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# Effects of Bromide-mixing in Methylammonium Lead Iodide on Photovoltaic Properties of ZnO-based Perovskite Solar Cells

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**Abstract.** To improve efficiency of ZnO-based perovskite solar cells, a mixture iodide-bromide (I-Br) of  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$  perovskite structure was prepared by two-step sequential deposition method and used as photo absorber layer. Solar cells with structure of ITO/ZnO/PCBM/perovskite/P3HT/Au were fabricated and characterized. The perovskite films were prepared by mixing precursor  $\text{PbI}_2$  and  $\text{PbBr}_2$  at various molar ratio. It was found that the grain sizes and crystallite sizes of perovskite crystal were comparable for different Br doping. The existence of Br ions in perovskite layer was confirmed. In addition, the increase in band gap energy was observed. The highest average power conversion efficiency (PCE) of 2.17% was achieved from the device with  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{2.8}\text{Br}_{0.2}$  layer. This PCE value is higher than the  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_3$  device which exhibited 1.53%-efficiency. The enhancement in PCE could be explained by the development of light absorption and charges transport.

## 1. Introduction

Organometal halide perovskite structured of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  ( $\text{MAPbI}_3$ ) is widely used as light absorber material for solar cells due to its various benefits such as high absorption coefficient, ease of synthesis, applicability for flexible substrate, and non-rare earth elements [1-3]. However, their durability is still problematic [4]. To deal with the issue, bromide (Br) ions were added into the structure of  $\text{MAPbI}_3$  [5] since they can improve the stability of solar cells, reduce charge recombination and enhance the efficiency [6-7].

In addition, the incorporation of formamidinium ( $\text{FA}^+$ ) cation to methylammonium ( $\text{MA}^+$ ) was another choice to develop the efficiency of solar cells because the existence of  $\text{FA}^+$  ions can reduce the band gap



energy of light absorber layer, increase the crystallite size [8] and enhance carrier lifetime [9]. Chen *et al.* proved that the  $\text{FA}^+:\text{MA}^+$  ratio of 4:6 provided the optimum PCE [9].

In this research the  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$  perovskite light absorber layer were prepared by two-step sequential deposition method. The  $\text{PbI}_{(1-x)2}\text{Br}_{2x}$  layer were first deposited on the ZnO layer. Then, the perovskite light absorber layer was formed with the mixture of FAI and MAI solution. With the benefits of Br ions and  $\text{FA}^+$  cation in the photo-absorber, the PCE of perovskite solar cells increased expectedly.

## 2. Experimental Details

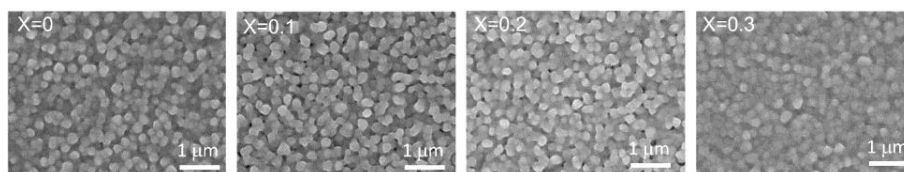
A ZnO compact layer was deposited on a UV-treated indium doped tin oxide (ITO) substrate by spin coating a colloidal ZnO solution. This deposition method was patterned after the procedure reported by Horachit *et al.* [10]. Then PCBM was deposited on the ZnO layer by spin-coating a solution of 10 mg/ml PCBM in chlorobenzene (CB) in a  $\text{N}_2$ -filled glovebox. A  $\text{PbI}_{2-2x}\text{Br}_{2x}$  precursor solution was prepared by mixing of  $\text{PbI}_2$  and  $\text{PbBr}_2$  in a mixture of 0.5 ml dimethylformamide (DMF) and 60  $\mu\text{l}$  of 4-*tert*-butylpyridine (tBP). The tBP was used as additive to form porous precursor layer [11]. The x values were varied as 0, 0.1, 0.2 and 0.3. Then, the precursor solution was spin-coated at 3000 rpm for 30 s and the films were annealed at 100  $^\circ\text{C}$  for 1 hr in a  $\text{N}_2$ -filled glovebox. Next a mixture of 4.3 mg/ml of FAI and 6 mg/ml of MAI solution in isopropanol was dropped on the  $\text{PbI}_{2-2x}\text{Br}_{2x}$  precursor layer and spun at 2000 rpm for 30s. films were then annealed at 75  $^\circ\text{C}$  for 20 min. A hole transporting layer (HTL) was prepared by spin coating a mixture of 20 mg/ml P3HT, 8  $\mu\text{l}$  of 280 mg/ml Co (II) in acetonitrile, 8  $\mu\text{l}$  of 4-tBP and 16  $\mu\text{l}$  of acetonitrile in 1 ml of CB at 1000 rpm for 30 s. Lastly Au metal electrode was coated on HTL layer for the electrode via thermal evaporation under  $10^{-4}$  bar vacuum condition.

The morphology of perovskite layer was observed by field emission scanning electron microscope (FE-SEM, JEOL JSM-6335F). Chemical composition of perovskite layer was analysed by energy-dispersive x-ray spectroscopy (EDS). Crystallite properties was investigated by X-ray diffraction (XRD) analysis. Optical properties of perovskite layer were studies via UV-visible spectroscopy and band gap energy ( $E_g$ ) of perovskite layer was calculated by Tac's equation [12]. Photovoltaic performance was measured under AM 1.5 condition with active area are about 38  $\text{mm}^2$ .

## 3. Results and Discussion

The FE-SEM images of the  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$  layer with different x content values were showed in Figure 1. It was found that the average grain sizes of these materials were comparable (241, 249, 247 and 237 nm for x= 0, 0.1, 0.2, and 0.3 respectively).

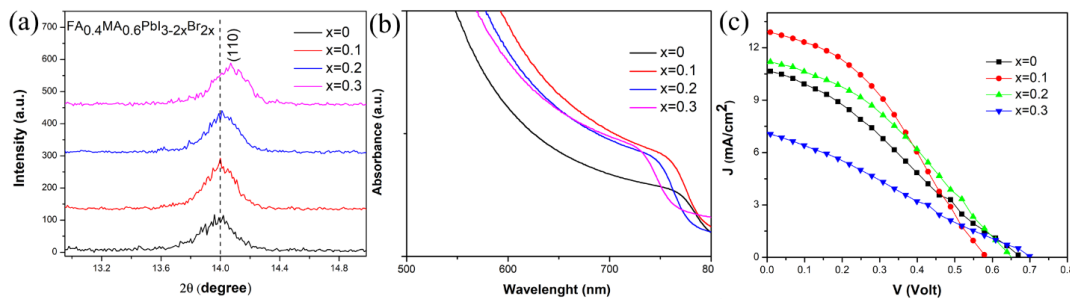
The element compositions analyzed by EDS for  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$  layer were summarized in Table 1. These results confirmed the presence of Br ions in the perovskite layer. It is seen that the atomic ratios of Br/Pb calculated from the detected data were comparable to the ratio of the initially mixed precursor. On the other hand, the ratio of I/Pb from the detected data were larger than the expected value. This maybe occurs due to the  $\text{PbI}_2$  residue in the film.



**Figure 1.** Top view FE-SEM images of  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$  layer for different x content value.

**Table 1.** Element compositions, atomic ratio and crystallite size of  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$  layers.

x	Structure	Atomic %			Theory		Experiment		Crystallite size (nm)
		Pb	I	Br	Br/Pb	I/Pb	Br/Pb	I/Pb	
0	$\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_3$	21.59	78.41	-	-	3	-	3.63	32
0.1	$\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{2.8}\text{Br}_{0.2}$	20.17	73.64	6.19	0.2	2.8	0.31	3.65	34
0.2	$\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{2.6}\text{Br}_{0.4}$	23.02	67.82	9.16	0.4	2.6	0.40	2.95	34
0.3	$\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{2.4}\text{Br}_{0.6}$	23.33	62.03	14.64	0.6	2.4	0.63	2.66	32

**Figure 2.** (a) XRD peaks at (110) plane and (b) absorption spectra of  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$  layers. (c) shows  $J$ - $V$  curves of perovskite solar cells with using  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$ .

As confirmed by XRD analysis, there were both tetragonal perovskite phase (XRD peaks at  $14^\circ$ ,  $28.2^\circ$  and  $31.6^\circ$ ) and residue  $\text{PbI}_2$  phase (XRD peak at  $12.6^\circ$ ) in the films. Figure 2a showed the diffraction peak at approximately  $14^\circ$  that refers to (110) plane [13] of the perovskite structure. It was seen that, when the  $x$  value increased, the diffraction peak shifted from lower peak position to a larger value. By using Bragg's equation [14, 15], it was found that the  $d$ -spacing and lattice constant decreased from  $6.33 \text{ \AA}$  to  $6.29 \text{ \AA}$  and  $8.95 \text{ \AA}$  to  $8.89 \text{ \AA}$  with increasing  $x$  content from 0 to 0.3. These phenomena can be explained by the substitutional of Br ions to I ions in the perovskite structure. In addition, calculated crystallite sizes of these materials (in Table 1) were comparable. This investigation is consistent with the FE-SEM observation, implying that the Br doping does not change the grain size and crystallite size of perovskite materials.

The absorption spectra of  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$  perovskite layers were in showed Figure 2(b). The increase in  $E_g$  (from 1.56 eV for  $x = 0$  to 1.62 eV for  $x = 0.3$ ) was found. This increment can be ascribed to the Br doping. Figure 2c showed current density-voltage ( $J$ - $V$ ) characteristic curves of perovskite solar cells using  $\text{FA}_{0.4}\text{MA}_{0.6}\text{PbI}_{3-2x}\text{Br}_{2x}$  as phot-absorber. The average photovoltaic parameters were summarized in table 2. It was found that the highest average PCE of 2.17% was obtained from the device with  $x = 0.1$ . In addition, open circuit voltage ( $V_{OC}$ ) for the devices with  $x = 0, 0.1$  and  $0.2$  were comparable but the  $V_{OC}$  value of the one with  $x = 0.3$  was higher. The increase in  $V_{OC}$  is attributed to the enlargement of  $E_g$  when more Br atoms incorporate into the crystal as confirmed by the calculated  $E_g$  and the results reported in reference [16].

Short-circuit current density ( $J_{sc}$ ) of the fabricated solar cells was relatively high for  $x = 0.1$  and  $0.2$ . The higher  $J_{sc}$  can be explained by two reasons. First, as seen in Figure 2b, the absorbance of the perovskite

layer with  $x = 0.1$  provided the strongest absorption so the perovskite layer has ability to generate more excitons than the other films. Finally, the series resistance ( $R_s$ ), which is commonly related to charge transportation [17], of the devices with  $x = 0.1$  showed the lowest value, therefore, better charge transport could be occurred

**Table 2.** The average photovoltaic parameters (over 6 cells prepaed at the same condition) at different x content value.

x	PCE (%)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	$R_s$ ( $\Omega$ cm <sup>2</sup> )
0	1.53 $\pm$ 0.33	0.61 $\pm$ 0.06	8.60 $\pm$ 1.67	0.30 $\pm$ 0.02	54.38 $\pm$ 10
0.1	2.17 $\pm$ 0.46	0.62 $\pm$ 0.02	9.95 $\pm$ 2.02	0.35 $\pm$ 0.03	36.27 $\pm$ 6.0
0.2	1.88 $\pm$ 0.44	0.61 $\pm$ 0.06	9.99 $\pm$ 1.32	0.31 $\pm$ 0.05	45.77 $\pm$ 25
0.3	1.39 $\pm$ 0.13	0.66 $\pm$ 0.03	6.94 $\pm$ 0.63	0.31 $\pm$ 0.03	40.62 $\pm$ 10

#### 4. Conclusion

The FA<sub>0.4</sub>MA<sub>0.6</sub>PbI<sub>3-2x</sub>Br<sub>2x</sub> perovskite solar cells based on ZnO ETL were successfully prepared via two-step sequential method. Br atoms were incorporated into the perovskite layer by using the mixture of PbI<sub>2</sub> and PbBr<sub>2</sub> as the precursors. The highest average PCE of 2.17 % was obtained from the device with  $x = 0.1$ . The improvement in PCE was due to the higher absorption, and the reduction of  $R_s$

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