Article

An Environmentally Stable Organic–Inorganic Hybrid Perovskite Containing Py Cation with Low Trap-State Density

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Abstract: The commonly-employed methylammonium-based perovskites are environmentally unstable, which limits their commercialization. To resolve this problem, a stable hybrid perovskite, pyrrolidinium lead iodide (PyPbI$_3$), was synthesized successfully via a simple drop casting method. The formed PyPbI$_3$ exhibited a hexagonal structure. It presented not only excellent phase stability, but also low trap-state density, as confirmed via the X-ray diffraction and space-charge-limited currents measurements. This novel perovskite may be applicable to perovskite photovoltaics to improve their environmental stability.

Keywords: pyrrolidinium lead iodide; organic–inorganic hybrid perovskite; environmental stability; low trap-state density; phase stability; perovskite solar cell

1. Introduction

With the growing demands for renewable energy, photovoltaics (PV) becomes a popular research area [1,2]. Among all PV materials, organic–inorganic hybrid perovskite (OIHP) has attracted much interest in recent years. In general, OIHP has a formula of ABX$_3$, where A represents monovalent cations, B for metals (e.g., Pb) and X for halides. Methylammonium lead iodide, with a chemical formula of MAPbI$_3$, has been considered one of the most important OIHP materials [3]. It has been studied and reported that MAPbI$_3$ has many superior properties including long diffusion length [4,5], tunable bandgap [6,7] and high defect tolerance [8], which results in the rapid development of its power conversion efficiency (PCE) from 3.8% to 25.2% [9] within only ten years, making OIHP one of the most promising PV materials.

Despite their excellent performance in terms of energy efficiency, the lifetime of the fabricated perovskite solar cell (PSC) is far from ideal [10]. For example, an unencapsulated PSC device would lose 10%–30% of its initial PCE within only several days in ambient conditions [11]. Comparing that with other already commercialized PV materials such as silicon, which has a lifetime of more than 25 years [12], the much shorter lifetime of PSCs confines them as a lab-scale product.

In order to fight against the MAPbI$_3$ instability problems, numerous methods have been attempted. Although strategies such as interface engineering [13–15] and doping [7,16,17] were shown to improve the environmental stability of MAPbI$_3$ effectively, they did not enhance the lifetime to any appreciable level, as MAPbI$_3$ is intrinsically unstable [10,18].

In this regard, replacing the unstable MA cations seems inevitable. In 2014, formamidinium lead iodide (FAPbI$_3$) [19] was introduced to improve the stability of PSC, but despite the enhanced thermal stability, they suffered severe moisture and phase instability issues [20]. Incorporating small
inorganic cations such as cesium (Cs) to form the perovskite structure was also reported in 2015 [21], and the formed CsPbI$_3$ exhibited improved moisture and thermal stabilities, yet its phase was not stable at room temperature [22]. Most recently, ring-based molecules with a strong hydrophobic nature were considered as an alternative in replacing the conventional unstable MA molecule. In 2017 [23], a four-membered ring-based azetidine (Az) molecule was introduced into the perovskite crystal structure to form AzPbI$_3$. According to the results, the AzPbI$_3$ exhibited excellent moisture stability. However, the structure of AzPbI$_3$ was highly distorted, and its bandgap was not ideal (~2.15 eV). Chao et al. (2018) [24] simulated a three-membered ring-based perovskite, namely aziridinium lead iodide (AzPbI$_3$). Their results indicated that such perovskite exhibited a low bandgap of 1.49 eV, as well as enhanced structural stability compared with MAPbI$_3$ and FAPbI$_3$ in terms of the formation enthalpy. A major issue for AzrPbI$_3$ was that the aziridine molecule was highly toxic, which made it not practical for application. We thus reported in our previous work [25] a five-membered ring-based pyrrolidine (Py) molecule could be used to form a new perovskite pyrrolidinium lead iodide (PyPbI$_3$). The PyPbI$_3$ not only exhibited a lower bandgap (~1.80 eV) than AzPbI$_3$, but also showed good water- and high-temperature-resistance [9], providing a possible answer to the long-term PSC instability problem. However, the phase stability of PyPbI$_3$, equally important to the moisture and thermal stability, remains unknown. Moreover, other properties such as defect states, which affect the perovskite PV performance significantly, also need further investigation.

It is, therefore, the purpose of the current report to investigate the phase stability of PyPbI$_3$. The results of our stability measurements showed that PyPbI$_3$ exhibited only one phase in an ambient environment, indicating its excellent phase stability. The optical properties and morphology of the PyPbI$_3$ film were also evaluated. By conducting the space-charge-limited currents (SCLC) measurement in a capacitor-like device, we revealed that PyPbI$_3$ demonstrated a low trap-state density of $\sim 2.3 \times 10^{16}$ cm$^{-3}$, which is comparable to that of MAPbI$_3$. Our results indicated that PyPbI$_3$ is an environmentally stable OIHP material with great potential to be employed in perovskite PV applications.

2. Materials and Methods

2.1. Materials

$N,N$-Dimethylformamide (DMF, 99.99%) and PbI$_2$ (99.999%) were purchased from Sigma-Aldrich. Pyrrolidine hydroiodide (PyI, 98%) was purchased from TCI America.

2.2. Film Formation and Device Fabrication

The film was fabricated via a simple drop casting method. First, the ITO substrate was sequentially washed with distilled water and ethanol, two times with each. After 20 min of UV–O$_3$ treatments, 80 $\mu$L of PyI (80 mg) and PbI$_2$ (60 mg) in a DMF solution were drop cast on the substrate. The fabricated films were next annealed on a hot plate at 120 °C for 30 min in air. In the capacitor-like device, the metal electrode was further deposited by thermal evaporation of gold under a pressure of $5 \times 10^{-5}$ Pa.

2.3. Characterizations

Powder XRD measurements were conducted on a Bruker D8 DISCOVER diffractometer (Bruker Corporation, Billerica, Massachusetts, USA). The steady state photoluminescence (PL) measurement was taken at room temperature with an excitation wavelength of 514.5 nm. The film morphology image was taken by a FEI Magellan 400 XHRSEM scanning electron microscope (SEM) (FEI Company Magellan™ XHR, Midland, ON, Canada). The current density–voltage characteristics of the devices were obtained using a Keithley 2400 source-measure unit. The light intensity was calibrated using a KG-5 Si diode.
3. Results

3.1. Fabrication and Characterizations of the Perovskite Film

The PyPbI₃ film was fabricated by employing a simple drop casting method as illustrated in Figure 1 (Details shown in experimental section), following the methods reported in our previous work [9]. The thickness of the formed film was measured as 1500 nm by a profilometer. To investigate the crystal structure of the film, we conducted powder XRD measurements. The results are shown in Figure 2, and suggest the formation of PyPbI₃ in the film [9]. The relatively low intensity of the first peak could be attributed to the texture in the powder film.

![Figure 1. The schematic illustration of the PyPbI₃ film fabrication process.](image)

![Figure 2. XRD results of the fabricated PyPbI₃ film.](image)

The optical property of the PyPbI₃ film was evaluated via steady state photoluminescence (PL) measurement. The excitation wavelength adopted in this study was 514.5 nm. The PL result is shown in Figure 3, which shows a peak at around 600 nm, exhibiting a blue shift compared to our previous results [25]. This could be attributed to the different thickness of the perovskite film (in this work 1500 nm), leading to a change of its absorption property, as reported in the literature [26–28]. The relatively broad emission characteristic of the peak further indicates that the structure type of PyPbI₃ belongs to 1D perovskite [29]. In addition, the PL luminescence of PyPbI₃ remained the same after one hour in ambient conditions, which indicated its good moisture stability.

The morphology of the film was studied via field emission scanning electron microscope (SEM). As shown in Figure 4, the film consisted of many grains of micrometer sizes and had low grain boundary coverage area, which is comparable with that of MAPbI₃ [30].
3.2. Trap-State Density of the PyPbI\textsubscript{3} Film

To investigate the defect states in PyPbI\textsubscript{3} film, SCLC measurements were taken. We fabricated capacitor-like devices following steps shown in the experimental section. The structure of the device is illustrated in Figure 5, and was composed of ITO/PyPbI\textsubscript{3}/Au. From the current density–voltage (CV) curve shown in Figure 6, it can be observed that the CV response is ohmic at low voltage. Upon reaching the intermediate voltage, the defect states are filled by the injected charge carriers (refers to TFL), resulting in a linear relationship between the voltage ($V_{TFL}$) and the density of defect states ($N_{DEF}$). Following the methods mentioned in previous reports ($N_{DEF} = 2 \varepsilon \varepsilon_0 V_{TFL}/eL^2$) [11], $\varepsilon_0$ is the vacuum permittivity, $\varepsilon$ (~4.90, determined by RUFUTO 871) is the dielectric constant of PyPbI\textsubscript{3}, L (~1500 nm) is the thickness of the perovskite film, and $e$ is the elementary charge. The defect density was estimated to be $2.3 \times 10^{16}$ cm\textsuperscript{-3}, which is comparable to that of MAPbI\textsubscript{3} (~$10^{16}$ cm\textsuperscript{-3}), indicating a low trap-state density in the polycrystalline film of PyPbI\textsubscript{3}. The origin of the trap-states in PyPbI\textsubscript{3} was assumed to be located at the grain boundaries, as suggested in the literature [31].
3.3. Stability Measurements of the PyPbI3 Film

To investigate the phase stability of PyPbI3, a set of stability measurements was conducted. According to previous reports on MAPbI3 and CsPbI3, the perovskite phase transition was triggered by either raising humidity [18,32] or temperature [22]. We therefore conducted the phase stability measurements in two different environments. First, we evaluated the phase stability of PyPbI3 in moisture with a relative humidity (RH) of ~50%. The formed film was kept in a desiccator for one week. The results are illustrated in Figure 7. As can be observed, after one week in ambient conditions with a RH of 50%, the XRD patterns of PyPbI3 remained unchanged, indicating the moisture and phase stabilities of PyPbI3.

Next, we raised the temperature of the environment. The fabricated film was placed on a hot plate at a temperature of 85 °C for 6 h. From the XRD results (Figure 8), a tiny peak appeared at around 14.78°, correspond to the PbI2 peak. The PbI2 peak was assumed to be originated from the surface of the PyPbI3 film, as suggested in literature [33]. Apart from that, we did not observe any other unknown diffraction peak. In addition, previous TGA measurements [9] further indicated the thermal stability of PyPbI3, which is consistent with our XRD results.

Figure 5. Current–voltage curves of the devices adopting the as-illustrated configuration. Inset: Device scheme of ITO/perovskite/Au.

Figure 6. Initial XRD results of PyPbI3, and results after one week in ambient conditions with a RH of 50%.
with previous results, we can therefore conclude that PyPbI$_3$ (31 g/mol), related to the perovskite can be attributed to the strong hydrophobic nature of its pyrrolidine rings [9], which can repel the invasion of water molecules, as schemed in Figure 8. The high thermal stability can be compared to the former molecule is less volatile [11].

The above stability measurement results indicate that PyPbI$_3$ is highly phase-stable. Combining it with previous results, we can therefore conclude that PyPbI$_3$ exhibits excellent environmental stability compared to MAPbI$_3$. The results are further summarized in Table 1. We also explored the reasons for the enhanced environmental stabilities found in PyPbI$_3$. The excellent moisture resistance of the perovskite can be attributed to the strong hydrophobic nature of its pyrrolidine rings [9], which can repel the invasion of water molecules, as schemed in Figure 8. The high thermal stability can be related to the greater molecular weight of the Py molecules (71 g/mol) compared to the MA molecules (31 g/mol), as the former molecule is less volatile [11].

| Formula | MAPbI$_3$ | FAPbI$_3$ | CsPbI$_3$ | AzPbI$_3$ | PyPbI$_3$ |
|---------|-----------|-----------|-----------|-----------|-----------|
| Moisture stability | Bad [18] | Bad [31] | Regular [21] | Good [23] | Good [25] |
| Thermal stability | Bad [34] | Regular [19] | Regular [35] | N/A | Good [9] |

5. Conclusions

In conclusion, a five-membered ring-based perovskite PyPbI$_3$ was synthesized and its properties were characterized. The trap-state density of the polycrystalline PyPbI$_3$ film was calculated to be $2.3 \times 10^{16}$ cm$^{-3}$. The stability measurements reveal that PyPbI$_3$ is an environmentally stable perovskite,
which shows great potential for employment in PSCs to resolve their long-term instability problems. In the future, it will be of great significance to fabricate and investigate the PyPbI$_3$-only solar cell device.

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