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Effects of Formamidinium and Bromide Ion Substitution in Methylammonium Lead Triiodide toward High-Performance Perovskite Solar Cells

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Abstract

Compositional engineering of organic-inorganic hybrid perovskite has attracted great research interests recently for seeking a better perovskite system to address existed challenges, such as the thermal and moisture instability, anomalous hysteresis, and toxic lead contamination, etc. In this study, we systematically investigated the structural, optophysical, and photovoltaic properties of the compositional $\text{MA}_x\text{FA}_{1-x}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ perovskite by sequentially introducing FA^+ and Br^- ions into the parental MAPbI_3 to elucidate their respective roles when they were inserted into the perovskite lattice. We unraveled that such dual compositional tuning in perovskite can improve the crystallinity of the resultant film and thus reduce its density of defect states as evidenced by admittance spectroscopy, resulting in a prolonged carrier lifetime over 500 ns. As a result, a promising average PCE (PCE_{AVG}) of 17.34% was realized in the optimized $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ -based PVSC with little hysteresis and stable photocurrent output. More significantly, another compositional $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite with a large bandgap of 1.69 eV can yield an impressively

high PCE_{AVG} over 15%. To the best of our knowledge, this performance is among the state-of-the-art large bandgap ($\sim 1.7\text{eV}$) PVSCs reported so far, which paves the way for the development of high-performance tandem cells using efficient large bandgap PVSCs as the top subcells. This study not only manifests the pivotal roles of dual compositional tuning in $MA_xFA_{1-x}Pb(I_yBr_{1-y})_3$ perovskites but also highlights the importance of compositional engineering for developing an even more efficient perovskite.

1. Introduction

Organic-inorganic hybrid perovskites have emerged as one of the most intriguing light-harvesting materials for solar energy due to their exceptional semiconducting properties and cost-effective solution processability.[1-5] Methylammonium lead triiodide perovskites ($MAPbI_3$) have received much attention, and high power conversion efficiencies (PCEs) of over 17% were reported recently.[6-7] However, $MAPbI_3$ still faces several complex challenges that need to be addressed, such as the thermal and moisture instability,[8-11] hysteretic current-voltage characteristics,[12-13] and toxic lead contamination[14-16], etc. In this regard, many researchers in this field have shifted their focus toward composition engineering of hybrid perovskites to seek a better system for photovoltaic applications.[9, 17-20] Tuning the organic cations or the halide anions of hybrid perovskites are the most common methods reported thus far.

Notably, formamidinium lead triiodide ($FAPbI_3$) perovskite shows promise as a photovoltaic material because its narrower bandgap (E_g) of 1.48 eV lies closer to the Shockley-Queisser ideal bandgap of ~ 1.40 eV for single-junction solar cells, meaning even higher PCEs can be realized. [21-22] However, controlling the phase purity of $FAPbI_3$ thin films is a significant hurdle to fabricating efficient $FAPbI_3$ -based perovskite solar cells (PVSCs). The appearance of the yellow non-perovskite δ -phase accompanies the formation

of black α -phase FAPbI_3 during annealing due to its relatively lower formation energy hinders the performance of the derived PVSCs due to its insulating properties.[1] Therefore, the most critical issue is to eliminate the formation of the δ -phase to obtain a pure black α -phase FAPbI_3 . Recently, Grätzel *et al.* partially substituted MA^+ with FA^+ ions in MAPbI_3 and reported higher PCEs for the perovskite $\text{MA}_{0.6}\text{FA}_{0.4}\text{PbI}_3$ than the parental perovskites.[19]

Halide substitution in MAPbI_3 has been widely investigated to date. Generally, the inclusion of chlorine in MAPbI_3 (denoted as $\text{MAPbI}_{3-x}\text{Cl}_x$) mainly results in the improved film coverage and crystallinity compared to the pristine MAPbI_3 as considering the fact that no detectable Cl is residual in the resultant film due to the release of MgCl during thermal annealing,[18, 23-24] while the inclusion of bromine ($\text{MAPbI}_{3-x}\text{Br}_x$) can effectively increase the E_g of the resultant perovskite thin films.[9] Recently, Seok *et al.* demonstrated a PVSC with a certified PCE of 20.1% using a perovskite with the composition of $(\text{FAPbI}_3)_{0.95}(\text{MAPbBr}_3)_{0.05}$, indicating the importance of composition engineering of perovskites.[17] Given the opposing impacts of the FA^+ and Br^- substitutions on the E_g of MAPbI_3 , the respective roles of these incorporated ions are still not readily understood at this stage.

In this communication, we systematically investigate the structural, photophysical, and photovoltaic properties of the compositional $\text{MA}_x\text{FA}_{1-x}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ perovskites and elucidate the respective roles of FA^+ and Br^- ions by sequentially introducing them into the compositional perovskites. The incorporation of FA^+ ions into MAPbI_3 to form $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ improved the crystallinity, carrier lifetime, and absorption of the resultant perovskite thin films. More importantly, the perovskite phase conversion temperature could be maintained at 100 °C despite the presence of FA^+ ions, which is much lower than that for forming pure black α -phase FAPbI_3 (150 °C). Subsequently, Br^- ions that were introduced to partially

replace Γ ions improved the crystallinity of the resultant film to reduce the density of trap states (N_T) as evidenced by the admittance spectroscopy. This enabled the optimized compositional $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ perovskite to possess a very long charge carrier lifetime of over 500 ns. As a result, a high average PCE (PCE_{AVG}) of 17.34% was realized in the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ -based PVSC with little hysteresis and stable photocurrent output, outperforming the cells derived from the parental perovskites and those with other compositions. More encouragingly, a compositional $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite with a large E_g of 1.69 eV exhibited a high PCE_{AVG} over 15%. To the best of our knowledge, this performance is among the state-of-the-art large E_g ($\sim 1.7\text{eV}$) PVSCs reported so far.[25] The synergistic effects in tuning perovskite composition revealed in this work signify that perovskites with different compositions in addition to MAPbI_3 deserve more in-depth understanding from physical and crystallographic aspects.

2. Experimental Section

2.1. Material preparation

Lead iodide, lead bromide, nickel acetate tetrahydrate, copper acetate monohydrate, PC_{61}BM and C_{60} were purchased from Sigma-Aldrich, and PC_{61}BM was purified before use. Methyl ammonium iodide and formamidinium iodide was synthesized according to previously reported methods.[18, 20] Bis- C_{60} was synthesized as reported in our previous work.[26]

A 0.1 M NiO_x precursor solution was prepared by dissolving nickel acetate tetrahydrate into ethanol, followed by adding 0.6 vol% ethanolamine into the solution. Separately, A 0.1 M Cu precursor solution was prepared by dissolving copper acetate monohydrate into ethanol. The final Cu-doped NiO_x precursor was prepared by mixing the NiO_x precursor and Cu precursor solutions at volume ratio of 95:5.[6] Compositional perovskite precursors (1 M) were prepared by dissolving MAI, FAI, PbI_2 and PbBr_2 with different ratio into a mixed solvent of dimethylsulfoxide and γ -butyrolactone (volume ratio of 3:7) and stirred at 60 °C

for 12 h. Mixed PC₆₁BM and C₆₀ solutions (15 mg mL⁻¹) were prepared by dissolving PC₆₁BM and C₆₀ into dichlorobenzene with a weight ratio of 1:1. Bis-C₆₀ surfactant solution (2 mg mL⁻¹) was prepared by dissolving Bis-C₆₀ into isopropyl alcohol followed by sonication for one hour.

2.2. Device fabrication

ITO glass (15 Ω sq⁻¹) was cleaned by sequentially sonication with a detergent solution and deionized water, acetone, and isopropyl alcohol for 10 min, respectively. After drying with a nitrogen flow, the ITO glass was further treated with UV ozone for 5 min. Subsequently, Cu-doped NiOx precursor was spin coated onto the ITO substrate at 3000 rpm for 60 s and annealed at 350 °C for 1 h in air. The coated substrates were transferred into the glove box with nitrogen atmosphere after cooling down to the room temperature. Sequentially, the compositional perovskite precursors (filtered with a 0.22 μ m PTFE filter) were spin coated onto the substrate at 1000 rpm for 15 s and 4000 rpm for 45 s sequentially. During the last 15 s of the second spin-coating step, the substrate was treated with toluene drop-casting (0.7 mL). The resulting thin films were annealed at 100 °C (150 °C for FAPbI₃) for 10 min. Then, the PC₆₁BM and C₆₀ mixed solution and bis-C₆₀ surfactant solution were spin coated on the perovskite films at 1000 rpm for 60 s and 3000 rpm for 60 s sequentially. Finally, silver electrodes with thickness of 100 nm were evaporated under high vacuum (<1 x 10⁻⁶ Torr) through a shadow mask. The cell area is defined as 3.14 mm².

2.3. Characterization

The structure of the perovskite films was characterized by SEM (FEI Sirion XL30 SEM operated at 5 kV) and XRD (Bruker F8 Focus Powder XRD). Elemental analysis was performed with the FEI Sirion XL30 SEM with an EDX detector operating at 20.0 keV. The absorption spectra were measured by using a Varian Cary 5000 UV-Vis-NIR. The J-V curves and steady-state photocurrent of the perovskite solar cells were measured by a Keithley

2400 Source Meter under illumination by a 450 W Oriel xenon lamp with an AM 1.5G filter solar simulator (100 mW cm^{-2}), and the light intensity was calibrated with a standard Si photodiode detector (equipped with a KG-5 filter). All devices are light soaked for 30 seconds without biasing before measurements. The EQE spectra were measured by combining a monochromated 450 W xenon lamp (Oriel) with a sourcemeter (Keithley 2400) and calculated using a calibrated Si photodiode (OSI-Optoelectronics). The steady-state photoluminescence spectra were measured by Horiba Fluorolog FL-3 with an excitation wavelength of 550 nm. For the time-resolved PL measurements, Samples were excited with 470 nm pulsed diode laser (FWHM $\approx$ 300 ps) with a frequency of 125 kHz and excitation intensity of 15 nJ cm^{-2} . The admittance spectroscopy was performed by CHI660e electrochemical workstation at a frequency between 1 to 1000 kHz.

3. Results and discussion

To systematically study the optical and photovoltaic properties of compositional $\text{MA}_x\text{FA}_{1-x}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ perovskites, FA^+ ions were gradually introduced into MAPbI_3 to form $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$. All the perovskite films in this study were prepared *via* a reported solvent engineering method.[27] Note that the denoted stoichiometry of compositional perovskites was defined according to the stoichiometry of the precursors; a more accurate definition of perovskite composition will be discussed later. **Figure S1** shows the UV-Vis absorption spectra of the compositional $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ perovskite, where the absorption edge gradually red-shifted from 790 to 840 nm as the FA^+ ion content increased from 0% (MAPbI_3) to 100% (FAPbI_3). Meanwhile, the corresponding E_g decreased from 1.61 eV to 1.51 eV, as displayed in the transformed Kubelka-Munk spectra (**Figure 1a**). It is important to note that the $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ perovskite with a MA^+ ion content above 20% formed after annealing at 100 °C for 10 min (**Figure S2**), which is much lower than the typical annealing temperature required for forming pure black α -phase FAPbI_3 (150 °C). Although, a small fraction of

δ -phase (11.8°) co-exists in the resultant films when the FA^+ ion content exceeded 60% as shown in the X-ray diffraction (XRD) spectra (**Figure 1b**). This can be inhibited when the $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ perovskite has a FA^+ ion content below 40%. The nearly threefold increase in XRD peak intensity of $\text{MA}_{0.8}\text{FA}_{0.2}\text{PbI}_3$ compared to that of other perovskites also suggests a higher crystallinity in its resultant polycrystalline film.

As displayed in the magnified XRD spectra (**Figure S3**), the 110 diffraction peak at 14.22° (assigned for MAPbI_3) gradually shifted to 13.95° (assigned for FAPbI_3) after increasing the FA^+ ion fractions in the compositional perovskites, representing a conversion from the tetragonal to the trigonal phase.[1] This gradual shift indicates a homogeneous compositional phase of $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ perovskite. Combined with the observation of red-shifted absorption onsets in the UV-vis spectra, we conclude that the FA^+ ions were homogeneously incorporated into the MAPbI_3 lattice. According to the literature, both the tetragonal and trigonal phases are considered to be the pseudocubic phase in lattice evolution.[9] In this view, the respective (110) spacing of tetragonal phase and (111) spacing of trigonal phase can be both defined as the (100) spacing of cubic phase in $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$. As shown in **Figure 1c**, the pseudocubic lattice parameter a^* increases from 6.23 Å to 6.33 Å with the gradually increased content of FA^+ ions in the targeted perovskites. According to Vegard's law, the lattice parameter of a homogeneous solid solution is linearly proportional to relative composition of each species in the absence of strong electronic effects.[28] Therefore, the actual composition of the denoted $\text{MA}_{0.8}\text{FA}_{0.2}\text{PbI}_3$ and $\text{MA}_{0.2}\text{FA}_{0.8}\text{PbI}_3$ was corrected to $\text{MA}_{0.7}\text{FA}_{0.3}\text{PbI}_3$ and $\text{MA}_{0.35}\text{FA}_{0.65}\text{PbI}_3$, respectively.

The photovoltaic performance of the compositional $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ were compared next in the derived solar cells with a device architecture of ITO/Cu-doped NiO_x /perovskite/ $\text{PC}_{61}\text{BM}:\text{C}_{60}(1:1)/\text{Bis-C}_{60}/\text{Ag}$ under AM 1.5 illumination (**Figures S4-S5 and Table 1**).[6, 29] **Note that in order to enhance the solution processability of C_{60} , PC_{61}BM is blended with**

C_{60} serving as the electron-transporting interlayer herein. The typical MAPbI₃-based cell yielded an open circuit voltage (V_{OC}) of 1.05 V, a short circuit current (J_{SC}) of 20.13 mA cm⁻², and a fill factor (FF) of 0.73, which corresponded to a PCE of 15.34%. A parental FAPbI₃-based cell delivered an average V_{OC} of 0.96 V, a J_{SC} of 20.76 mA cm⁻², and a FF of 0.63, which corresponded to a PCE of 12.56%.

For the targeted MA_xFA_{1-x}PbI₃ systems, the V_{OC} of the derived cell increased as the FA⁺ ion content decreases, which was consistent with the corresponding E_g evolution (**Table 1**). Among the targeted MA_xFA_{1-x}PbI₃ systems, MA_{0.4}FA_{0.6}PbI₃, MA_{0.35}FA_{0.65}PbI₃ and FAPbI₃ perovskites particularly yielded relative low J_{SC} s and FFs due to the presence of δ -phase in the films; on the contrary, the δ -phase-free cells based on MA_{0.7}FA_{0.3}PbI₃ and MA_{0.6}FA_{0.4}PbI₃ exhibited improved J_{SC} and FF, respectively (**Figure S6**). The increased J_{SC} observed in the MA_{0.7}FA_{0.3}PbI₃- and MA_{0.6}FA_{0.4}PbI₃-based cells compared to the parental MAPbI₃-based cell can be clearly interpreted as a consequence of the broadened light absorption range induced by the FA⁺ ion incorporation (**Figure S1**). On the other hand, the improved FF observed in the MA_{0.7}FA_{0.3}PbI₃-based cell can be correlated with the enhanced overall crystallinity of the perovskite film after the insertion of FA⁺ ions into the MAPbI₃ lattice as discussed earlier. Both enhancements in J_{SC} and FF compensated the potential loss in the resultant V_{OC} due to the reduction of E_g . Consequently, the MA_{0.7}FA_{0.3}PbI₃-based cell yielded the highest PCE_{AVG} of 16.42%. These results demonstrated the advantages of incorporating FA⁺ ions into MAPbI₃ lattice and encouraged us to fine-tune the halide ratio based on this top-performing perovskite composition.

As mentioned previously, the homogenous incorporation of bromide into MAPb(I_xBr_{1-x})₃ widens the E_g of MAPbI₃.^[9] A recent report suggested that the insertion of bromide into MAPbI₃ lattice can change the potential barrier at grain boundaries (GBs) to reduce recombination loss within perovskite.^[30] After clarifying the role of FA substitution in

MAPbI₃, Br⁻ ions were sequentially introduced into the top-performing MA_{0.7}FA_{0.3}PbI₃ perovskite to elucidate the influence of bromide incorporation in the composition.

As shown in **Figures S7** and **1d**, the absorption onset of the targeted perovskites blue-shifted from 800 to 750 nm when the Br⁻ ion content was increased from 0% to 20%, which corresponded to an increase in E_g from 1.57 to 1.69 eV. According to the XRD spectra, higher intensity suggests the improved crystallinity after partial Br⁻ ion substitution in MA_{0.7}FA_{0.3}PbI₃ (**Figure 1e**). With the increased Br⁻ ion content in the compositional perovskites, the characteristic diffraction peak at 14.10° gradually shifted to 14.30°, representing the tendency to convert the tetragonal phase toward the cubic phase (~15°) (**Figure S8**). The enhanced crystallinity induced by Br⁻ ion insertion might result in part from such a symmetry change in crystal lattice. The pseudocubic lattice parameter a^* was calculated, which decrease from 6.26 Å to 6.19 Å when the Br⁻ ion content was increased from 0% to 20%. This shift agrees well with Vegard's law, as depicted in **Figure 1f**. These results indicate the formation of homogeneous compositional phase of MA_{0.7}FA_{0.3}Pb(I_yBr_{1-y})₃, in which MA⁺, FA⁺, I⁻, and Br⁻ ions are all inserted into the same lattice framework. The Br⁻ ion content in the compositional perovskites was evaluated with energy dispersive X-ray spectroscopy (EDX). Elemental mapping for I and Br atoms in MA_{0.7}FA_{0.3}Pb(I_{0.9}Br_{0.1})₃ demonstrates a homogeneous distribution of both halide ions without detectable phase separation (**Figure S9**). Quantitative EDX measurements reveal the halide atomic fraction of Br to be 0.1 (**Figure S10**), which match the halide stoichiometry used in precursor (10% Br⁻). Hence, the denotation based on stoichiometry used in the precursor preparation for the MA_{0.7}FA_{0.3}Pb(I_yBr_{1-y})₃ system was left unchanged.

Then, the photovoltaic performance of these compositional MA_{0.7}FA_{0.3}Pb(I_yBr_{1-y})₃ perovskites was investigated (**Figures S11-S12**) and the photovoltaic parameters are summarized in **Table 2**. The V_{OC} of the derived PVSCs increases from 1.02 eV to 1.11 eV

while the E_g of the corresponding perovskite increases from 1.57 eV to 1.69 eV. Encouragingly, the FFs of all the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ -based cells are superior to that of the control $\text{MA}_{0.7}\text{FA}_{0.3}\text{PbI}_3$ -based cell. The enhanced V_{OC} and FF of the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ -based cells compensate the slightly decreased J_{SC} resulting from the narrower absorption window. Consequently, the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ -based cell exhibits a promising PCE_{AVG} of 17.34%, with a peak V_{OC} of 1.10 V, a J_{SC} of 20.21 mA cm^{-2} , and a FF of 0.78. More importantly, the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ -based cell with a large E_g of 1.69 eV can still exhibit a high PCE_{AVG} of over 15%, which is among the state-of-the-art large E_g ($\sim 1.7\text{eV}$) PVSCs reported so far.[25] Previous reports have demonstrated that large E_g PVSC can serve as an efficient top sub-cell in a high-performance tandem solar cell with crystalline silicon (1.12 eV) employed as the bottom sub-cell.[25, 31]

In order to systematically understand the fundamental roles of FA^+ and Br^- ions in high-performance compositional perovskite solar cells, the photovoltaic performance of a device based on MAPbI_3 was compared with that of devices based on $\text{MA}_{0.7}\text{FA}_{0.3}\text{PbI}_3$ and $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$, respectively. As shown in **Figure 2a**, the introduction of FA^+ ions into MAPbI_3 improve the J_{SC} of the derived cells due to the extended absorption spectra, as is evident in the corresponding external quantum efficiency (EQE) spectra (**Figure 2b**). After further incorporation of Br^- ions, the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ -based cell shows a decreased J_{SC} from that of $\text{MA}_{0.7}\text{FA}_{0.3}\text{PbI}_3$; however it is still comparable to the pristine MAPbI_3 -based cell despite its smaller absorption spectrum range. The EQE spectra indicates its slightly narrower light-harvesting window is well compensated by its superior absorption of red light (670 to 770 nm), which could have resulted from the improved thin-film crystallinity. In addition, it is worth noting that the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ -based cell possesses a smaller potential loss ($E_g/e - V_{OC}$) than that of the MAPbI_3 -based cell (0.53 V vs 0.56 V), in which the improvement in V_{OC} between $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ - and MAPbI_3 -based PVSCs is ~ 0.05 V,

which is larger than their E_g/e difference (~ 0.02 V). Another important observation is that the FF improves from 0.73 to 0.75 with the introduction of 30% FA^+ ions in MAPbI_3 and further rises to 0.78 by substituting 10% I^- with Br^- ions in $\text{MA}_{0.7}\text{FA}_{0.3}\text{PbI}_3$. These phenomena require further investigation.

Scanning electron microscopy (SEM) was carried out to compare the morphological differences of these three perovskite films and to gain insight into the differences in photovoltaic performance (**Figure 3a-3c**). The average perovskite domain size gradually increased after sequentially introducing FA^+ and Br^- ions into the perovskite lattice. As known, the ideal grain growth can be approximately expressed by the following formula: $d^2 - d_0^2 = k_0 \exp(-Q/RT)$, where d and d_0 are the initial and final grain size, k_0 is a constant, and T , R and Q are the absolute temperature, radius of the sphere, and activation energy for boundary mobility, respectively.[32] Given the k_0 , Q and T are almost the same, it can be speculated that the introduction of FA^+ and Br^- may can decrease the activation energy for boundary mobility to result in the bigger grain size. Since XRD reveals that crystallinity was also increased, a reduction of grain boundaries and a decreased density of defect states inside the perovskite thus can be inferred. It is known that steady state photoluminescence (PL) of organic-inorganic hybrid perovskite primarily results from radiative recombination of free carriers. For equally thick perovskite films, stronger PL intensity could imply less non-radiative decay and fewer defects inside perovskites. As shown in **Figure 4a**, the PL intensity follows the trend of $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3 > \text{MA}_{0.7}\text{FA}_{0.3}\text{PbI}_3 > \text{MAPbI}_3$ for equally thick films. Therefore, it can be speculated that the incorporation of FA^+ and Br^- ions could help reduce the density of non-radiative centers and defects in the perovskite films. Consequently, the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ possesses the fewest non-radiative center and defects, which is beneficial for its photovoltaic performance.

To support this hypothesis further, time-resolved PL was conducted to estimate the charge recombination behavior in the perovskites. As shown in **Figure 4b**, the average carrier lifetime was respective 103, 252 and 507 ns for MAPbI₃, MA_{0.7}FA_{0.3}PbI₃ and MA_{0.7}FA_{0.3}Pb(I_{0.9}Br_{0.1})₃, suggesting the diminished charge recombination as a result of the improved thin-film crystallinity. DFT calculations by *Buin et al.* suggested that high concentrations ($>10^{18}$) of the deep-level trap state Pb_I (an antisite where I atoms substitute Pb) were formed in iodine-rich conditions.[33-34] Therefore, we propose the concentration of these Pb_I antisites can be reduced by substituting partial I⁻ with Br⁻ ions, resulting in favorable iodine-poor conditions.

To further confirm the effects of FA⁺ and Br⁻ ions substitution in perovskite, admittance spectroscopy was performed accordingly to quantitatively estimate the N_T in the studied perovskite films (**Figure 4c** and **4d**). It has been reported that the admittance spectroscopy is an effective method to analyze the N_T in thin-film photovoltaics,[34-35] where the N_T can be estimated from the angle frequency dependent capacitance, i.e.

$$N_T(E_\omega) = -\frac{V_{bi}}{qW} \frac{dC}{d\omega} \frac{\omega}{kT}$$

where V_{bi} , W , C , ω , k and T are built-in potential, depletion width, capacitance, angle frequency, Boltzmann constant, and temperature respectively.[35-36] V_{bi} and W can be obtained from the C^2 - V plots according to literature[37] and E_ω is the energy demarcation determined by the applied angular frequency.

$$E_\omega = kT \ln\left(\frac{\omega_0}{\omega}\right)$$

E_ω are defined as trap energy minus the valence band edge. As show in **Figure 4d**, after substituting the FA⁺ and Br⁻ ions in MAPbI₃, the N_T in perovskite becomes less and is in the order of MA_{0.7}FA_{0.3}Pb(I_{0.9}Br_{0.1})₃ < MA_{0.7}FA_{0.3}PbI₃ < MAPbI₃, clearly manifesting the less defects was formed in these compositional perovskites. Moreover, we notice that the

differences in the lower trap band region (0.05 to 0.15 eV) are smaller than those in the higher trap band region (0.15 to 0.25 eV), which suggests that the pristine MAPbI₃ plays a more dominant effect in the lower trap band region while the FA⁺ and Br⁻ ions substitution can effectively decrease the trap density in the higher trap band region.[38] Note that the high trap band region, to certain degree, represents the deep traps states in perovskite, which might result from the defects or grain boundary.[39-40] This result clearly shows the reduced N_T in the compositional perovskites, especially for MA_{0.7}FA_{0.3}Pb(I_{0.9}Br_{0.1})₃, confirming the efficacy of the dual substitution of FA⁺ and Br⁻ ions in MAPbI₃ to enhance the photovoltaic performance of the derived devices.

As mentioned earlier, the MA_{0.7}FA_{0.3}Pb(I_{0.9}Br_{0.1})₃-based cell showed a reduced potential loss compared to MAPbI₃-based device. It is possibly correlated with the influence of the Br⁻ incorporation related to the GBs' properties discuss earlier. The insertion of Br⁻ ions in MA_{0.7}FA_{0.3}PbI₃ could change the band bending at the GBs to facilitate charge separation in the perovskite, leading to the reduced potential loss in the photovoltaic device.[30] At this stage, it is still not readily understood that this enhancement in reducing potential loss resulted from the inserted Br⁻ ions or the cooperative effect of both FA⁺ and Br⁻ ion substitution. More detailed physical and crystallographic studies pertaining to the new compositional perovskites will be conducted.

Finally, photo-stability and hysteresis tests of were performed on the top-performing MA_{0.7}FA_{0.3}Pb(I_{0.9}Br_{0.1})₃-based cell. As shown in **Figure 5a**, the cell display insignificant hysteresis even at a very low scan rate of 0.01 V s⁻¹. In addition, the steady-state photocurrent measurement shown in **Figure 5b** demonstrates the cell yields a stable photocurrent at the maximum power point (applied voltage of 0.93 V) for 10 min without showing any degradation.

5. Conclusions

In summary, the structural, photophysical, and photovoltaic properties of the compositional $\text{MA}_x\text{FA}_{1-x}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ perovskite were systematically studied by gradually introducing FA^+ and Br^- ions into MAPbI_3 . The results show that the a substitution of ~30% MA^+ ions with FA^+ ions in MAPbI_3 can improve the crystallinity, absorption, and carrier lifetime of the perovskite. Importantly, the perovskite phase conversion temperature can be maintained at 100 °C despite the incorporation of FA^+ ions that usually requires a higher annealing temperature of 150 °C to form pure black α -phase FAPbI_3 . the subsequent insertion of Br^- in the $\text{MA}_x\text{FA}_{1-x}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ lattice continued to improve the crystallinity of resultant film and thus reduced the N_T as evidenced by the admittance spectroscopy, resulting in a prolonged carrier lifetime of over 500 ns. As a result, a PCE_{AVG} of 17.34% was achieved in the optimized $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ -based PVSC with little hysteresis and stable photocurrent output. More encouragingly, the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ -based PVSC with a large E_g of 1.69 eV exhibited a high PCE_{AVG} over 15%, which is among the state-of-the-art large E_g (~1.7eV) PVSCs reported thus far.

Figure 1. (a) Kubelka-Munk spectra of $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$, where α is the absorption coefficient and E_{photon} is the photon energy. (b) XRD spectra of $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ perovskite. (c) Evolution of pseudocubic lattice parameters on FA^+ ion content in $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$. (d) Kubelka-Munk spectra of $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$. (e) XRD spectra of $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ perovskite. (f) Evolution of pseudocubic lattice parameters on Br^- ion content in $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$.

Figure 2. *J*-*V* characteristics (measured under AM 1.5 illumination) (a) and EQE spectra (b) of PVSCs based on compositional perovskites of MAPbI₃, MA_{0.7}FA_{0.3}PbI₃ and MA_{0.7}FA_{0.3}Pb(I_{0.9}Br_{0.1})₃.

Figure 3. SEM images of the perovskite films with the compositions of MAPbI_3 (a), $\text{MA}_{0.7}\text{FA}_{0.3}\text{PbI}_3$ (b) and $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ (c).

Figure 4. Steady-state PL (a) and normalized time-resolved PL spectra (b) of the perovskite films with different compositions of MAPbI₃, MA_{0.7}FA_{0.3}PbI₃ and MA_{0.7}FA_{0.3}Pb(I_{0.9}Br_{0.1})₃. Capacitance-frequency (c) and calculated N_T (d) of the perovskite films with different compositions of MAPbI₃, MA_{0.7}FA_{0.3}PbI₃ and MA_{0.7}FA_{0.3}Pb(I_{0.9}Br_{0.1})₃, which were measured under room temperature.

Figure 5. (a) Hysteresis measurement of the PVSCs based on $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ perovskite at a scan rate of 0.01 V s^{-1} under AM 1.5 illumination. (b) The steady-state photocurrent measurement of the PVSCs was conducted on the top-performing $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ PVSC with an applied voltage of 0.93 V (the maximum power point).

Table 1. Photovoltaic parameters of the PVSCs with different compositional $\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$ perovskites measured under AM 1.5 illumination.

$\text{MA}_x\text{FA}_{1-x}\text{PbI}_3$	E_g (eV)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
x=1	1.61	1.05±0.01	20.13±0.41	0.73±0.01	15.43±0.41
x=0.7	1.57	1.02±0.01	21.47±0.52	0.75±0.01	16.42±0.52
x=0.6	1.55	1.00±0.01	21.98±0.61	0.72±0.01	15.83±0.47
x=0.4	1.54	0.99±0.02	20.38±1.26	0.65±0.02	13.11±0.89
x=0.35	1.52	0.98±0.01	19.43±1.33	0.58±0.03	11.04±1.07
x=0	1.51	0.96±0.02	20.76±0.64	0.63±0.03	12.56±0.62

Average values with standard deviation.

Table 2. Photovoltaic parameters of the PVSCs with different compositional $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ perovskites measured under AM 1.5 illumination.

$\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$	E_g (eV)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
y=0	1.57	1.02±0.01	21.47±0.32	0.75±0.01	16.42±0.54
y=0.05	1.60	1.06±0.01	20.48±0.42	0.77±0.01	16.72±0.63
y=0.10	1.63	1.10±0.01	20.21±0.49	0.78±0.01	17.34±0.49
y=0.15	1.66	1.11±0.01	18.94±0.54	0.78±0.01	16.40±0.43
y=0.20	1.69	1.11±0.01	17.34±0.67	0.78±0.01	15.01±0.55

Average values with standard deviation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Effects of Formamidinium and Bromide Ion Substitution in Methylammonium Lead Triiodide toward High-Performance Perovskite Solar Cells

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The structural, optophysical, and photovoltaic properties of the compositional $\text{MA}_x\text{FA}_{1-x}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ perovskite were systematically studied by gradually introducing FA^+ and Br^- ions into the MAPbI_3 to elucidate the roles of FA^+ and Br^- ions in the compositional perovskites. Benefitting from the improved thin-film crystallinity, prolonged carrier lifetime, and extended absorption introduced by such dual compositional engineering, a high average PCE of 17.34% was realized in the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ -based solar cell. More importantly, the $\text{MA}_{0.7}\text{FA}_{0.3}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ perovskite with a large bandgap of 1.69 eV can exhibit a high PCE over 15%, which is among the state-of-the-art large bandgap ($\sim 1.7\text{eV}$) PVSCs reported to date.