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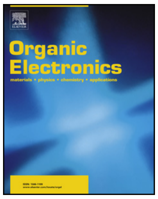

Impact of excess lead on the stability and photo-induced degradation of lead halide perovskite solar cells

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ABSTRACT

The stability of perovskite solar cells exposed to prolonged solar irradiation is a major concern that has not been thoroughly investigated in the past. In this investigation, devices fabricated with the architecture, glass/ITO/PEDOT:PSS/$MAPbI_3$/PCBM/Ag using Pb acetate as a source material, were found to operate with an efficiency of about 13%. Adding excess amounts of Pb to the precursor resulted in a presence of Pb in the perovskite (PVS) active layer. In addition, the impact of photo-induced degradation on the device efficiency was investigated. X-ray Diffraction and Time-resolved Photoluminescence analyses were used to evaluate the impact of excess Pb before and after illumination. The results indicate that changes in the crystallinity occur without any significant decrease in charge carrier lifetimes, and this is attributed to the formation of the degradation product, $PbI_{2.}$ This by-product has been shown to have beneficial effects due to its influence in passivating grain boundaries and in altering the band structure at the interface between the active layer and the electron transport layer. This work demonstrates that 5 mol% excess Pb is the optimal concentration with respect to efficiency and stability of these devices. The devices can retain more than 50% of their initial efficiency after 1 h of simulated solar exposure, when compared to 0 mol% and 10 mol% excess Pb samples.

1. Introduction

Organic-Inorganic lead halide perovskite solar cells (PSC) have emerged as one of the most promising thin film photovoltaic technologies. This is because of the cost-effectiveness of their manufacturing methods and low-temperature synthesis processes [1–3], and their high power conversion efficiencies (PCE) [4–9]. However, instability in device performance due to photo-degradation is a major concern for the advancement of perovskite solar cells [10–12]. Several reports show that prolonged illumination to sunlight leads to device degradation [13,14]. Such degradation is attributed to several factors. Ito et al. have reported that perovskite film degradation could be a key reason [15]. Device degradation has also been attributed to a combination of light and thermal influences [16]. Interfacial degradation between the transport layer and the corresponding electrode has also been reported [17]. In this investigation, the formation of trap states due to ion migration is also a reason for the degradation in device performance [18–20]. Hence, the analysis of these defects [21] is important, and so is the elucidation of their impact on the stability of PSCs.

Lead iodide residue is commonly formed during solar-radiation induced degradation of PSCs, together with trap states in different environments [16,22]. A group of investigators have demonstrated improved device stability by using crosslinking additives, compositional engineering and the addition of other precursor materials [23–25]. Additives such as Benzoquinone are added to suppress the occurrence of trap states, and thereby, to improve device stability [26]. However, solar-radiation induced degradation needs to be further explored, since solar cells typically operate under constant illumination.

In this work, glass/ITO/PEDOT:PSS/$MAPbI_3$/PCBM/Ag devices were fabricated with an inverted architecture, using lead acetate as a source material. Characterization of the devices shows that adding excess lead into the precursor solutions (that were used for the perovskite active layer) results in higher stability (for exposure to prolonged illumination) compared to samples fabricated with no excess Pb in their precursor solutions. This increased stability against prolonged exposure is attributed to the formation of PbI_3 in the perovskite layers.

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2. Experimental procedure

The experimental procedure in this study was similar to that reported for our previous work [27]. Methylammonium iodide was purchased from Dyesol, and lead acetate trihydrate ($Pb(OAc)_2 \cdot 3H_2O$) was purchased from Alfa Aesar. Both materials were used as received. An initial perovskite precursor solution was prepared by dissolving 3.0 mmol MAI and 1 mmol $Pb(OAc)_2 \cdot 3H_2O$ in 1 mL of anhydrous DMF solution. Starting with this initial perovskite precursor solution, three different solutions were then prepared with differing excess Pb concentrations: 0 mol%, 5 mol% and 10 mol%.

Indium-doped tin-oxide (ITO) coated glass substrates were cleaned in the following sequence: detergent solution, deionized water, acetone, and isopropyl alcohol, followed by UV-ozone treatment for 10 min for each process step. The substrate was 2.5 cm × 2.5 cm in size, and the active device area (defined by the overlapping of ITO and Al electrodes) was 0.2 cm^2. Poly (3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS, Clevious PVP Al4083 filtered through a 0.45 μm filter) was spin-coated onto the ITO substrates at 4000 rpm, followed by a thermal anneal at 130 °C, for 15 min in a glovebox. $Pb(OAc)_2$:MAI solutions were then spin-coated onto the PEDOT layers for 60 s at 4000 rpm. A thermal anneal was then performed at either 80 °C for 15 min or 90 °C for 5 min to form the perovskite films. Phenyl-C_{61}-butyric acid methyl ester (PCBM, Aldrich) was dissolved in chlorobenzene, to result in a concentration of 20 mg/mL, and was then spin-coated on top of the perovskite layer at 1000 rpm for 30 s. The devices were then completed, with thermal evaporation of a 80 nm thick Al electrode.

The as-prepared samples were characterized using scanning electron microscopy (SEM-XL30 Environmental FEG (FEI)). X-ray diffraction (XRD) measurements were performed with an X-ray Diffractometer using an anode tension of 40 kV and a filament current of 45 mA to produce Cu $K\alpha$ radiation. A step-size of 0.01° was used during the analysis.

UV-Vis Absorption spectra were recorded using a Cary 5000 UV/VIS spectrometer. The lifetimes of charge carriers were determined from Photoluminescence (PL) characteristics, using a Picosecond Time-Correlated Single Photon Counting (TCSPC) Spectrofluorometer. The PL decay time for each perovskite film was monitored at 775 nm with a femtosecond Ti:S laser (Spectra Physics) with a frequency doubler and a pulse selector. The excitation wavelength was fixed at 425 nm.

Current density-voltage (J-V) characteristics of the solar cells were measured using simulated AM 1.5 global solar irradiation (100 mW/cm^2) from a xenon-lamp solar simulator (Spectra Physics, Oriel Instruments, USA). For illumination aging, the samples were placed under the solar simulator for prolonged time intervals before recording the J-V characteristics. In order to minimize the influence of moisture, the devices were placed into sealed environments and transferred to characterizations tools.

3. Results and discussion

The degradation of the current density of the devices as a function of time under constant illumination is shown in Fig. 1. As reported in our previous work, 5% excess Pb content resulted in the highest PCE, with a value of 12.9%, initially [27]. Following the 5% device were the 10% and 0% excess Pb devices with PCE values of 8.8% and 7.2%, respectively. Under simulated solar illumination, the device's PCE followed a similar trend of degradation over time as shown in Fig. 2. The degradation trend of the PCE shows that the 5% Pb structure retained the highest efficiency after 1 h of constant illumination when compared to the other samples. Various solar cell device parameters before and after degradation are tabulated in Table 1. While the J_{sc} degraded significantly, the V_{oc} and FF remained similar for all of the devices after illumination aging. The degradation trends of V_{oc} and FF of devices (measured every 10 min for 1 h) are plotted in Fig. S1 in the supplementary information.

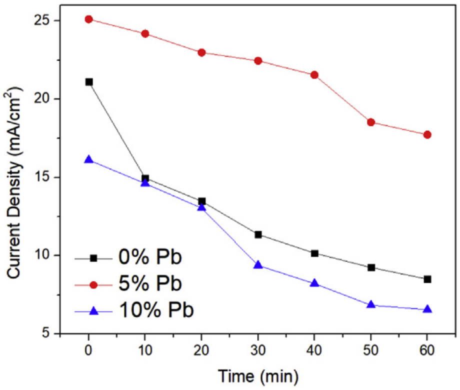

Fig. 1. J_{sc} degradation with time.

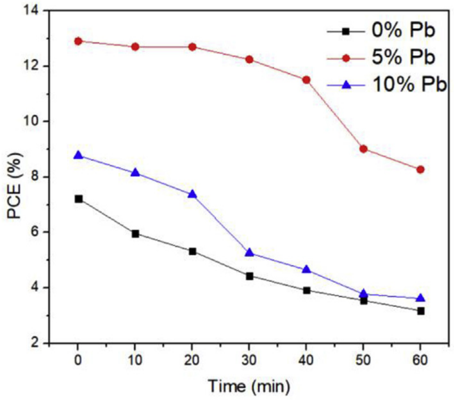

Fig. 2. PCE degradation with time.

Table 1
Solar cell device parameters for samples before and after degradation from 1 h illumination.

Sample details	PCE (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF
0% Initial	7.23	−21.12	0.84	0.48
0% degraded	3.18	−8.50	0.81	0.45
5% Initial	12.91	−25.11	0.81	0.63
5% degraded	8.27	−17.73	0.80	0.57
10% Initial	8.78	−16.11	1.00	0.56
10% degraded	3.62	−6.54	0.95	0.54

To further investigate the behavior of the devices, absorbance spectra were measured before and after illumination, and are shown in Fig. 3. The absorbance does not show any significant reduction with time, for all of the samples. However, a distinct hump is observed around 500 nm [22] for both 5% and 10% excess Pb samples. This can be attributed to an increased presence of PbI_2 in these samples, when compared to the 0% excess sample [22,28]. The higher PbI_2 is a direct result of higher Pb precursor concentrations. The reaction for the formation of $MAPbI_3$ and its decomposition can be summarized as follows [22,27]:

$$Pb(CH_3COO)_2 + 3CH_3NH_3I \rightarrow CH_3NH_3PbI_3 + 2CH_3NH_3CH_3COO\uparrow \quad (1)$$

$$CH_3NH_3PbI_3 \rightarrow PbI_2 + CH_3NH_2 + HI \quad (2)$$

The formation of PbI_2 is further evident from the XRD data shown in Fig. 4. The initial patterns showed that the $MAPbI_3$ peak is highest for the 5% excess Pb sample when compared to the 0% and 10% excess Pb samples. Photo-degraded samples show a decrease in the crystallinity of the (110) peak. This indicates structural degradation occurring due to