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Using photoluminescence to monitor the optoelectronic properties of methylammonium lead halide perovskites in light and dark over periods of days

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A B S T R A C T

The degradation of methyl-ammonium lead iodide ($MAPbI_3$) upon exposure to air is a potentially limiting effect for large scale $MAPbI_3$ photovoltaic production. Here, we report a systematic study on effects of air-exposure on the structural and optical properties of $MAPbI_3$ thin films. The X-ray diffraction studies indicate a shrinking volume of $MAPbI_3$ upon air-exposure as the material decomposes back to its precursors, methyl amine (CH_3NH_2) and lead iodide (PbI_2). However, the photoluminescence (PL) yield and carrier lifetime measured with time-resolved photoluminescence, show an increasing trend upon air-exposure. These phenomena can be explained by self-passivation of $MAPbI_3$ grains by PbI_2 layer that reduces the number of non-radiative recombination centres at the grain boundaries. However, this process is not self-limiting and it eventually leads to a film that has completely reverted back to its precursor state. It is shown that this conversion of $MAPbI_3$ film back to its precursors is also accelerated by exposure to laser illumination. Furthermore, we report unusual variation of PL intensity on a shorter time scale of a few seconds in all the films used for the experiment. The variations are found to follow different trends in the encapsulated samples as compared to the un-encapsulated samples. We propose that the decomposition followed by the ionic diffusion through film is responsible for such unusual behaviours.

1. Introduction

Hybrid organic-inorganic metal halide perovskite has rapidly emerged to be one of the most promising solar photovoltaic materials recently. A few outstanding properties which enable these materials to yield high efficiency solar cells are optical absorption coefficients > $10^4\ cm^{-1}$, doping tunability from n- to intrinsic to p-type [1–3], long minority carrier lifetimes, efficient ambipolar carrier transport properties [4], and tunable band gaps across the solar spectrum. Moreover, a low-cost synthesis process adds to making this material a preferable ingredient for inexpensive and efficient solar cell technology. This is evident from the steep progress in power conversion efficiency (PCE) of lead based perovskite solar cells from mere 3.8% [5] to more than 21% [6] in just over half a decade.

Studying the nature of I-V curves may reveal important information regarding perovskite solar cells leading to a better understanding. More

specifically, there are some unusual characteristics such as a strong hysteresis in I-V curve and slow dynamic responses, which make research into this material system a worthwhile effort. Snaith et al. [7] reported anomalous hysteresis in the lead iodide perovskite cells and proposed three possible mechanisms to explain it, viz. charge trapping at the surface or interfaces, applied field dependent polarization of the material and migration of excess interstitial ions under the applied field. On the other hand, Gottesman et al. [8] proposed that the cause of hysteresis could be photo-induced structural changes in the materials. On a very similar note and as a re-establishment of Snaith's findings, Chen et al. [9] explained the hysteresis on basis of ferroelectric polarization of the material whereas Shao et al. [10] holds the trap states at the surface and grain boundaries responsible for the I-V hysteresis. Jacobs et al. [11] also explained the hysteresis behaviour in light of complex responses from charge trapping and ion migration.

Thus, there is no consensus among the research groups regarding

the specific physics behind these seemingly unusual behaviours of perovskite based solar cells, which may be because most studies were carried out with non-identical parameters such as different device structures and different growth routes. Furthermore, another point of interest rises from the fact that it is also necessary to isolate the effects of contacts and other materials in the stack in order to establish whether the effect is inherently caused by the perovskite layer or as a result of the combination of perovskite with interfacing materials.

In addition, as far as the technology development is concerned, the major road-block in development of commercially viable solar PV devices, despite of its advancing efficiency, is poor stability and reproducibility of MAPbI$_3$. The fast degradation of perovskites under ambient conditions is largely related to the irreversible formation of PbI$_2$, CH$_3$NH$_2$ and HI materials at room temperature [12]. Yang et al. [13] reported reduction of 20% in the initial efficiency within 24 h and 80% within 6 days for high efficiency cell (19.3%) kept in dry, inert environment. The cells kept in ambient air showed more than 80% reduction in the initial efficiency just within 24 h. However, Philippe et al. [14] showed that the degradation triggers right at the annealing stage and slow degradation continues even in the inert atmosphere with good encapsulations. Efforts are now being put up to improve the long term stability. Recently some promising results have been reported by using butylphosphonic acid 4-ammonium chloride as an additive into the perovskite lattice [15] and carbon as hole transporting material [16] and counter electrode instead of gold or silver [17,18]. Reported data strongly suggests that degradation of lead perovskite is due to decomposition of material back to the precursors [19]. However, the exact rapid-degradation mechanism is still the subject of further investigations.

One potential way to probe the degradation and decomposition mechanisms in the hybrid organic-inorganic perovskites is to observe the optical properties of the material as a function of time. The luminescence emitted by the material can yield a strong hint towards the changes taking place during degradation. Interestingly, there are reports of light assisted degradation in the literature [20,21]. The applied bias can also help ion migration that could lead to permanent changes in the material [11]. Thus it requires a very carefully designed and controlled experiment to understand the complex effects of degradation due to light, applied bias and ambience.

Here, we report a systematic investigation on illumination and air-exposure induced degradation of isolated methyl ammonium lead iodide (CH$_3$NH$_3$PbI$_3$) films. We used two sets of samples of CH$_3$NH$_3$PbI$_3$ films, one was encapsulated in glove box immediately after deposition and the other was left un-encapsulated in ambient air. Both samples were subjected to the X-ray diffraction (XRD), time-resolved photo-luminescence (TRPL), and PL at certain time intervals for a few days. We also studied the variation of PL intensity on a shorter time scale as a function of exposure-time to laser on both the samples by turning the laser-shutter on and off for various time intervals. The experiment was repeated for at least three pairs of samples to check the reproducibility. The results are systematically analysed and presented here.

2. Experimental

Methyl ammonium lead iodide films were prepared on quartz substrate by a standard spin-coating procedure [22] in a glove box (O$_2$ < 1 ppm, H$_2$O < 1 ppm). The CH$_3$NH$_3$PbI$_3$ precursor was prepared by dissolving 0.28 g PbCl$_2$ (Sigma Aldrich) and 0.48 g MAI (Solarmer) in 1.25 mL N,N-dimethylformamide (DMF). The solution was stirred and placed on a hot plate at 70 °C overnight. The quartz substrate was cleaned and treated with O$_2$ plasma for 15 min before use. Subsequently the precursor solution was spin coated at 2000 rpm followed by annealing at 105 °C for 120 min. A color change of the film from light yellow to dark brown was observed during the annealing process. One of the sample films was encapsulated with a quartz coverslip inside the glove box in inert atmosphere ensuring no exposure to the ambient air.
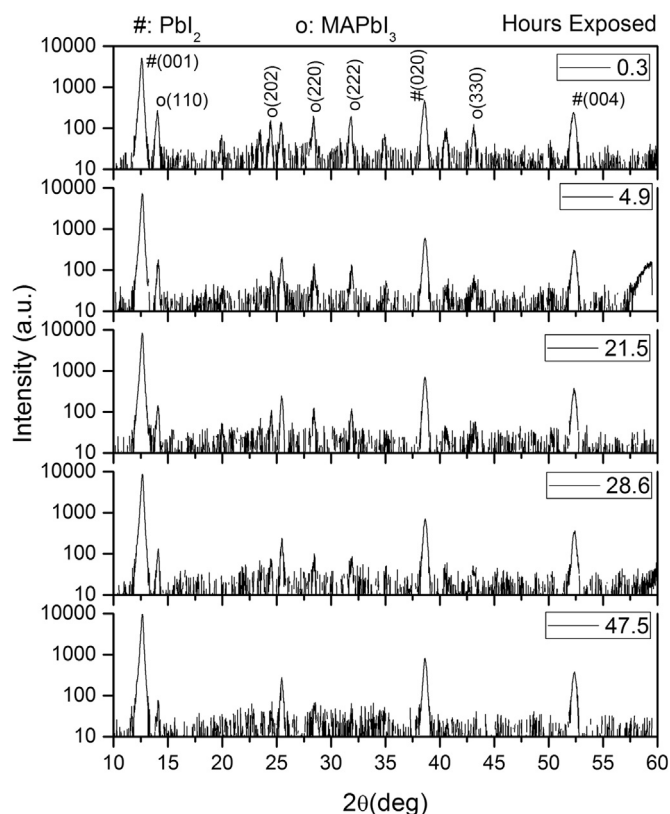

Fig. 1. Relative evolution of diffraction peaks corresponding to PbI$_2$ and MAPbI$_3$ over time in the XRD patterns of un-encapsulated sample on exposure to ambient air. The XRD peaks corresponding to PbI$_2$ and MAPbI$_3$ are indicated with # and o, respectively.

Whereas the other sample film was kept un-encapsulated. The XRD measurements were carried out with diffractometer with Cu Kα radiation. For TRPL, the samples were excited by 650 nm wavelength, 100 ps laser pulses at 50 MHz repetition rate with average power of 0.1 mW using BHL-600 ps laser diode. The PL decay was recorded using time-correlated single photon counting using SPC-630 module. The Photoluminescence measurements were carried out using 532 nm wavelength CW excitation source and the emission was recorded using Ocean Optics USB-2000 spectrometer. The power density of excitation source was maintained at about 15 mW/cm^2, which is too low to cause any significant structural or morphological changes in the films [23]. All the characterizations were carried out in air ambience at 300 K temperature, 32% humidity, 690 mmHg atmospheric pressure and with oxygen partial pressure of about 140 mmHg.

3. Results and discussion

Fig. 1 shows the XRD profiles of the un-encapsulated samples measured over time. The sample was kept in ambient air at room temperature. Strong peak observed at 2θ = 14° pertaining to CH$_3$NH$_3$PbI$_3$ [24]. We note the lack of peak at 12.6° that corresponds to PbI$_2$ phase [24] in the XRD profile measured at time zero (t = 0) i.e. immediately after removing the film from glove-box (not shown here); this confirms that the conversion of CH$_3$NH$_3$PbI$_3$ from the precursors was complete at t = 0. At t > 0 the XRD profiles shown shrinking volume of CH$_3$NH$_3$PbI$_3$ with increasing peak of PbI$_2$. Since the PbI$_2$ peak is very strong as compared to the CH$_3$NH$_3$PbI$_3$ peaks, the XRD profile is shown on logarithmic scale to emphasize the relative variations over time. This indicates that the film converts back to its precursor state, i.e. PbI$_2$, in the presence of air at room temperature. However, the decreasing volume of CH$_3$NH$_3$PbI$_3$ and expanding volume of PbI$_2$ with time as indicated by the XRD spectra was accompanied by