

Effect of temperature on light induced degradation in methylammonium lead iodide perovskite thin films and solar cells



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ABSTRACT

In this study we investigate the light and heat-induced degradation of methylammonium lead iodide (MAPbI₃) perovskite films in an inert atmosphere to exclude the effect of oxygen and humidity. Films aged under solar intensities started to degrade above 75 °C, while films in the dark degraded at 95 °C. To investigate the temperature-induced degradation mechanism, spectroscopic techniques such as Ultraviolet-Visible (UV-Vis) absorption spectroscopy, X-Ray Diffraction (XRD), Extended X-ray Absorption Fine Structure (EXAFS), and Fourier Transform Infrared (FT-IR) were used. Results show that the films aged under light at 75 °C degraded to a mixture of PbI₂ and metallic Pb. In contrast, films aged thermally in the dark, or with light and oxygen, degraded to PbI₂ only. MAPbI₃ solar cells were aged to show the effect of the metallic lead on the charge transfer mechanism.

1. Introduction

Organometal halide perovskites (OMH-perovskite) with the structure ABX₃ (A = organic cation, B = metal cation, and X = halide anion) have unique properties such as a tunable band gap, easy fabrication process, high extinction coefficients, low recombination rate, high carrier mobility, and enhanced power conversion efficiency (PCE) up to 22.1%, indicating that OMH-perovskite has a great potential in photovoltaics applications [1–6]. However, the rapid instability of the material in the presence of environmental elements, such as light, oxygen, heat, and moisture, limits its application in industry [7–9]. Different types of environmental exposure can induce different degradation pathways, so it is important to examine the degradation of the OMH-perovskite samples under each condition to have a full assessment of the stability of the material. Many degradation studies have focused on oxygen and water, however both can be kept from interacting with the perovskite layer using proper encapsulation. However, solar cells are all subject to operation under light and elevated temperatures. To date, only a few studies have been done on the stability of OMH-perovskite films and solar cells with light in the absence of water [10–12]. Based on these studies, oxygen is critical in the light induced degradation of MAPbI₃ films, while in the absence of oxygen, the perovskite films were found to be stable. However, the stability of

perovskites under light at varying temperatures has not been fully addressed.

In this work, we examined the degradation of MAPbI₃ perovskite films and solar cells with light in an inert atmosphere at two different temperatures (55 °C and 75 °C). In addition, we evaluated the thermal stability of perovskite films in the dark at three temperatures (75 °C, 85 °C, and 95 °C) to have an accurate assessment of the thermal factor in the light degradation mechanism. Our data show the MAPbI₃ perovskite to be stable under intense light of approximately 360 mW/cm² at 55 °C, but under the same conditions at an elevated temperature of 75 °C, it degrades to a mixture of PbI₂ and metallic Pb. The influences of different degradation processes on the samples were investigated in detail.

2. Material and methods

The materials used in these experiments include N,N-dimethylformamide (DMF, spectroscopic grade, OmniSolv), 2-propanol (spectroscopic grade, Fisher Scientific), Lead iodide (PbI₂, 99%, ACROS Organics, Fisher Scientific), and methylammonium iodide (MAI, Dyesol), TiO₂ nanoparticles (Solaronix), and Poly-3-hexylthiophene (P3HT, Sigma-Aldrich). All chemicals were used as received without any further purification. The methylammonium lead iodide (MAPbI₃)

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films were prepared in air at humidity level of $40\% \pm 2\%$ RH on cleaned borosilicate glass and quartz slides using a slightly modified two step method [13]. The films were prepared by spin coating $50 \mu\text{l}$ of dissolved PbI_2 in DMF (461 mg/ml) at 6000 rpm for 5 s, then dried at 80°C for 30 min in air. $150 \mu\text{l}$ MAI solution (10 mg/ml in 2-propanol) was spin-coated on the films for 1 min at 0 rpm (loading time), then for 20 s at 3000 rpm to remove the excess. The films were dried again at 80°C for 30 min in air. This preparation method gives MAPbI_3 thin films with thickness of ~ 250 nm. MAPbI_3 solar cell fabrication is detailed in the [Supplementary information](#).

The degradation process was induced by heating the samples with light using a mercury lamp (spectrum in [Fig. S1](#)), with illumination intensity of $360 (\pm 10) \text{ mW/cm}^2$ (high intensity compared with 100 mW/cm^2 AM1.5 solar light, though heavily weighted in the UV) in a nitrogen filled environment with very low oxygen and humidity levels (< 10 ppm and < 0.1 ppm, respectively). For samples characterized by temperature degradation without light, samples were placed on a hotplate and heated to the desired temperature in an N_2 glovebox. Surface temperatures of the thin film were recorded over time, and are considered the temperature of the sample.

To facilitate the comparison of samples aged at different conditions, we will use the formula X-Y-Z to label the samples, where X is D (dark) or L (light) to indicate whether the sample was subjected to light or kept in the dark; Y is N_2 or O_2 , representing whether the sample was aged in nitrogen or dry air; and Z is the temperature of the sample substrate, in Celsius. For example, the sample label D-N_2-95 represents the sample aged in a dark, N_2 filled environment with a substrate temperature of 95°C , and the label L-O_2-22 represents the sample aged in dry air at 22°C with light exposure. [Table \(S1\)](#) in [Supplementary information](#) provides the details of each sample according to its label.

The optical absorption spectra of the films were measured using a Jasco V-670 spectrophotometer. XRD analysis (XRD, Rigaku Americas Miniflex Plus powder diffractometer) was performed at a voltage of 40 kV and current of 44 mA, with a scanning angle range of $10\text{--}60^\circ$ (2θ) with a rate of $3^\circ/\text{min}$. Fourier Transform Infrared (FT-IR) spectra were recorded with a Perkin Elmer Spectrum One FT-IR spectrophotometer using KBr pellets as substrates. The Pb L_{III} edge EXAFS data were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 4-1 using a Si (220) double monochromator, detuned 50% at 13,200 eV to reduce harmonics. The data were collected in fluorescence mode with a Ge multi-channel detector at a temperature of 8 K. Slit heights were approximately 0.4 mm, which gives an energy resolution of ~ 1.3 eV. The data were reduced using standard techniques (RSXAP) [8], converted to k -space, and Fourier transformed to r -space. The Fourier transform range for all the samples is $3.5\text{--}12.5 \text{ \AA}^{-1}$ with a window rounding of 0.3 \AA^{-1} .

3. Results and discussion

The light induced degradation of MAPbI_3 perovskite films was examined in a dry, N_2 environment to exclude the role of oxygen and to avoid the destructive effect of humidity. The stability of the perovskite films exposed to light of $360 \pm 10 \text{ mW/cm}^2$ was monitored over the course of 4 days at two different temperatures ($55^\circ\text{C} \pm 2^\circ\text{C}$ and $75^\circ\text{C} \pm 2^\circ\text{C}$). The experimental setup is detailed and illustrated in the [Supplementary information](#). The perovskite films aged at 55°C were stable, showing no visible change; meanwhile, films aged at 75°C were visibly degraded. We found this interesting, as previous publications investigating light induced degradation of perovskite material in N_2 atmosphere concluded that it had either a negligible or no sign of decomposition [10–12,27]. The film aged at the lower temperature is in agreement with those previous studies; however, the film aged at the higher temperature showed the opposite result, indicating an additional factor initiated this unanticipated decomposition. Furthermore, the degraded film had a unique gray-yellow color post degradation, which

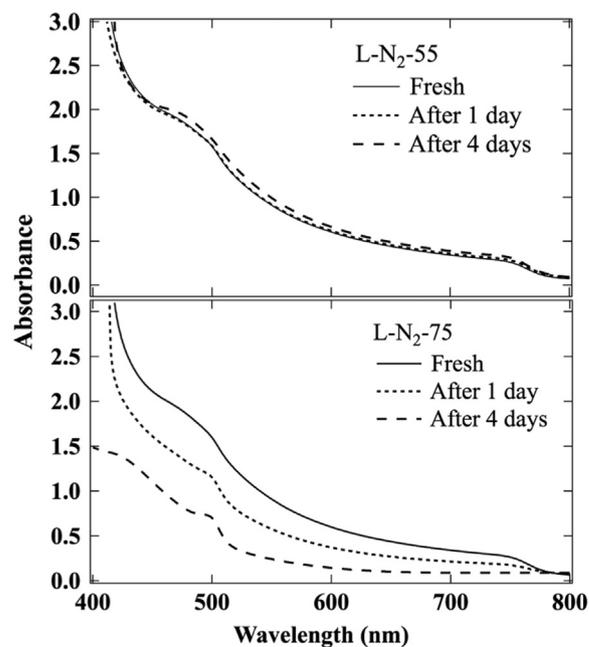


Fig. 1. The UV-Vis absorbance spectrum of MAPbI_3 perovskite films aged with intense light in N_2 filled environment in different positions. Top: the curves represent the perovskite film aged facing away from the lamp (face down) with temperature of 55°C . Bottom: the curves represent the perovskite film aged facing the lamp (face up) with temperature of 75°C .

is uncommon and does not resemble the bright yellow color of PbI_2 films - the typical remnant material after MAPbI_3 degradation. An image of the film before and after degradation process, compared with films aged in different setups, is shown in the [Supplementary information](#) ([Fig. S3](#)). By taking the UV-Visible absorbance spectra of the aged samples for 4 days of continuous illumination, as seen in [Fig. 1](#), we confirmed that only the sample exposed to light with elevated temperature was degraded and lost the signature perovskite onset at 790 nm that reflects the optical bandgap ($E_g = 1.56$ eV) [14].

To understand the role of heat in the degradation process, the stability of MAPbI_3 films were observed at different temperatures (75°C , 85°C , and 95°C) without light exposure. The perovskite films were aged on a hotplate in a dark, N_2 filled setup; their UV-Vis absorbance spectra are illustrated in [Fig. 2](#). It is clear that after 1 day the perovskite started to show slight degradation at 85°C , and showed almost complete degradation at 95°C . This result is in agreement with previous studies that reported thermal decomposition in MAPbI_3 at 85°C in an inert atmosphere [15,16]. Meanwhile, the sample kept at 75°C , the same temperature as the degraded sample under light, did not show any sign of degradation. Therefore, it is likely that the intensity of the light added energetic effects to trigger degradation of the perovskite at 75°C .

To determine the degradation pathway, the changes in the perovskite structure aged under these various conditions were measured via XRD analysis, as shown in [Fig. 3](#). For comparison purposes, MAPbI_3 films were prepared and aged under light in dry air at room temperature (22°C) using the same setup detailed in a previous paper [10]. It is well documented that O_2 plays a crucial role in light induced degradation of perovskite, where free radicals such as superoxides are generated and subsequently interact with the organic cation of the perovskite molecule, which leads to degradation to PbI_2 [10–12]. As shown in [Fig. 3](#), The fresh sample showed the expected diffraction peaks assigned to (110), (220), (310) and (330) at 14.23° , 28.47° , 31.85° , and 43.08° respectively, with lattice parameter values of $a = 12.5 \text{ \AA}$, $b = 26.6 \text{ \AA}$, and $c = 8.92 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$ that indicate an orthorhombic structure [17]. The XRD spectra of the degraded MAPbI_3 films (light in dry air and in dark with high temperature

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