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# Influence of organic cations on high-performance $CH_3NH_3PbI_3$ based photovoltaics

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ABSTRACT

A comprehensive study was carried out to understand the influence of organic cations on high-performance $CH_3NH_3PbI_3$ based photovoltaics. Scanning electron microscope, X-ray diffractometer, Hall measurement, absorbance spectrum, photoluminescence (PL) spectrum and nanosecond time-resolved PL measurements were used to explore the structural, electrical, optical and excitonic characteristics of $CH_3NH_3PbI_3$ thin films fabricated under different thermal annealing temperatures from 60 °C to 140 °C. The decrease in the open-circuit voltage ($V_{OC}$) with an increase in the thermal annealing temperature can be explained as due to the reduced work function of the $CH_3NH_3PbI_3$ thin film. The short-circuit current density ($J_{SC}$) of the $CH_3NH_3PbI_3$ based photovoltaics is dependent on the efficiencies of light absorption and carrier collection, which results in an optimized $J_{SC}$ when the thermal annealing temperature is 120 °C. The atomistic interaction between the organic cations and Pb–I framework strongly influences the absorbance of $CH_3NH_3PbI_3$ thin films, as confirmed by the libration of $CH_3NH_3$ cations shown by Raman scattering spectroscopy. In addition, the experimental results indicate that the power conversion efficiency can be further improved when the absorption strength of the $CH_3NH_3PbI_3$ thin film and the energy-level alignment of each photovoltaic layer are simultaneously fulfilled.



## 1. Introduction

Lead halide perovskite absorber ($CH_3NH_3PbI_3$, $CH_3NH_3PbI_{3-x}Cl_x$, and $CH(NH_2)_2PbI_3$) based photovoltaics which can be fabricated using one-step and two-step solution processes under low temperatures have been intensively investigated owing to their high power conversion efficiency (PCE). The high PCE of perovskite absorber (PA) based photovoltaics can be understood as due to two main reasons. The absorption bandgap of the PA is smaller than 1.6 eV [1–3], resulting in at least half of the sunlight being absorbed when the PA thickness is greater than 350 nm. For $CH_3NH_3PbI_3$ thin film, the small exciton binding energy (20–50 meV) [4], due to the larger Bohr radius [5], leads to a long exciton diffusion length (300 nm) [6] and a high efficient carrier generation at the interface between the $CH_3NH_3PbI_3$ and the electron transport layer (hole transport layer). In the first attempt at using $CH_3NH_3PbX_3$ (X=Br and I) as a light harvester it was fabricated in a dye-sensitized liquid-type solar cell structure [7]. There are three PA based photovoltaic structures with a PCE of more than 17%: the dye-sensitized solar cell structure, the regular-type organic photovoltaic (OPV) structure, and the inverted-type OPV structure. The highest PCEs for the above mentioned photovoltaic structures are 20.2% [8], 17.8% [9], and 19.3% [10], respectively. Among the three photovoltaic structures, the regular-type OPV structure has the lowest PCE due to the lower $V_{OC}$ which is smaller than 0.9 V. However, its advantage is that the PEDOT:PSS and PCBM thin films are used as the hole and electron transport layers, respectively. This means that a high PCE for flexible photovoltaics [11] can be achieved using a regular-type OPV structure because the fabrication temperatures of PEDOT:PSS and PCBM thin films are less than 120 °C.

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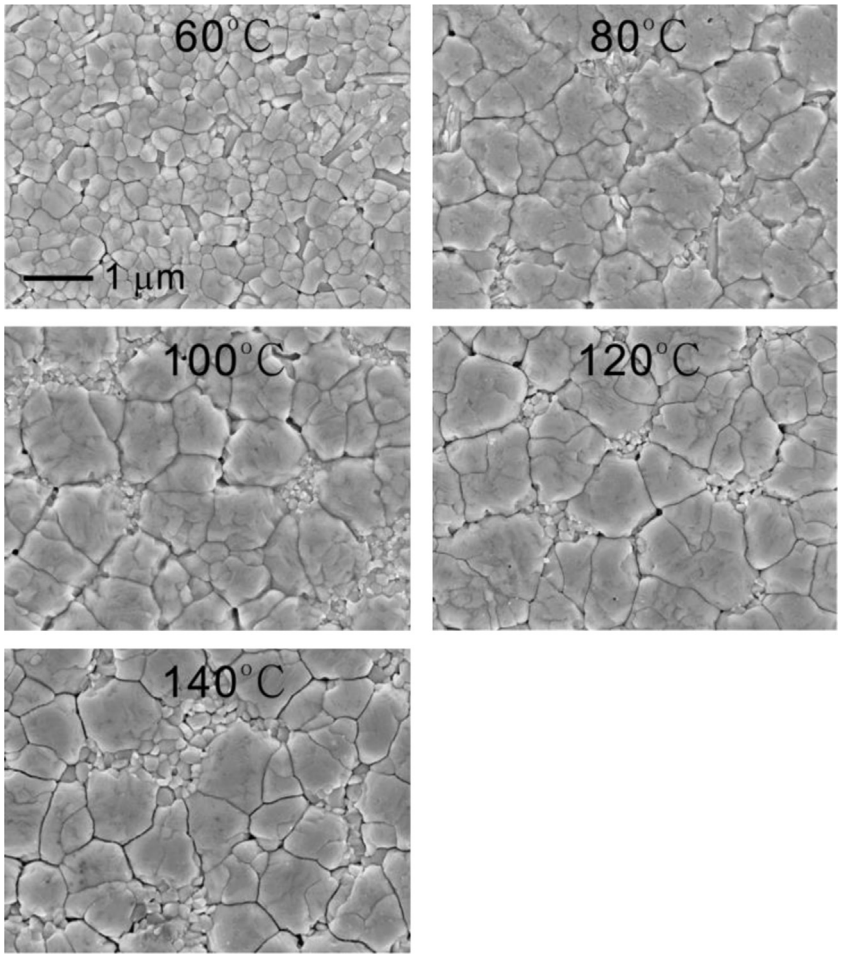


**Fig. 1.** SEM images of $CH_3NH_3PbI_3$ thin films fabricated with difference annealing temperatures.

The optimized thermal annealing temperature of PA is about 100 °C for high efficiency photovoltaics. In the two-step solution process, a long inter-diffusion time and moisture-controlled environment are needed for the formation of pinhole-free $CH_3NH_3PbI_3$ thin film, but the $V_{OC}$ ($J_{SC}$) is degraded (enhanced) by increasing the thermal annealing time at 105 °C. The $V_{OC}$ is decreased with an increase in the thermal annealing time due to the reduced work function in the $CH_3NH_3PbI_3$ thin film, as has been confirmed by UPS experiments [12]. The enhancement of the $J_{SC}$ with an increase in the thermal annealing time at 105 °C is strongly related to the increased absorption strength of the $CH_3NH_3PbI_3$ thin film. However, it is not yet completely understood why the absorption strength of the $CH_3NH_3PbI_3$ thin film is so highly influenced by the thermal annealing temperature and time. According to the first-principles calculation [13], $CH_3NH_3$ and Pb provides one and two electrons to $I_3$, respectively. The structure of $CH_3NH_3$ and Pb–I can maintain electric neutrality by the van der Waals force. Therefore, the absorption strength of the $CH_3NH_3PbI_3$ thin film might be related to the atomistic interaction between the $CH_3NH_3$ cations and Pb–I framework. One goal of this study is to explore the atomistic interaction of the $CH_3NH_3$ cations on the high-performance $CH_3NH_3PbI_3$ based photovoltaics.

## 2. Experiments

In the photovoltaic fabrication process, a 40 nm-thick PEDOT:PSS (1:6 wt%, AI4083) film was spin-coated onto transparent conductive indium tin-oxide (ITO) glass before being subjected to thermal annealing at 120 °C for 10 min, to act as the hole transport layer. $PbI_2$ (Sigma-Aldrich, 99%) and $CH_3HN_3I$ (Ruilong, 99.9%) were dissolved in a γ-butyrolactone/dimethyl sulfoxide mixture (1:1, v/v) as the $CH_3NH_3PbI_3$ precursor. The $CH_3NH_3PbI_3$ precursor was spin-coated on top of the PEDOT:PSS/ITO/glass with an in-situ non-polar solvent washing treatment [11,14,15]. The toluene was used as the washing solvent at room temperature. The fabrication process of the $CH_3NH_3PbI_3$ thin film is described in detail in our previous report [16]. After this, a 50 nm-thick $PC_{61}BM$ film was spin-coated on top of the $CH_3NH_3PbI_3$ film. The $CH_3NH_3PbI_3$ and PCBM thin films were prepared in a nitrogen-filled grove box which has a low relative humidity ( $< 2\%$). Finally, a 70 nm-thick Ag film was evaporated on top of the $PC_{61}BM$ film, to act as the cathode electrode. The active area of the photovoltaic device was $0.2 \times 0.5\ cm^2$. The current density–voltage ($J$–$V$) curves were recorded using a Keithley 2400 source-measurement unit. The intensity of the simulated sunlight was calibrated using an NREL-certified Si solar cell (Oriel, 91150V) with a KG-5 bandpass color filter to have an intensity of 100 $mW/cm^2$ (AM 1.5G). The surface morphologies and crystallizations of the $CH_3NH_3PbI_3$ thin films were analyzed by a high-resolution scanning electron microscope (SEM) (GeminiSEM, ZEISS) and X-ray diffractometer (XRD) (D8 Discover, Bruker), respectively. The absorbance spectrum of the $CH_3NH_3PbI_3$/glass was measured using a UV-visible spectroscopy (U-4100, HITACHI). The photoluminescence (PL) spectra, nanosecond time-resolved photoluminescence (NTR-PL) and Raman scattering spectra of the $CH_3NH_3PbI_3$ thin films were measured using an optical microscope system (UniRAM, Protrustech). For the PL and NTR-PL experiments, the wavelength, pulse duration, and