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THE STABILITY STUDIES OF MIXED HALIDE PEROVSKITE $CH_3NH_3PbBr_XI_{3-X}$ THIN FILMS IN AMBIENT WITH AIR HUMIDITY 70% USING UV-VIS SPECTROSCOPY AND X-RAY DIFFRACTION

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ABSTRACT

Perovskite Solar Cells (PSC), with the efficiency of more than 22%, has shown promising prospects for the future of environmentally friendly technology. However, low stability on humidity is a major problem limiting the commercialization of PSC. The perovskite material commonly used as a perovskite solar-cell active material is methylammonium lead tri-iodide ($CH_3NH_3PbI_3$ or $MAPbI_3$) prepared with a mixture of methylammonium-iodide (MAI) and lead iodide (PbI_2). Perovskite material $MAPbI_3$ is hygroscopic and easily decomposed into its constituent material, thereby reducing the performance of the PSC. Meanwhile, perovskite methylammonium lead-bromide ($MAPbBr_3$) has higher moisture stability than $MAPbI_3$ because it has a cubic crystal structure that has high symmetry. However, the efficiency of solar cells using $MAPbBr_3$ as active material is lower than that of $MAPbI_3$, due to a higher bandgap (~2.2 eV) than that of $MAPbI_3$ (~1.5 eV). Therefore the wavelength range of sunlight absorbed by $MAPbBr_3$ is shorter. We have studied the effect of the ratio of Bromium ion (Br^-) insertion into $MAPbI_3$ perovskite, forming mixed perovskite halide $MAPbBr_xI_{3-x}$ on the stability of thin perovskite films in ambient with air humidity 70%. The value of x is varied from x = 0, 0.25, 0.5, 0.75 and 3. We measured the evolution of UV-Vis spectra and XRD patterns of thin perovskite films. The $MAPbBr_3$ perovskite film is the most stable in high air relative humidity (> 70%). While mixed perovskite films with x = 0.5 are more stable as compared to the other x values based on absorption spectra. The XRD results showed that the stability of mixed halide perovskite is decreased with the increasing of x value.

Keywords: mixed halide perovskite, absorption spectra, crystal structure, humidity, stability

INTRODUCTION

Perovskite solar cells have been developing very rapidly and have been able to produce power conversion efficiency (PCE) above 22% since it first developed in 2009 with PCE 3.9% [1,2]. Recently, PCE 26% has been generated for tandem solar cells with silicon [3]. The most commonly used perovskite material for solar cells is methylammonium lead triiodide $CH_3NH_3PbI_3$ or $MAPbI_3$. This is because $MAPbI_3$ has a bandgap of around 1.50 eV and has a range of light absorption ranging from the ultra-violet to near-infrared (800 nm) [4]. Therefore, it is expected to produce solar cells with the same PCE with silicon solar cells that currently dominate the market. The advantages of perovskite are that it is easy to process, low cost, and optoelectronic properties can be controlled by replacing halide ions [5,6]. Although the PCE of perovskite solar cells is the same as silicon solar cells, the problem of stability, especially against humidity, temperature, and UV radiation, hinders it for mass production and commercialization of perovskite solar cells [7,8]. Perovskite material is hygroscopic, and easily decomposed into its constituents, thereby reducing solar cell performance. Previous studies have shown that perovskite solar cells are strongly influenced by humidity [9,10]. Therefore, it is necessary to develop perovskite material, which is stable to humidity, especially high humidity above 70%.

Perovskite material $MAPbI_3$ has three crystalline structures/phases that are stable at different temperatures, namely orthorhombic, tetragonal, and cubic [11]. Perovskite will be stable in the pseudo-tetragonal crystal structure, which is between the tetragonal and cubic crystal structure. Perovskite $MAPbI_3$ has a tetragonal crystal structure at room temperature, whereas $MAPbBr_3$ has a cubic structure at room temperature. The mixture of Bromide ion and Iodide ions will form perovskite mixed-halide $MAPbBr_XI_{3-X}$ is expected to increase the stability of the perovskite film and also the stability of solar cell to humidity. Our previous study showed that the insertion of Br ion increased the optical bandgap, and the crystal structure changed from tetragonal to cubic [12].

In this paper, we report our stability studies on mixed-halide perovskite $MAPbBr_XI_{3-X}$ thin films. The stability studies have been performed in ambient with a temperature of 27°C and air relative humidity larger than 70%. We measured the evolution of UV-Vis absorbance and X-Ray Diffraction (XRD) pattern of mixed perovskite thin films. The values of ion Br fraction (x) were 0, 0.25, 0.5, 0.7 and 3. We evaluated the changes of UV-Vis peak absorption of thin films and the changes of XRD main peak of thin films to observe the impact of Br-ion insertion on the stability of mixed perovskite films against humidity.

METHOD

Methylammonium iodide (MAI > 99%), methylammonium bromide (MABr > 99%), lead iodide (PbI_2, 99.999%) were purchased from Lumtec Technology Corp. Taiwan. Dimethylformamide (DMF) solvent was purchased from Sigma Aldrich. All materials are used as received directly without any further purification.

The preparation of perovskite halide was carried out stoichiometrically according to the reaction:

$$(1-x)\, MAI + PbI_2 + xMABr \rightarrow MAPbBr_xI_{3-x} \tag{1}$$

where x is calculated in molars, and its value was varied from 0, 0.25, 0.5, 0.75, and 3. For the calculation of the molarity of each material, molecular weight quantities for MAI, MABr, and PbI_2 were 159 gr/mol, 112 gr/mol, and 461 gr/mol, respectively. The $MAPbI_3$ perovskite solution was prepared by dissolving 159 mg of MAI and 462 mg of PbI_2 in 1 mL DMF. The solution was then stirred with a magnetic stirrer at 300 rpm while heated at a temperature of 70°C for 30 minutes. The solution was then centrifuged at 300 rpm for 15 minutes. Perovskite thin films were prepared by the spin-coating technique of solution on the substrate at 5000 rpm for UV-Vis spectroscopy measurements, while for XRD film measurements, the films were spin-coated at 1000 rpm. $MAPbBr_3$ solution was carried out by mixing 112 mg MABr and 461 mg PbI_2 in 1 mL DMF. The preparation of $MAPbBr_3$ thin films was carried out using a similar procedure as $MAPbI_3$ thin films. While the manufacture of perovskite halide $MAPbBr_XI_{3-X}$ mixture was done by adjusting the value of x according to the reaction equation (1). After the spin-coating process, the perovskite film was heated on a hot plate at 70°C for 60 minutes. Thin perovskite films for UV-Vis spectroscopy measurement were spin-coated on a quartz substrate, while for XRD measurements, thin films were spin-coated on a glass substrate. The XRD measurements were conducted from different films.

UV-Vis absorbance spectra of thin films were carried out using T70+UV/Vis spectrometer at the Material Physics Laboratory, Department of Physics, Universitas Padjadjaran. XRD measurements were conducted using X-ray Diffraction PANalytical X'Pert PRO 40 kV 30 mA PW3040/x0 Cu-Kα with wavelength 1.54 Å at Pusat Survey Geology Bandung. Perovskite film stability study using UV-Vis spectroscopy was carried out by measuring the absorbance of thin films every 2 hours after the preparation of films (0 hours) to 8 hours and then measuring again after 24 hours. The films were stored in a dark room at a temperature of 27°C and relative humidity of larger than 70%. At the same time, the XRD measurements were done every 24 hours from just prepared to 48 hours after thin film preparation. Those UV-Vis and XRD measurements were performed to study the effect of Br-ion insertion on the stability of mixed perovskite films against humidity.

RESULT AND DISCUSSION

UV-Vis absorbance spectra of perovskite thin films $MAPbI_3$ and $MAPbBr_3$ as a function of time are shown in FIGURE 1. The absorbance of thin films $MAPbI_3$ decreases with increasing time, which shows that the films degrade after stores at room temperature with humidity larger than 70%. While the absorption spectra of $MAPbBr_3$ films almost do not change after 24 hours.

This study shows that $MAPbBr_3$ is more stable than $MAPbI_3$ against humidity. From FIGURE 1, we also observe that the absorption range of $MAPbI_3$ is wider than that of $MAPbBr_3$, which shows that the optical bandgap of $MAPbBr_3$ is larger than $MAPbI_3$. Our previous study showed that the insertion of Br-ion into $MAPbI_3$ changed the optical bandgap (E_g) according to equation [12]:

$$E_g(eV) = 1.58 + 0.28x \tag{2}$$

where x is the fraction of Br-ion. Our results showed that the optical bandgap of mixed-halide perovskite well agreed with reported results by *Atourki et al.* [13], except for $MAPbI_3$ due to our degraded film. They prepared the films in a vacuum to avoid degradation due to oxygen and humidity, while our films were prepared in ambient with humidity higher than 70%.

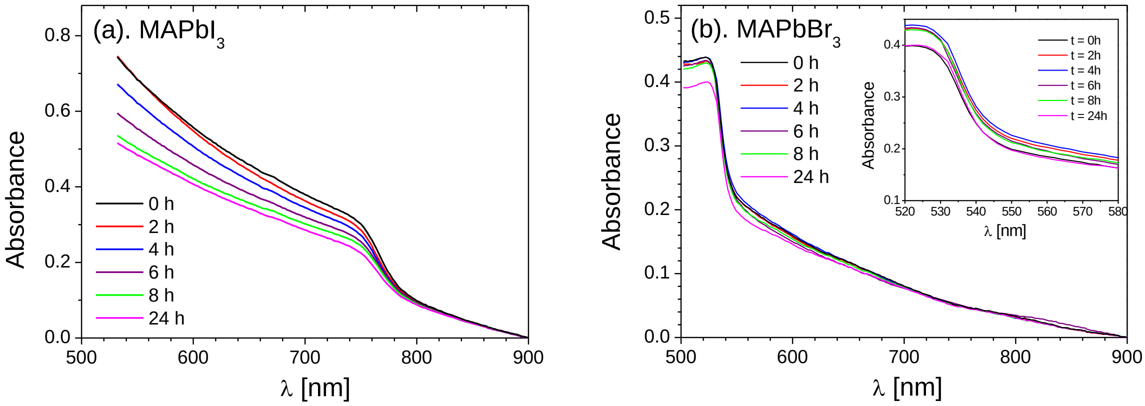

FIGURE 1. The absorbance of perovskite thin films as a function of time (a). $MAPbI_3$, and (b). $MAPbBr_3$. The insert is UV-Vis spectra of $MAPbBr_3$ in the range of wavelength from 520 nm to 580 nm to observe the different spectra clearly.

The absorbance spectra of mixed perovskite $MAPbBr_XI_{3-X}$ films show decreasing their absorbance with increasing time. To study the optical stability of mixed halide $MAPbBr_XI_{3-X}$ films, we evaluate the changes of absorbance peaks of all films at a certain wavelength. The wavelength for each x value is different because it has a different absorbance range. For variations x = 0, 0.25, 0.50, 0.75 and 3, the absorbance differences are measured at wavelengths of 740 nm, 734 nm, 710 nm, 672 nm and 524 nm, respectively. The absorbance value is normalized to its initial value (film just prepared or 0 h) to observe changes in absorbance value as a function of the storage time of the perovskite film. The changes of absorbance of perovskite film at a certain wavelength as a function of time are displayed in FIGURE 2.

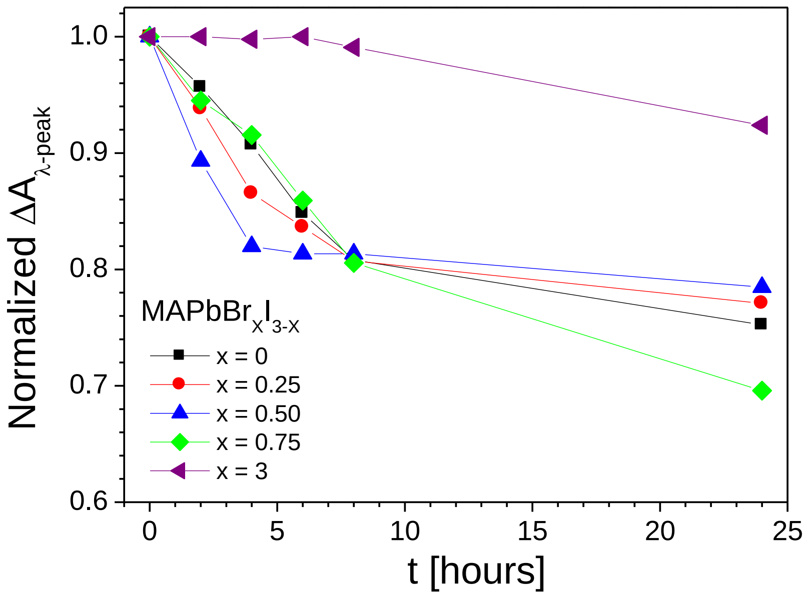

FIGURE 2. Normalized absorbance of perovskite thin films at a certain wavelength as a function of time.

It can be seen from FIGURE 2, that the $MAPbBr_3$ perovskite film is the most stable against air humidity larger than 70%, which is indicated by a small change in absorbance with increasing storage time. While, mixed perovskite halide films with x = 0.50 have higher stability compared to x = 0, 0.25 and 0.75 after being stored for 24 hours. In order to observe more clearly the effect of Br ions insertion into the stability of the films, we plot the difference of absorbance peak at a certain wavelength ($\Delta A_{\lambda\text{-peak}}$) as mention above as a function of Br-ion fraction x, as shown in FIGURE 3. Perovskite $MAPbBr_3$ film has the highest moisture stability after being stored for 24 hours, indicated by the lowest value of $\Delta A_{\lambda\text{-peak}}$.

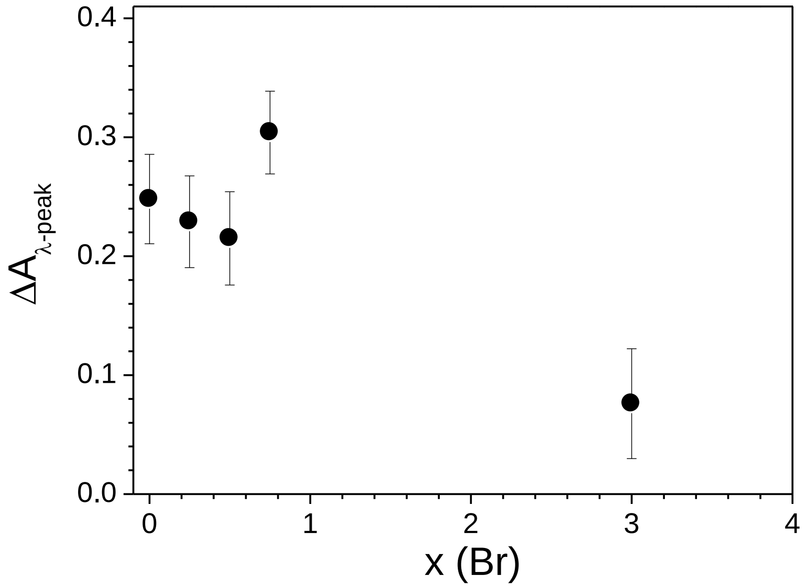

FIGURE 3. Changes in absorbance of thin mixed-halide perovskite films as a function of x after being stored 24 hours at room temperature and air humidity larger than 70%.

The effect of Br ions insertion on air humidity was carried out by *Noh et al.* [5]. They tested the stability of solar cells made from perovskite halide mixed $MAPb(I_{1-x}Br_x)_3$ against 33% relative humidity and room temperature. On the 4th day, the solar cells were exposed to 55% humidity. The results showed that solar cells with the insertion of Br (x) ions are 0.20 or x = 0.6 is the most stable after being stored for 20 days. Whereas for solar cells with perovskite x = 0 or $MAPbI_3$, the efficiency decreased by 60% to its initial value due to the degradation of perovskite film. Their study has the same result with our study that the mixed perovskite film is stable to the humidity for value x = 0.50.

XRD patterns of $MAPbI_3$ and $MAPbBr_3$ perovskite films measured after preparation (as-prepared or 0 hours) and after storage at room temperature with air humidity larger than 70% for 24 hours and 48 hours are shown in FIGURE 4.

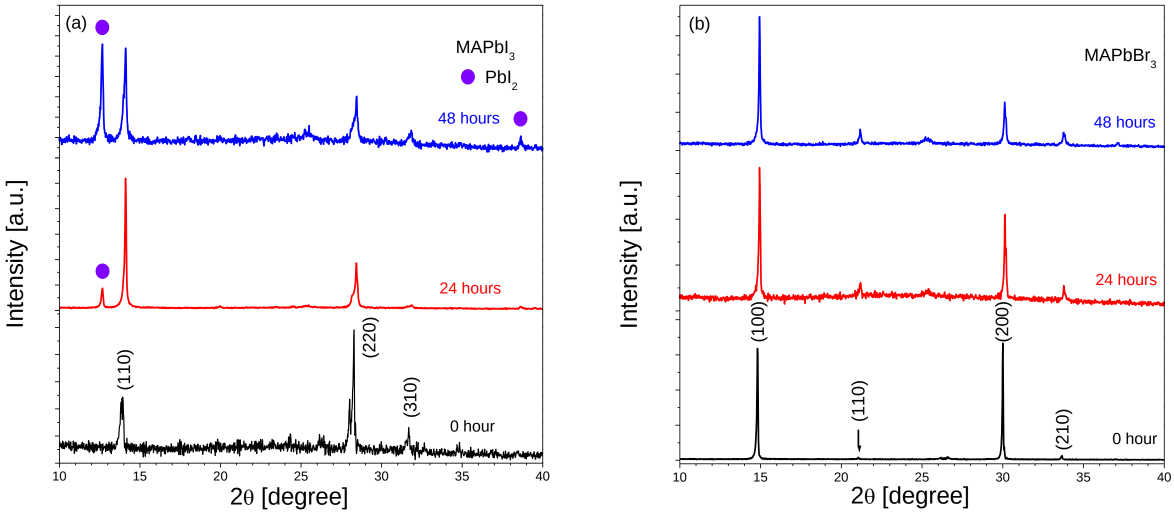

FIGURE 4. XRD patterns of $MAPbI_3$ and $MAPbBr_3$at just as prepared (0 h), after 24 and 48 hours being stored 24 hours at room temperature and room humidity larger than 70%.

$MAPbI_3$ perovskite XRD pattern shows three-main diffraction peaks at an angle of 14.15°, 28.50° and 31.94° corresponding to the diffraction peaks of the crystal fields (110), (220), and (310). Our previous study showed that $MAPbI_3$ perovskite has a tetragonal crystal structure with an I4mcm space group and majority crystal orientation in the x-y plane [4,14]. No PbI_2 peak at around 12.66° is observed which shows that PbI_2 is completely converted into perovskite $MAPbI_3$. Meanwhile, $MAPbBr_3$ shows a cubic crystal structure with a Pm3m space group [15], which is characterized by diffraction peaks at an angle of 14.8°, 21.0°, 30.0°, and 33.6°, corresponding to the diffraction peaks of the crystal plane (100), (110), (200), and (210), respectively [15]. The XRD pattern shows that the crystal field is predominantly oriented toward the x-axis. There is no diffraction peak that originates from $PbBr_2$ (at 18.61°), meaning that all $PbBr_2$ is converted to $MAPbBr_3$.

After being stored for 24 h, the peak at 12.62° has appeared and a new additional peak at 38.70° is observed after 48 h. Those peaks are originated from the PbI_2 crystalline plane (001) and (002), respectively. The peak intensity of PbI_2 also increases with increasing storage time. This study shows that the oxidation process of perovskite film due to humidity has occurred, indicating by the decomposition of perovskite into PbI_2. MAI ion bond is released due to reacting with water (H_2O) from humidity. However, the different behavior of the XRD pattern is observed in $MAPbBr_3$ film. The XRD pattern of $MAPbBr_3$ does not change with time and does not show the appearance of diffraction peaks originating from $PbBr_2$. This means that the $MAPbBr_3$ perovskite film is very stable to high humidity, as confirmed already by optical stability, as explained above.

To assess the effect of Br ions insertion on the stability of the mixed perovskite halide film using XRD, a diffraction intensity ratio calculation was performed at the peak of PbI_2 (12.62°) with the peak of the diffraction perovskite with the crystal plane (110) at an angle of 14°. The change in intensity ratio I (12.62°/14°) as a function of storage time (t) is shown in FIGURE 5. It appears that the $MAPbBr_3$ film is the most stable to high humidity, as also confirmed from UV-Vis absorbance (FIGURE 1). $MAPbI_3$ films are more stable than mixed halide $MAPbBr_XI_{3-X}$ perovskite with x = 0.25, 0.50 and 0.75. This result is different from the optical stability tests (absorbance of thin films), which showed that the more stable mixed-halide perovskite film is obtained with x = 0.50. This difference results are due to the XRD measurements are carried out on different films, while the UV-Vis absorbance measurements of thin films are carried out on the same film. Therefore, in order to confirm changes in XRD patterns due to oxidation, in-situ measurements with the same film are required.

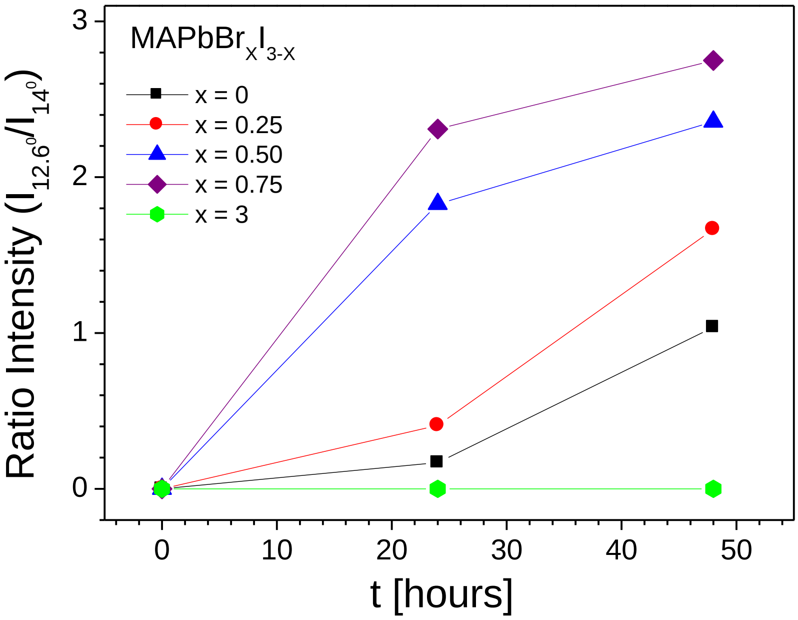

FIGURE 5. Changes in the ratio of diffraction peak intensities at angles of 12.6° (PbI_2) and 14° (perovskite) of perovskite film as a function of storage time.

CONCLUSION

We have studied the stability of mixed halide $MAPbBr_XPbI_{3-X}$ perovskite films with variations in the value of x = 0, 0.25, 0.50, 0.75, and 3 using UV-Vis spectroscopy and XRD to assess the effect of Br ions insertion on the stability of the perovskite film against high relative humidity above 70%. The UV-Vis spectroscopy and XRD measurements of perovskite films showed that $MAPbBr_3$ film is the most stable against high air humidity. The UV-Vis absorbance stability measurement showed that for mixed-halide perovskite films, the x = 0.5 is more stable than other x values including $MAPbI_3$ (x = 0), except if comparing with x = 3 ($MAPbBr_3$). The XRD study, however, showed different results that the perovskite is increasingly unstable with an increased value of x, except for x = 3 or MAPbBr.

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