by the partial substitution of iodide ions by bromide ions within the perovskite lattice.

The crystallite sizes, estimated using the Scherrer method, nevertheless confirm the positive effect of moderate bromide incorporation on the crystalline quality of the films $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$.

Table 1. Scherrer table of MAPb(I_{1-x}Br_x)₃.

Br (%)	Plan	2 θ (°)	FWHM (°)	Size D (nm)
0%	(110)	14.183	0.311	25.544
	(220)	28.484	0.200	39.722
	(310)	31.968	0.249	31.905
5%	(110)	14.215	0.308	25.793
	(220)	28.618	0.248	32.034
	(310)	32.015	0.242	32.828
10%	(110)	14.250	0.311	25.544
	(220)	28.642	0.247	32.163
	(310)	32.074	0.232	34.243
15%	(110)	14.273	0.294	27.021
	(220)	28.686	0.239	33.240
	(310)	32.137	0.220	36.111

The size of the crystallites D is obtained using Scherrer's formula:

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos(\theta)}$$

where:

D = crystallite size (nm)

K = form factor equal to 0.9

λ = wavelength of X-ray radiation (1.5406 Å for Cu K α)

β = FWHM in radians

θ = Bragg angle (°) converted to radians ($\theta = \frac{1}{2} \times 2\theta$)

3.2. Optical Properties: UV-Visible Absorbance

UV-Visible absorbance spectra show a high absorption coefficient in the visible region of the electromagnetic spectrum, characteristic of organometallic hybrid perovskites and favorable to photovoltaic applications [14]. A progressive shift of the absorption edge towards shorter wavelengths is also observed with increasing bromide content (Figure 3), reflecting a broadening of the optical band gap of the thin films MAPb(I_{1-x}Br_x)₃ [14].

3.3. Photoluminescence (PL) Properties

The photoluminescence (PL) spectra recorded at room temperature show intense and relatively narrow emission peaks for all the compositions studied. A progressive shift of the emission maximum towards shorter wavelengths is observed with increasing bromide content (Figure 4), consistent with the widening of the optical band gap highlighted by UV-Visible absorbance measurements.

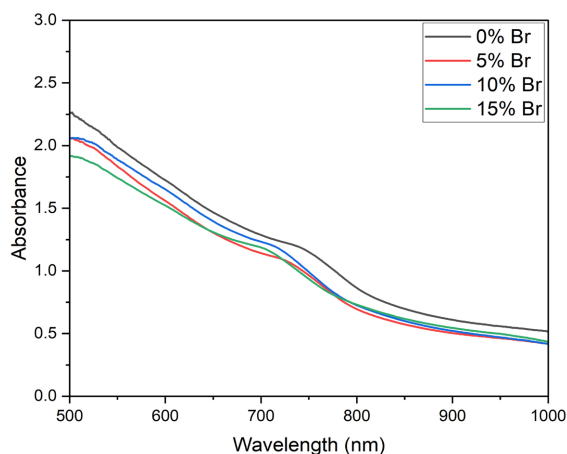


Figure 3. Absorbance spectra of thin films $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$.

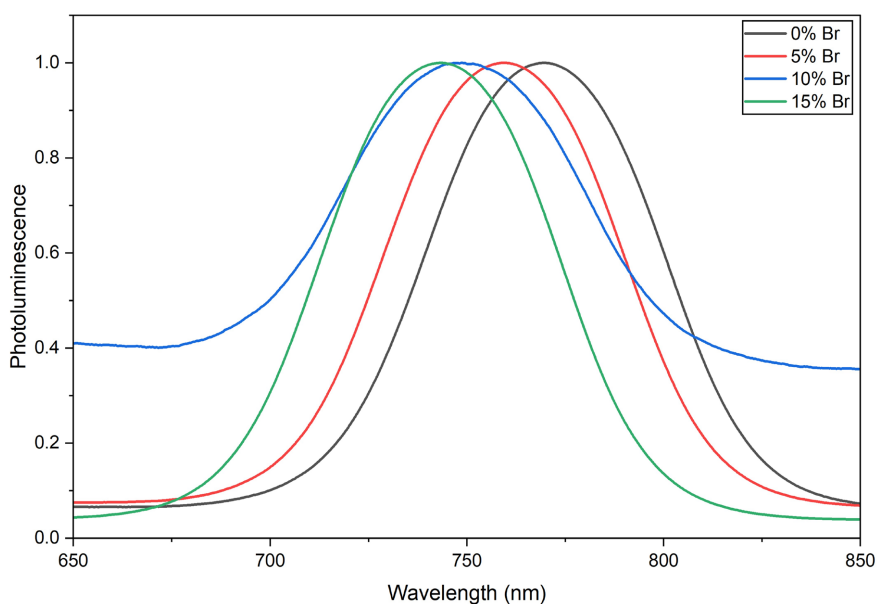


Figure 4. Normalized photoluminescence for perovskite films $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$.

The gap energy increases almost linearly with the bromide fraction x (**Figure 5**), in agreement with the results previously reported for $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ [14]. This evolution reflects the changes in the electronic structure, in particular the shift in the valence and conduction band levels induced by halogenated substitution.

Furthermore, the intensity of photoluminescence (PL) is closely linked to the crystalline quality and morphology of thin films. A decrease in the density of non-radiative defects as well as better passivation of grain boundaries promotes more efficient radiative recombination, resulting in more intense PL emission [17] (**Table 2**).

Figure 6 shows a progressive increase in the band gap energy $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ with increasing bromine content, reflecting the band gap widening by the partial substitution of I^- by Br^{2-} . Indeed, the band gap energy increases from 1.60 eV for the bromine-free film (0%) to 1.68 eV for an incorporation rate of 15%.

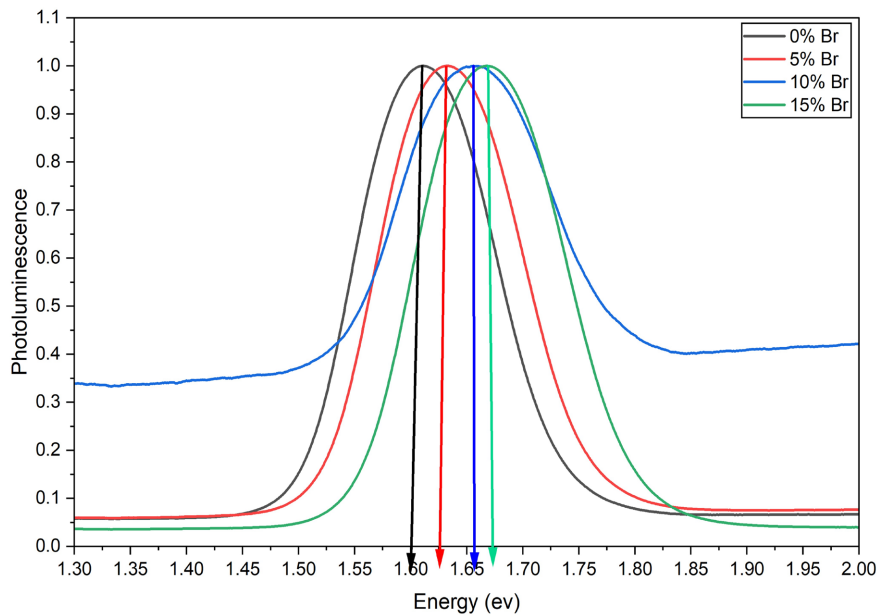


Figure 5. Normalized photoluminescence of MAPb(I_{1-x}Br_x)₃ as a function of energy.

Table 2. Band gap energy of MAPb(I_{1-x}Br_x)₃.

Br (%)	Eg (eV)
0%	1.60
5%	1.63
10%	1.66
15%	1.68

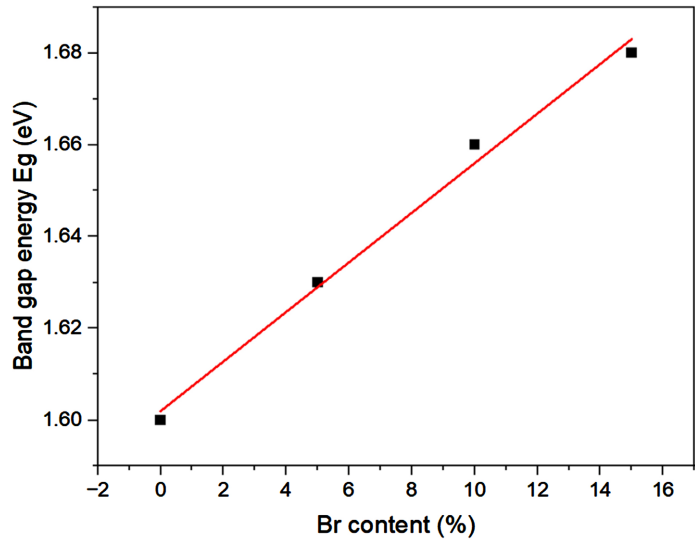


Figure 6. Variation of the band gap energy as a function of the Br concentration.

3.4. Surface Morphology (SEM)

The SEM images (**Figure 7**) show that the thin films are continuous and well-

covered, composed of polycrystalline grains. The average grain size decreases slightly as the bromide content increases. This behavior could be associated with changes in nucleation and growth kinetics during solution deposition. A more homogeneous morphology and better substrate coverage generally help limit non-radiative recombination pathways, which may partly explain the trends observed in photoluminescence (PL) measurements. These observations highlight the importance of precise control of the halogen composition to simultaneously optimize the structural, optical, and morphological properties of the films.

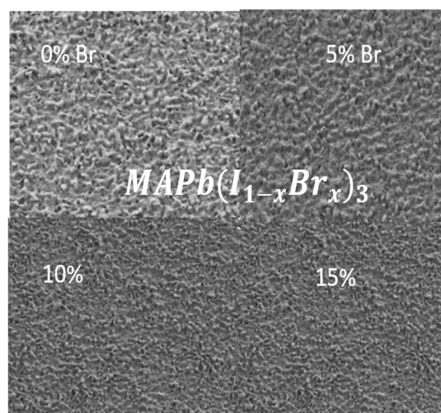


Figure 7. SEM images of thin films $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$.

3.5. Structural Evolution (Monitored by X-Ray Diffraction over 21 Days)

The long-term stability of the films $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ was assessed by weekly monitoring of X-ray diffraction under ambient conditions.

To accurately assess the degradation kinetics without the substrate crushing effect, the XRD diagrams were normalized (**Figure 8**). Comparative analysis of the curves after 3 weeks of exposure (green curves) highlights the superiority of the 10% Br sample. While the main perovskite peaks at approximately 14.2° and 28.5° collapse almost completely for the pure compound (0% Br) and weaken for the 15% Br, they maintain their resolution and maximum relative intensity for the 10% Br composition. This result confirms the existence of an optimum at 10% bromine, limiting network amorphization while avoiding the local mechanical stresses suspected at the higher 15% concentration.

3.6. Optical Stability Analysis (Absorbance over 28 Days)

Monitoring by UV-Vis spectroscopy confirms structural trends while revealing the surface condition of the films.

For the 0% Br sample A progressive blurring of the absorption edge and a dramatic increase in the baseline are observed after 14 days. This vertical shift may not be an actual increase in absorption, but rather a sign of strong light scattering caused by physical degradation and increased film roughness following its structural collapse.

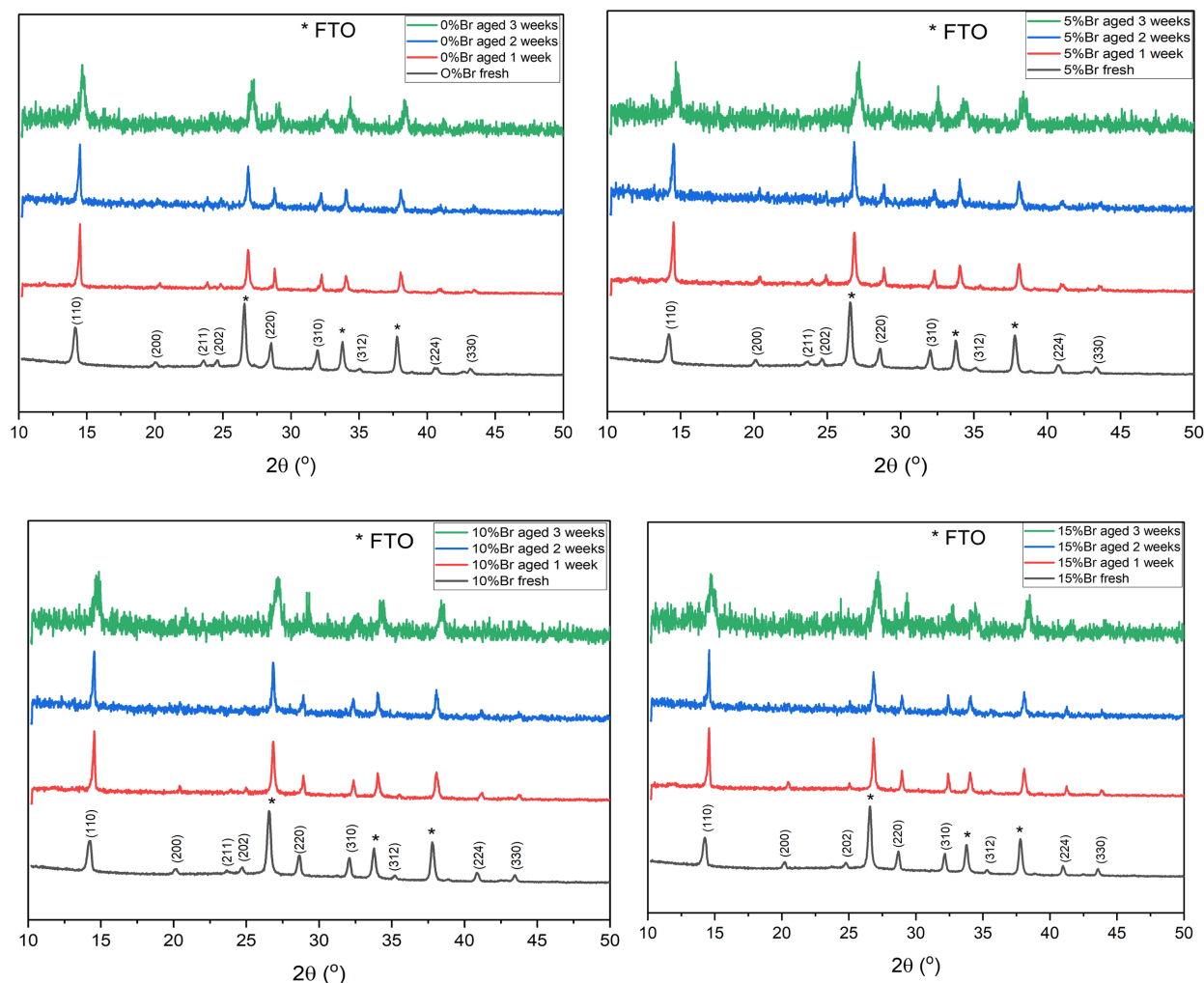


Figure 8. Diffractograms of fresh and 3-week-old thin layers $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$.

For mixed compositions (5% - 15% Br), the absorption front remains stable and sharp for at least 21 days. For the 10% Br sample, the spectrum retains its initial profile even after 28 days, showing only slight scattering at the end of the period. This could demonstrate that bromine not only stabilizes the internal structure but also preserves the optical quality of the interface [15] [18] (Figure 9).

3.7. Photoluminescence Dynamics and Passivation (28 Days)

Photoluminescence (PL) spectra offer the finest understanding of electronic quality during aging.

A remarkable phenomenon of “humidity-assisted passivation” was observed for all bromine-doped samples. By the second week, the PL intensity increased significantly. This effect was maximal for the 10% Br sample, whose intensity was four times greater than that of the undamaged film. This luminescence peak suggests that controlled exposure to ambient humidity allows for the passivation of surface defects or the rearrangement of grain boundaries, thereby reducing non-radiative recombination.

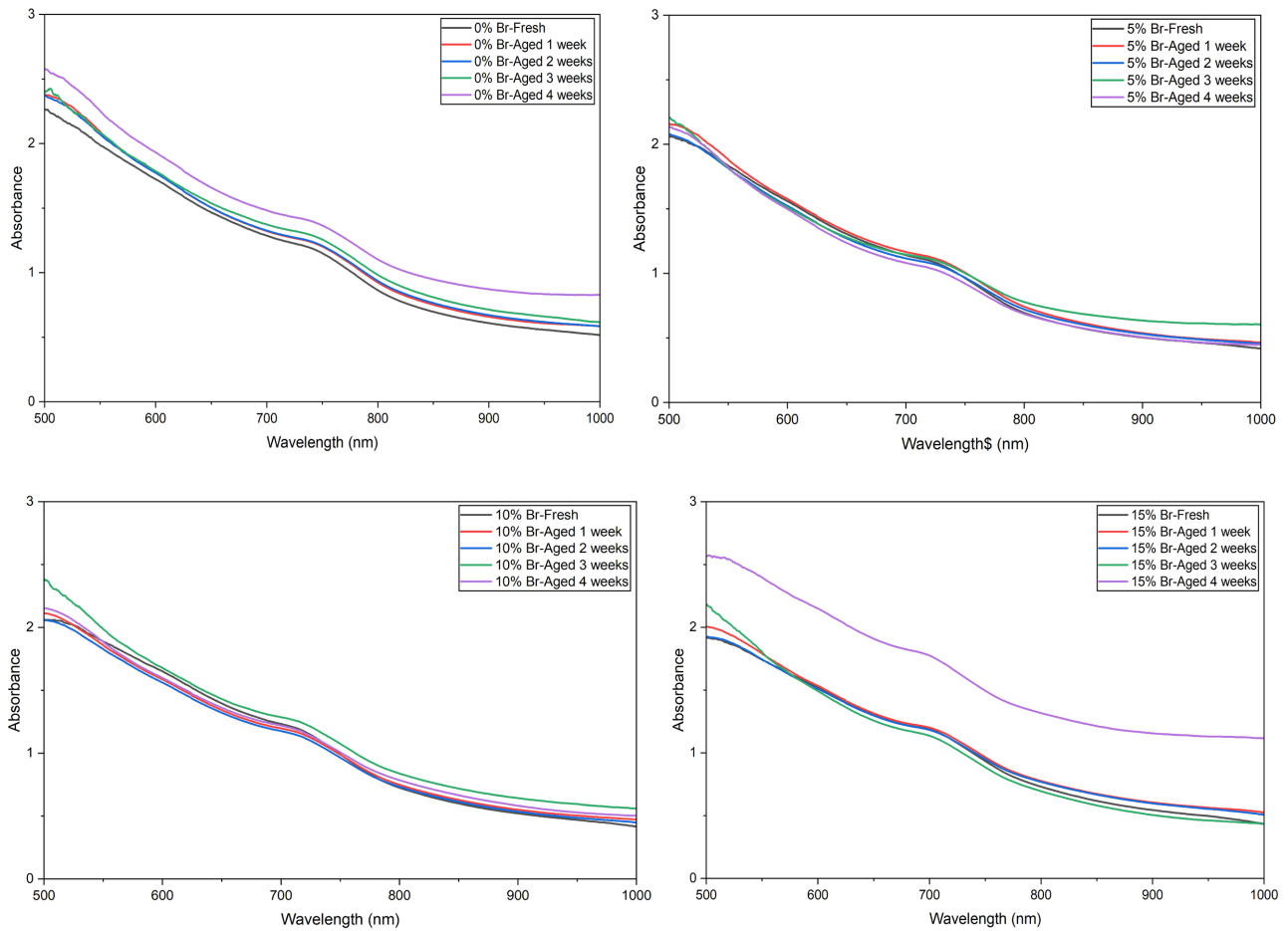
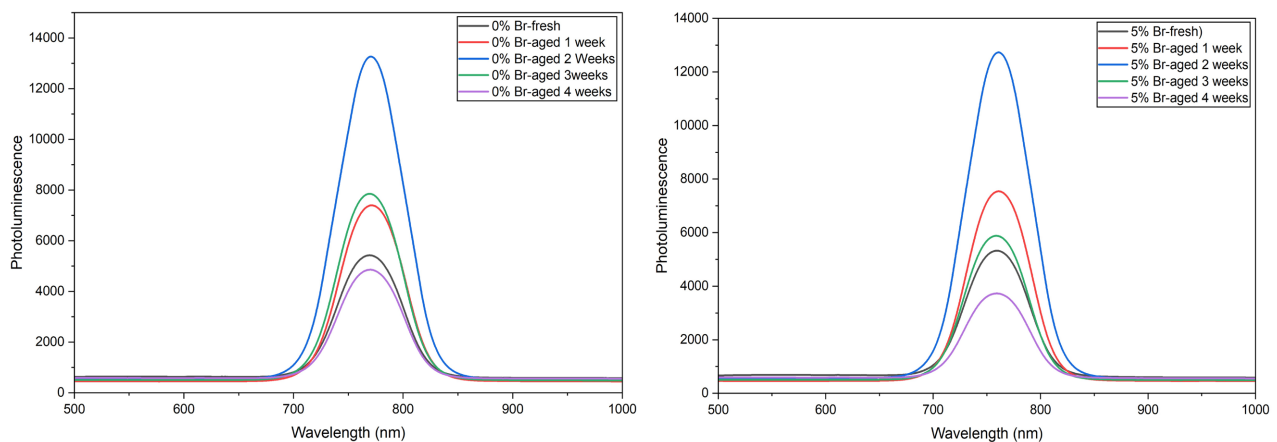


Figure 9. Absorption of the different thin layers of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ fresh and old.

However, after 21 days, a competition arises between this passivation and chemical degradation. While the 15% Br sample experiences a rapid drop in PL intensity by week 4, the 10% Br sample maintains robust emission. This crucial result identifies the 10% Br ratio as the optimal threshold: it provides sufficient protection against moisture while avoiding excessive network stresses or microscopic segregation that could occur at higher bromine levels (**Figure 10**).



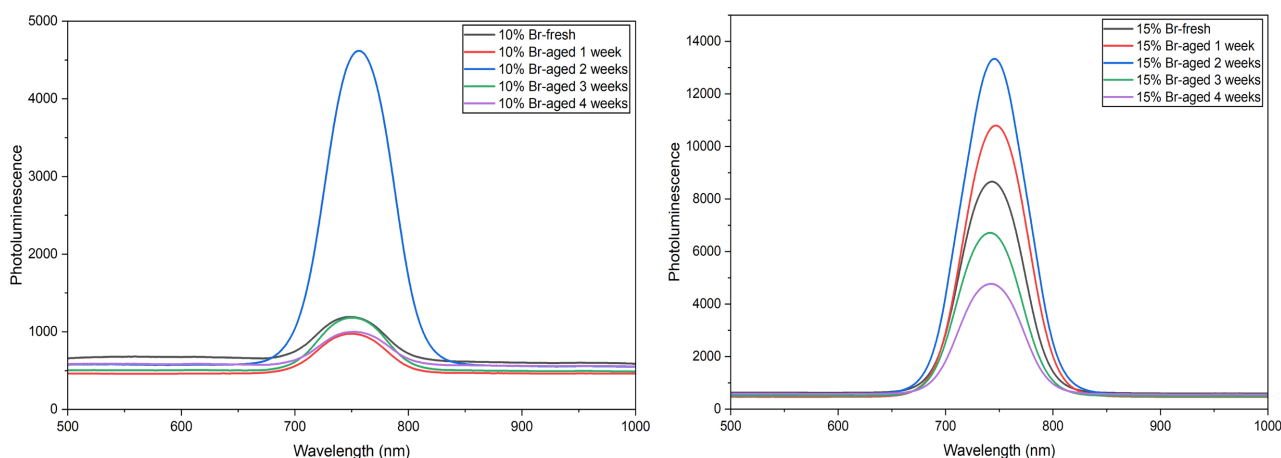


Figure 10. Photoluminescence of different thin layers of $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ fresh and old.

4. Conclusions

In conclusion, this study has allowed us to precisely quantify the influence of bromine incorporation on the structural properties and environmental stability of perovskite thin films $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$. Our results confirm that halide engineering is a key lever for overcoming the intrinsic limitations of MAPbI_3 pure perovskite.

Structural analyses by XRD and optical analyses by UV-Vis demonstrated homogeneous integration of bromine within the lattice, enabling precise band gap adjustment from 1.60 eV to 1.68 eV. This *band gap control* is essential for the development of high-efficiency tandem solar cells. Morphologically, SEM images confirmed that halogenated substitution preserves the uniformity and compactness of the films, prerequisites for photovoltaic applications.

The major contribution of this work lies in the comparative monitoring of degradation over 28 days. We have demonstrated that:

The MAPbI_3 pure form undergoes total amorphization in less than a week without an intermediate crystalline phase.

The addition of bromine delays this process by strengthening the cohesion of the crystal lattice through lattice contraction.

The 10% Br sample represents the optimal ratio, even surpassing the 15% sample in terms of electronic resilience. This 10% threshold allows for a beneficial humidity-assisted passivation mechanism, tripling the lifetime of the photoluminescence signal compared to the pure compound.

These findings suggest that there is a critical trade-off between structural rigidity and the quality of electronic interfaces. Above 10% Br, although the structure remains robust, emission properties begin to decline earlier, likely due to internal network stresses.

This work paves the way for more precise optimization of photovoltaic devices operating in humid environments. Future research could explore the impact of this optimal 10% ratio under combined thermal and light stress, in order to validate its viability for the industrial production of durable perovskite modules.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Jeong, J., Kim, M., Seo, J., Lu, H., Ahlawat, P., Mishra, A., *et al.* (2021) Pseudo-Halide Anion Engineering for α -FAPbI₃ Perovskite Solar Cells. *Nature*, **592**, 381-385. <https://doi.org/10.1038/s41586-021-03406-5>
- [2] Berhe, T.A., Su, W., Chen, C., Pan, C., Cheng, J., Chen, H., *et al.* (2016) Organometal Halide Perovskite Solar Cells: Degradation and Stability. *Energy & Environmental Science*, **9**, 323-356. <https://doi.org/10.1039/c5ee02733k>
- [3] Leguy, A.M.A., Hu, Y., Campoy-Quiles, M., Alonso, M.I., Weber, O.J., Azarhoosh, P., *et al.* (2015) Reversible Hydration of CH₃NH₃PbI₃ in Films, Single Crystals, and Solar Cells. *Chemistry of Materials*, **27**, 3397-3407. <https://doi.org/10.1021/acs.chemmater.5b00660>
- [4] Zhu, Z., Hadjiev, V.G., Rong, Y., Guo, R., Cao, B., Tang, Z., *et al.* (2016) Interaction of Organic Cation with Water Molecule in Perovskite Mapb₃ : From Dynamic Orientational Disorder to Hydrogen Bonding. *Chemistry of Material*, **28**, 7385-7393. <https://doi.org/10.1021/acs.chemmater.6b02883>
- [5] Noh, J.H., Im, S.H., Heo, J.H., Mandal, T.N. and Seok, S.I. (2013) Chemical Management for Colorful, Efficient, and Stable Inorganic-Organic Hybrid Nanostructured Solar Cells. *Nano Letters*, **13**, 1764-1769. <https://doi.org/10.1021/nl400349b>
- [6] Aziz, A., Aristidou, N., Bu, X., Westbrook, R.J.E., Haque, S.A. and Islam, M.S. (2019) Understanding the Enhanced Stability of Bromide Substitution in Lead Iodide Perovskites. *Chemistry of Materials*, **32**, 400-409. <https://doi.org/10.1021/acs.chemmater.9b04000>
- [7] Jung, E.H., Jeon, N.J., Park, E.Y., Moon, C.S., Shin, T.J., Yang, T., *et al.* (2019) Efficient, Stable and Scalable Perovskite Solar Cells Using Poly(3-Hexylthiophene). *Nature*, **567**, 511-515. <https://doi.org/10.1038/s41586-019-1036-3>
- [8] Jošt, M., Köhnen, E., Morales-Vilches, A.B., Lipovšek, B., Jäger, K., Macco, B., *et al.* (2018) Textured Interfaces in Monolithic Perovskite/Silicon Tandem Solar Cells: Advanced Light Management for Improved Efficiency and Energy Yield. *Energy & Environmental Science*, **11**, 3511-3523. <https://doi.org/10.1039/c8ee02469c>
- [9] Xing, G., Mathews, N., Lim, S.S., Yantara, N., Liu, X., Sabba, D., *et al.* (2014) Low-Temperature Solution-Processed Wavelength-Tunable Perovskites for Lasing. *Nature Materials*, **13**, 476-480. <https://doi.org/10.1038/nmat3911>
- [10] Sadhanala, A., Ahmad, S., Zhao, B., Giesbrecht, N., Pearce, P.M., Deschler, F., *et al.* (2015) Blue-Green Color Tunable Solution Processable Organolead Chloride-Bromide Mixed Halide Perovskites for Optoelectronic Applications. *Nano Letters*, **15**, 6095-6101. <https://doi.org/10.1021/acs.nanolett.5b02369>
- [11] Draguta, S., Sharia, O., Yoon, S.J., Brennan, M.C., Morozov, Y.V., Manser, J.S., *et al.* (2017) Rationalizing the Light-Induced Phase Separation of Mixed Halide Organic-Inorganic Perovskites. *Nature Communications*, **8**, Article No. 200. <https://doi.org/10.1038/s41467-017-00284-2>
- [12] Suchan, K., Merdasa, A., Rehmann, C., Unger, E.L. and Scheblykin, I.G. (2020) Complex Evolution of Photoluminescence during Phase Segregation of MAPb(I_{1-x}Br_x)₃ Mixed Halide Perovskite. *Journal of Luminescence*, **221**, Article ID: 117073. <https://doi.org/10.1016/j.jlumin.2020.117073>
- [13] Mao, W.X., *et al.* (2019) Visualizing Phase Segregation in Mixed-Halide Perovskite

- Single Crystals. *Angewandte Chemie International Edition*, **58**, 2893-2898.
- [14] Atourki, L., Vega, E., Marí, B., Mollar, M., Ait Ahsaine, H., Bouabid, K., *et al.* (2016) Role of the Chemical Substitution on the Structural and Luminescence Properties of the Mixed Halide Perovskite Thin $\text{Mapb}_{1-x}\text{Br}_x$ ($0 \leq x \leq 1$) Films. *Applied Surface Science*, **371**, 112-117. <https://doi.org/10.1016/j.apsusc.2016.02.207>
 - [15] Doumbia, Y., Bouich, A., Soucasse, B.M. and Soro, D. (2023) Boosting the Stability and Growth of Methylammonium Lead Bromide Perovskites Film Doped with FA for Solar Cells. *Optical Materials*, **137**, Article ID: 113563. <https://doi.org/10.1016/j.optmat.2023.113563>
 - [16] Jeon, N.J., Noh, J.H., Kim, Y.C., Yang, W.S., Ryu, S. and Seok, S.I. (2014) Solvent Engineering for High-Performance Inorganic-Organic Hybrid Perovskite Solar Cells. *Nature Materials*, **13**, 897-903. <https://doi.org/10.1038/nmat4014>
 - [17] Herz, L.M. (2016) Charge-Carrier Dynamics in Organic-Inorganic Metal Halide Perovskites. *Annual Review of Physical Chemistry*, **67**, 65-89. <https://doi.org/10.1146/annurev-physchem-040215-112222>
 - [18] Soro, D., Doumbia, Y., Bouich, A. and Mari Soucase, B. (2023) Surface Morphology and Optical Properties of Ma-Doped FAPbBr_3 Thin Films for Photovoltaic Applications. *International Journal of Advanced Research*, **11**, 1523-1527. <https://doi.org/10.21474/ijar01/16818>