

Article

Persistent PbI₂-Passivated Microdomains in As-Prepared MAPbI₃ Perovskite Thin Film Revealed by Spatially Resolved Photoluminescence and Raman Maps

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Abstract

Methylammonium lead iodide (MAPbI₃) perovskite has been widely studied for its optoelectronic properties, but its polycrystalline thin films inevitably contain grain boundaries and defects that degrade performance and stability. PbI₂ is often considered a destabilizing agent in perovskites, yet it has also been reported to act as a passivation agent, making its role a subject of debate. Here, we performed integrated optical, photoluminescence (PL), and ultra-low-frequency Raman mapping on a 100 μm² region of MAPbI₃ thin films to study the roles of PbI₂. The analyses resolved α-phase MAPbI₃-rich, PbI₂-rich, and mixed-phase domains, revealing heterogeneous PbI₂ distribution with PL quenching at defect sites. In addition, after light-induced degradation, PL changes were governed by both the local microstructure and PbI₂ distribution. Notably, PbI₂-rich regions retained PL, evidencing a protective passivation effect. These findings demonstrate that the beneficial role of PbI₂ is key to designing more stable perovskite devices.

Keywords: MAPbI₃ thin film; hybrid organic-inorganic halide perovskites; PbI₂ passivation; photoluminescence mapping; Raman mapping



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1. Introduction

Hybrid organic-inorganic halide perovskites (HOIPs) exhibit a set of outstanding optoelectronic properties. Owing to these advantages, HOIPs have been extensively employed in diverse optoelectronic devices [1–3]. Among various halide perovskites, methylammonium lead iodide (MAPbI₃) has been studied as one of the most representative materials for optoelectronic applications. MAPbI₃ possesses a direct bandgap of 1.57 eV [4], which can be readily tuned by halide substitution or halide mixing [5]. Its exciton binding energy (37–50 meV) is comparable to or smaller than the thermal energy at room temperature (~25 meV), enabling efficient exciton dissociation under ambient conditions [6–8]. Moreover, the fabrication process for MAPbI₃ is relatively simple and cost-effective compared to other semiconductors [9,10].

However, MAPbI₃ thin films are intrinsically polycrystalline [11], which introduces performance degradation associated with grain boundaries and related defects. Traps and non-radiative recombination centers—originating from chemical impurities or structural defects—are primary factors that limit device efficiency [5,12]. In particular, structural defects can act as Shockley-Read-Hall recombination centers, reducing carrier lifetimes and lowering the open-circuit voltage [13,14], and initiating progressive degradation when subjected to extreme operation conditions such as high temperature during laser lasing processes [15]. These defects can also accelerate environmental instability by increasing susceptibility to moisture and light [16]. Although MAPbI₃ has been reported to show some tolerance to defects, they remain a main limitation for the performance of perovskite-based devices [17].

Additives such as PbI₂ [18–21], phenethylammonium iodide [11,16,22], and dibenzopentacene (C₆₄H₃₆) [23] have been reported to suppress defects. Among them, PbI₂ has been considered a destabilizing agent in perovskites, yet recently been reported to act as a passivation agent, thus leaving its role controversial.

A variety of characterization techniques have been utilized to clarify the passivation role of PbI₂ distributed on a thin film [18]. Techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM), and mapping mode energy dispersive X-ray spectroscopy provide spatial information, but integrated multimodal mapping on identical sample locations remains uncommon.

In this regard, ultra-low frequency Raman (<100 cm^{−1}) is highly advantageous, as it allows direct discrimination between PbI₂ and α -phase MAPbI₃, making it an ideal tool for addressing the debated role of PbI₂ in thin films [24–30].

In this work, we demonstrate that the debated role of PbI₂ in MAPbI₃ thin films can be clarified through integrated spatially resolved optical, PL, and Raman mapping for a 100 μ m² area. This approach revealed heterogeneous PbI₂ distributions and the emergence of persistent PbI₂-passivated microdomains that retain PL even under degradation conditions. These findings demonstrate that the beneficial role of PbI₂ is key to designing more stable perovskite devices.

2. Materials and Methods

2.1. Perovskite Thin Film Preparation

PbI₂ was purchased from TCI (Tokyo, Japan) and used as received. All other chemicals were obtained from Sigma-Aldrich (Darmstadt, Germany) and also used as received.

MAPbI₃ perovskite thin films were fabricated via an anti-solvent-assisted spin-coating method, with methylammonium chloride (MACl) as an additive to stabilize the intermediate phase and improve crystallographic orientation. MACl largely evaporates during annealing and does not disturb the intrinsic structure [31]. Glass substrates were pretreated with oxygen plasma before film deposition.

The precursor solution was prepared by dissolving 1.53 M PbI₂, 1.40 M methylammonium iodide (MAI), and 0.50 M MACl in a mixed solvent of DMF and DMSO (DMF:DMSO = 8:1, *v/v*). The solution was stirred continuously at 70 °C for 6 h. For film preparation, the precursor solution was spin-coated on the ozone-etched glass substrate in two steps, which was secured on the spin-coater (EF-40p, E-flex, Bucheon, Republic of Korea), using a micropipette: 1000 rpm for 10 s, followed by 4000 rpm for 30 s. During the second step, 200 μ L of diethyl ether was dripped onto the spinning substrate 10 s after the start of the second step. The films were then annealed at 120 °C for 60 min in a nitrogen atmosphere. After annealing, the sample was allowed to cool to room temperature inside the glovebox before characterization. The film thickness was approximately 250 nm. The overall fabrication process is schematically illustrated in Figure 1.

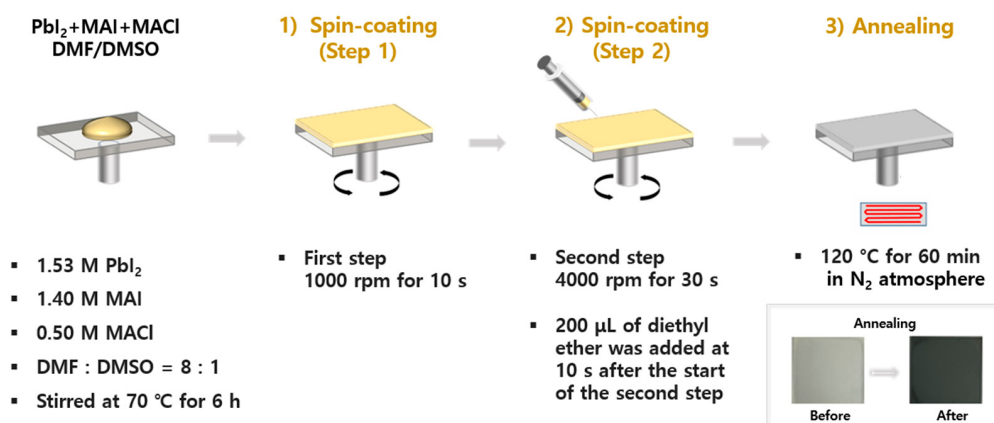


Figure 1. Schematic illustration of the perovskite thin film fabrication process via the anti-solvent-assisted spin-coating method.

2.2. Optical Characterization

X-ray diffraction (XRD) patterns were recorded using a powder diffractometer (X'Pert³, PANalytical, Almelo, The Netherlands) equipped with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). UV-Vis absorption spectra were acquired with a spectrophotometer (V-770, JASCO, Tokyo, Japan).

Raman and PL mapping were performed using a confocal Raman microscope (LabRAM HR Evolution, Horiba Jobin-Yvon, Palaiseau, France) equipped with an Olympus SMPLN 100 $\times$ objective lens. A 633 nm He-Ne laser was used as the excitation source for both Raman and PL measurements. The laser spot diameter at the sample surface was $\sim 0.86 \text{ }\mu\text{m}$. For PL mapping, the laser power was reduced to 0.0137 W cm^{-2} @ 633 nm, and the integration time was set to 0.05 s per point to minimize photodegradation. For Raman measurements, Raman pump power was reduced to 12 W cm^{-2} @ 633 nm, with an integration time of 30 s. All spatially resolved measurements were conducted over a $10 \text{ }\mu\text{m} \times 10 \text{ }\mu\text{m}$ area with a step size of $1 \text{ }\mu\text{m}$.

3. Results and Discussion

3.1. Optical and Structural Characterization of MAPbI₃ Thin Films

The UV-Vis absorption and steady-state PL spectra of the MAPbI₃ perovskite thin film were measured at room temperature. As shown in Figure 2a, the emission peak is centered near 780 nm, closely matching the absorption onset, and the absorption spectrum extends across most of the visible range, together indicating the successful formation of the MAPbI₃ perovskite thin film on the substrate [32]. This emission is consistent with the tetragonal phase of MAPbI₃, which has a band gap of approximately 1.60 eV (corresponding to PL near 775 nm); the observed $\sim 5 \text{ nm}$ redshift may arise from slight variations in film quality or measurement conditions [33]. The X-ray diffraction (Figure 2b) further supports the formation of the MAPbI₃ perovskite phase, showing distinct peaks at 14.08° (110), 28.5° (220), and 32° (310), characteristic of the tetragonal crystal phase (space group I4/mcm) [5,12,32].

A minor peak at 12.6° , attributed to the (001) plane of lead iodide [34], was also observed, indicating the presence of a small amount of lead iodide, presumed to originate either from incomplete conversion of the PbI₂ precursor during crystallization or from the degradation of the perovskite thin film after synthesis. Because MAPbI₃ has a low formation enthalpy, it is prone to degradation into PbI₂ and volatile MAI [16]. Thus, these diffraction results suggest that the fabricated film predominantly consists of the α -phase MAPbI₃, with a small amount of PbI₂.

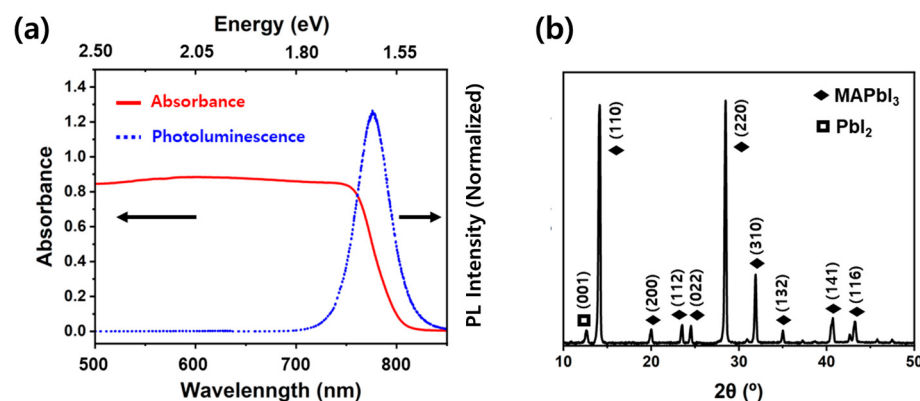


Figure 2. (a) UV-Vis absorption and normalized steady-state photoluminescence (PL) spectra, and (b) X-ray diffraction (XRD) patterns of methylammonium lead iodide (MAPbI₃) perovskite thin film. Diffraction peaks corresponding to PbI₂ and MAPbI₃ are marked by □ and ♦, respectively.

3.2. Correlation Analysis of Optical Microscopy and Spatially Resolved PL Mapping

To spatially investigate the structural heterogeneity of the polycrystalline MAPbI₃ perovskite thin film, optical microscopy and microscale PL mapping were acquired from the same region of the film to allow direct spatial correlation between morphological and photoluminescence features. Figure 3a,b present an optical microscope image and the corresponding PL intensity contour map, respectively, focusing on a surface defect and its surrounding region. The optical microscope image in Figure 3a clearly reveals pronounced surface defects localized at the junctions. Due to the inherent polycrystalline nature of MAPbI₃, grain boundaries are commonly formed [16]. Since individual grains of MAPbI₃ thin films can typically be identified at SEM-level resolution, the fracture observed in Figure 3a is more likely a relatively large crack, which is often associated with the film processing steps, rather than a typical grain boundary. Nevertheless, because the internal width of this crack is only ~2 μm at most, there is a possibility that it might be overlooked even at a resolution of about 1 μm in Raman mapping that covers larger areas [35]. Similar to typical grain boundaries, these defects can hinder charge carrier transport and often serve as sites for further defect formation [16]. The PL contour map in Figure 3b exhibits a clear spatial correlation with the optical features. For instance, region A, which appears relatively smooth in the optical image, shows the strongest PL emission, while region C, associated with defective regions, displays the weakest and most redshifted PL signal (Figure 3c). This correlation suggests that the optical response, including both PL intensity and spectral position, is strongly influenced by surface morphology and the local defect environment exemplified by cracks. The reduced PL intensity and redshift near defect sites can be attributed to enhanced nonradiative recombination and possible bandgap reduction due to compositional variations or strain [36].

3.3. Spatially Resolved Raman Mapping of Composition Distribution in Thin Films

To further investigate chemical information in the regions analyzed in Figure 3, Raman mapping was conducted on the same areas of the MAPbI₃ perovskite thin film previously examined by optical and PL measurements. Figure 4a shows ultra-low frequency Raman spectra (40–200 cm^{−1}) measured at three representative spots (A, B, and C) marked in Figure 3. Notably, no Raman feature near 143 cm^{−1}, typically attributed to PbO vibrational modes, was detected in any region [37]. This absence indicates that the PL and Raman measurements employed here did not induce photodegradation under our experimental conditions [12,27].

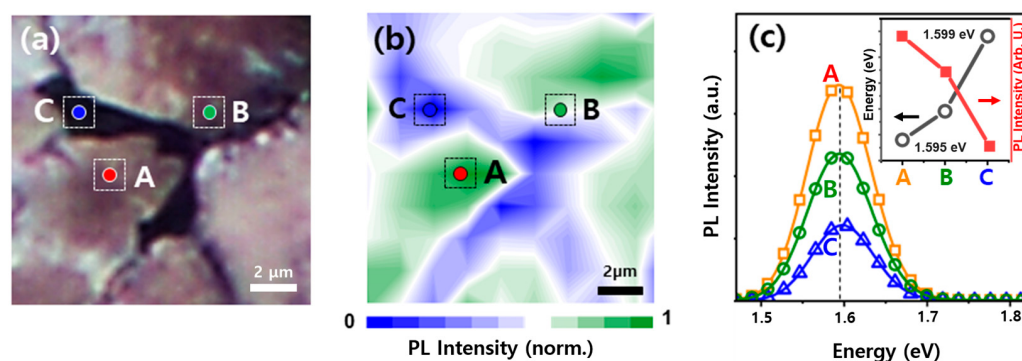


Figure 3. (a) Optical image of MAPbI₃ thin film, (b) PL intensity map acquired from the same area as shown in (a), and (c) representative PL spectra measured at spots A, B and C. The inset presents a comparison of the PL intensities (a.u., red line) and the corresponding optical bandgap values (eV, black line) for each of the three spots (A, B, and C).

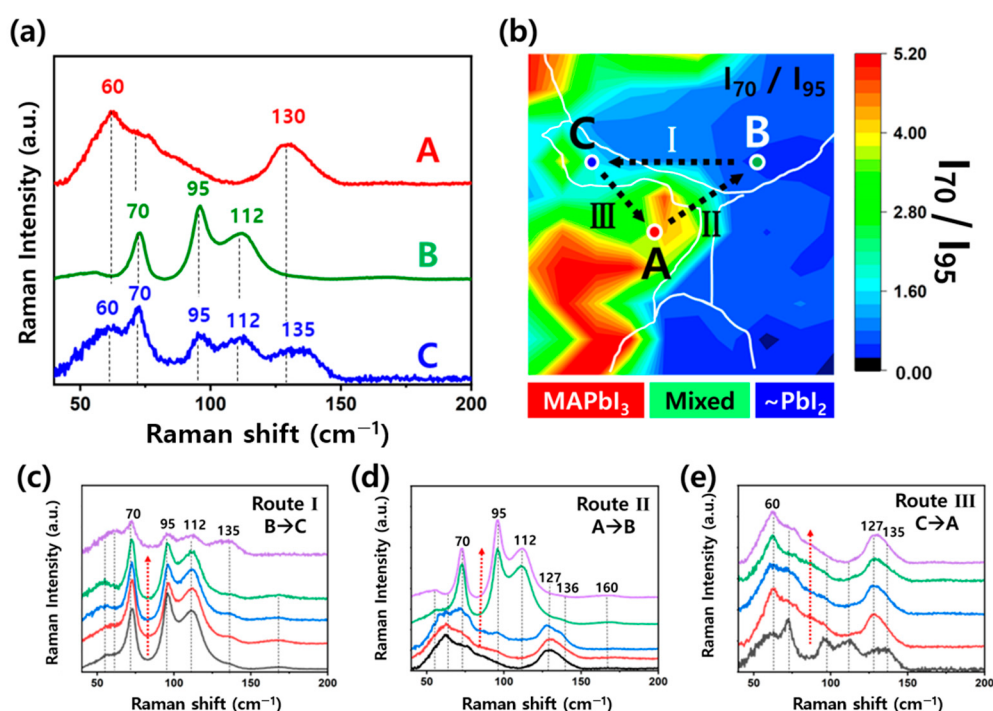


Figure 4. (a) Ultra-low frequency Raman spectra (40–200 cm^{−1}) measured at the representative points A–C shown in Figure 3, corresponding to α -phase MAPbI₃-rich (A), PbI₂-rich (B), and mixed-phase (C). (b) Raman intensity ratio (I_{70}/I_{95}) map with white line boundaries defined from the optical image, showing the distribution of chemical species. (c) Raman spectra along the dashed arrows in Route I (B $\rightarrow$ C), (d) Route II (A $\rightarrow$ B), and (e) Route III (C $\rightarrow$ A).

Spots A and B, located on different grains, exhibit distinct Raman signatures. Spot A shows peak at 60 cm^{−1}, assigned to the I-Pb-I bending mode in MAPbI₃, which is a significant marker of its α -phase inorganic component [38]. A second peak at ~135 cm^{−1} is assigned to a librational mode of the MA cation confined within the inorganic cage of the perovskite lattice, consistent with previous reports [39]. The Raman features of α -phase MAPbI₃ were clearly distinguished from those of MAI (see Figure S1) [40]. In contrast, spot B displays the peaks at 70 and 95 cm^{−1}, characteristic of crystalline PbI₂ and associated with the symmetric and asymmetric stretching vibrations of Pb–I bonds in edge-sharing PbI₆ octahedra [38,41]. It shows good agreement with the Raman of PbI₂ (see Figure S1) [42]. The Raman spectrum at spot C, located at the defect region, exhibits mixed features observed at spots A and B, indicating the coexistence of both α -phase MAPbI₃ and PbI₂. This implies that the defect contains residual PbI₂ precursors or PbI₂ formed

by degradation. If excess PbI_2 is present during the annealing process, it can be driven toward grain boundaries by perovskite grain growth, leading to its accumulation near defect sites [18,19].

With the incorporation of MACl additive, incomplete conversion thermodynamically results in residual PbI_2 in the film. The PbI_2 observed at spot C can be explained by its migration during annealing, while the strong signal at spot B likely arises from the same mechanism, leading to accumulation at grain boundaries or point defects beyond the current optical resolution [18]. This indicates that PbI_2 is not uniformly distributed but accumulates locally within the film. Therefore, in spatially resolved analyses of MAPbI_3 thin films using optical techniques such as Raman mapping, both structural defects (e.g., cracks) and the heterogeneous distribution of residual PbI_2 must be carefully considered. Figure 4b presents a relative ratio map of the Raman peak intensities at 70 and 95 cm^{-1} (I_{70}/I_{95}) to distinguish the chemical species. As shown in Figure 4a, the peak at 70 cm^{-1} originates from crystalline PbI_2 , while the 95 cm^{-1} peak becomes dominant in PbI_2 -rich regions. Accordingly, higher I_{70}/I_{95} ratios correspond to α -phase MAPbI_3 -rich domains, whereas lower ratios mark PbI_2 -rich domains. Figure 4c–e show the Raman spectra along the paths connecting the three points. The spectral changes occur abruptly, rather than gradually, upon crossing the interfaces between regions, consistent with the boundaries between compositionally distinct domains.

3.4. Integrated Multimodal Analysis at Identical Surface Locations

To provide a comprehensive comparison, the optical, PL, and Raman map data corresponding to the same region of the film were combined (Figure 5). It is evident that structural degradation is clearly correlated with the reduced PL intensity in the dark region (Figure 5a,b). These defect regions contain some PbI_2 showing mixed Raman features (Figure 5c). Thus, the reduced PL is more reasonably explained by the presence of structural defects, such as cracks or voids, which increase non-radiative recombination rates. However, PbI_2 -rich regions can also emit bright PL comparable to that of α -phase MAPbI_3 -rich areas. The PL emission of pristine PbI_2 powder or crystals deposited on a substrate, occurring at 2.50–2.43 eV, is distinct from the PL peak in this study and thus cannot account for the observed emission. Although PbI_2 in coordinating solvents such as DMSO or DMF can form emissive polyiodide plumbate complexes. However, this emission is unlikely to be retained in a thin film due to the evaporation of the solvents during annealing [34,43]. To visualize the correlation between α -phase MAPbI_3 -rich and PbI_2 -rich regions on the Raman map and the PL intensity, we constructed a heat map by multiplying the PL and Raman signal values obtained at each spot (see Figure S2). Because higher PL intensity can be found in both pure α -phase MAPbI_3 -rich and PbI_2 -rich domains, Raman intensities were assigned negative values for PbI_2 -rich domains and positive values for MAPbI_3 -rich domains during the normalization of PL and Raman maps. Figure S2 demonstrates that blue regions represent negative correlation (i.e., strong PL associated with PbI_2 -rich domains) while red regions indicate positive correlation (i.e., strong PL associated with α -phase MAPbI_3 domains). This analysis confirms that the PL intensity is correlated with both PbI_2 - and MAPbI_3 -rich regions.

PbI_2 has been reported to passivate MAPbI_3 , showing the reduction in defect density and suppression of degradation initiated at surface defects [23]. If the PbI_2 -rich regions observed in Figure 5c indeed reflect PbI_2 concentrated at grain boundaries or local surface defects, it is plausible that PbI_2 acts as a protective barrier against environmental degradation-inducing factors such as moisture, oxygen, or light, thereby mitigating further deterioration of the perovskite thin film.

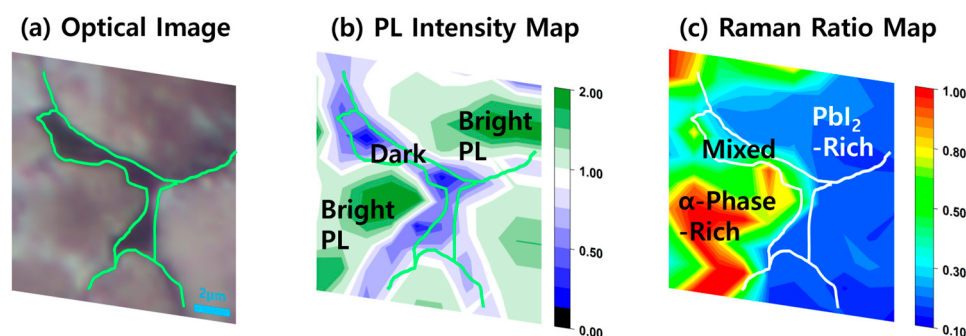


Figure 5. Comparison of (a) optical image, (b) PL intensity map, and (c) Raman intensity ratio (I_{70}/I_{95}) map, reproduced from Figure 3a, Figure 3b, and Figure 4b, respectively. All images correspond to the same region of the film, enabling direct correlation of morphology, PL response, and phase distributions.

3.5. Spatially Dependent Response of Thin Films to Light-Induced Degradation

To examine the passivation effect on the PL of MAPbI₃ thin film, the sample was irradiated with an intense laser (120 W cm^{-2} @633 nm) under ambient conditions. The irradiation power is approximately 1200 times higher than the standard one-sun illumination (100 mW cm^{-2} , AM 1.5G) [23].

The PL intensity and the red-shift magnitude maps were obtained (Figure 6a,b) after the irradiation. The α-phase MAPbI₃ (A) and defect (C) regions exhibited no detectable PL after the irradiation, indicating photo-bleaching (③ in Figure 6c). In contrast, the PbI₂-rich region (B) exhibited a slight red-shift upon irradiation yet retained a detectable PL signal (② in Figure 6c), indicating that the presence of PbI₂ contributes to preserving the PL of the MAPbI₃ thin film [20]. Although previous studies have reported that excessive PbI₂, under specific conditions [18,44,45] such as light-induced decomposition or electric poling, increase the defect density of the film, our measurements indicate that the dominant effect of PbI₂ is more consistent with passivation. Accordingly, the preserved PL emission in region (B) can originate from partial protection by PbI₂ against irradiation-induced degradation.

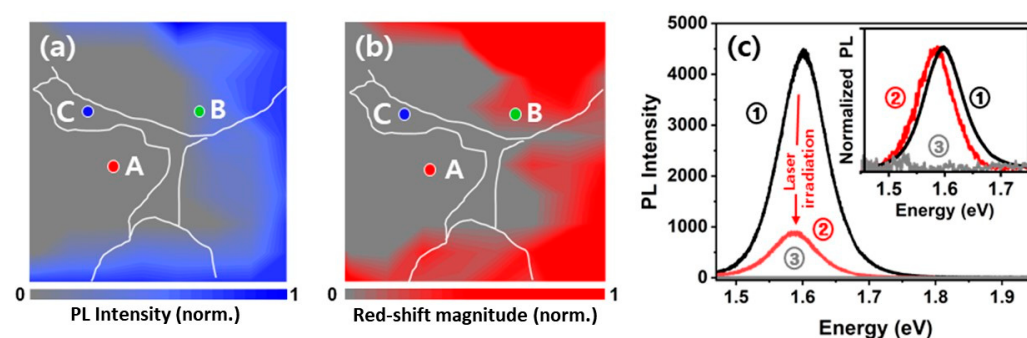


Figure 6. (a) Normalized PL intensity and (b) red-shift magnitude heatmaps after intense irradiation. (c) Representative PL spectra before and after laser irradiation. Spectrum ① corresponds to the PL from spot B before irradiation, while spectra ② and ③ represent the PL from spots B and A after irradiation, respectively. The inset shows normalized PL spectra.

The influence of PbI₂ on the performance and stability of MAPbI₃ thin films remains debated, with both beneficial and detrimental effects reported [46–50]. Previous studies have addressed this issue either at the grain level using SEM or at broader scales using Raman mapping, often leading to ambiguous interpretations [18,35]. In contrast, our study demonstrates at an intermediate scale ($10 \mu\text{m} \times 10 \mu\text{m}$) that PbI₂ mitigates light-induced degradation, and that PL changes after irradiation are jointly governed by the local PbI₂ distribution and the microstructure of MAPbI₃ thin films.

4. Conclusions

In summary, we integrated optical, PL, and Raman mapping on identical surface regions of MAPbI₃ thin films within a 10 μm $\times$ 10 μm field of view, enabling precise spatial correlation between local morphology and composition. Through this analytical approach, we observed that PbI₂-rich microdomains retained PL even under light-induced degradation. These results highlight the critical role of spatially resolved, multimodal characterization in elucidating passivation mechanisms in polycrystalline perovskites.

This capability to perform multimodal measurements at the same location before and after light-induced degradation distinguishes our method from conventional techniques that either focus on highly localized features at high magnification (e.g., SEM and AFM) or characterize the entire film at low magnification. Accordingly, we anticipate that this nondestructive approach will serve as a powerful platform for preliminary evaluation of passivation strategies, including screening of passivation agents and their loading amounts, prior to more detailed characterization.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst15110991/s1>, Figure S1: Ultra-low Raman spectra of MAI and PbI₂, Figure S2: PL–Raman correlation map. Red: PL–MAPbI₃ correlation; Blue: PL–PbI₂ correlation.

Author Contributions: Conceptualization, B.-G.K. and M.P.; Methodology, B.-G.K., J.C., T.S., and M.P.; Software, J.C.; Validation, B.-G.K., J.C., T.S., H.S.K., M.K., and J.J.; Formal Analysis, B.-G.K., J.C., and T.S.; Investigation, B.-G.K., J.C., T.S., and S.L.; Resources, M.K. and S.L.; Data Curation, H.S.K., M.K., J.J., and S.L.; Writing—Original Draft, B.-G.K., J.C., T.S., S.L., and M.P.; Writing—Review and Editing, J.C., T.S., H.S.K., M.K., J.J., S.L., and M.P.; Visualization, T.S., H.S.K., M.K., J.J., and M.P.; Supervision, S.L. and M.P.; Project Administration, S.L. and M.P.; Funding Acquisition, J.J., S.L., and M.P. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflicts of interest.

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