Effect of chlorine and bromine on the perovskite crystal growth in mesoscopic heterojunction photovoltaic device

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Abstract

Organic-inorganic hybrid perovskite solar cells are within the emerging photovoltaic technologies. The combination of different halogen ions, in certain fill fractions, is one of the methods to improve the perovskite film properties. Herein, fabrication and characterization of perovskite cells in standard mesoscopic architecture using one-step deposition method has been done. The role of the halogen ions (Chlorine or Bromine) on crystal structure growth and photoelectric performance has been investigated. X-ray diffraction, scanning electron microscopy, atomic force microscopy and optical microscopy analysis were performed.

1. Introduction

Organic-inorganic hybrid perovskite solar cells (PSCs) have attracted significant attention as a promising material for photovoltaic applications due to their photo-physical properties, high defect tolerance, a tunable band gap by compositional engineering, and their simple solution fabrication process using low-cost materials [1-7]. Their high-power conversion efficiency (PCE) has achieved an impressive improvement, and presently the best cells go beyond 25% [8,9].

Methylammonium lead triiodide (CH₃NH₃PbI₃) is one of the most studied perovskite materials in photovoltaics perovskite field. The perovskite solar cells based on this perovskite type has demonstrated the relevant stable and efficient devices [10-12]. The heterojunction solar cells based on CH₃NH₃PbI₃ have a considerable advantage in terms of synthesis and performance, in combination with mesoporous TiO₂ as electron transport layer and spiro-OMeTAD and hole transport layer [13,14].

Improving the morphology, homogeneity and microstructure of the perovskite film are among the most important assements to obtain devices with high efficiency. Many scientific publications state that the photovoltaic performance of PSCs is directly correlated with the perovskite deposition parameters, such as the annealing treatment [15-17], the molar ratio of the precursors [18-20] and the deposition procedure [21-23]. Other studies suggest that for an easy to scale-up "one-step" deposition process, the CH₃NH₃PbI₃ hybrid perovskite must contain small amounts of chloride or bromide [24-28].

Recently, it has been suggested that compositional engineering by using other halogens such as chlorine (Cl) or bromine (Br), which leads to mixed halide perovskites, is one of the most used strategies to improve the PCE in solar cells [29-44]. On the other hand, the band gap of the perovskite depends on halogens concentrations [45-47], while the choice of organic cations impacts the stability of the devices [48-50].

The addition of Br and/or Cl increases the generation and diffusion length of the carriers, reducing charge recombination in the perovskite absorber film, leading to better photovoltaic performance [24]. Moreover, Cl and Br slow down the nucleation process and speed up the crystal growth rate, thus, having a impact on the microstructure (crystallinity) of the perovskite film [51, 52]. Br ions have a higher activation energy of the ionic migration than I ions, and consequently, reduced movement within the perovskite film, while Cl ions improve the diffusion length of the free carriers [53]. Therefore, mixing the halogens in the perovskite structure is a key to obtain superior photovoltaic properties with lower hysteresis effects than devices with CH₃NH₃PbI₃ only [54,55]. Previous work has demonstrated the potential of the mixt halide perovskites I and Cl halogen mixtures, *Tombe et al.* [56], *Po-Wei Liang et al* [57] and *Spalla et al* [58] reported their work with planar inverted geometry devices.

This paper focuses on the mixt halogenated perovskites with either I : Cl or I : Br in the same proportion of 1.8:1.2. This work focuses on the perovskite films with the composition CH₃NH₃PbI_{1.8}Br_{1.2}, and how the properties of the perovskite film change when Cl is used instead of Br in the same amount. The role of the halogen's composition on the morphology, microstructure, and optical properties as well as on photovoltaic performance and stability in solar cells in a mesoscopic geometry is studied.

2. Experimental section

2.1. Materials

Pre-cut fluorine tin oxide (FTO, 2.5x 1.5 cm²) coated glass with a sheet resistance of $15\Omega/sq$ were purchased from Xin Yan Technology LTD, China. Lead chloride (PbCl₂, 99.99%), lead Bromide (PbBr₂, 99.99%), N,N-Dimethylformamide (DMF), Dimethylsulfoxide (DMSO), Chlorobenzen (CB), acetone, isopropanol (IPA) and anhydrous ethanol, 4-tert-butylpyridine (tBP, 99.99%) and titanium diisopropoxide bis(acetylacetonate) (Ti(iProp)₂AcAc₂ were purchased from Sigma Aldrich. Methylammonuim iodide (MAI, 99%) was purchased from Dyesol. Ti-Nanoxide T/SP was purchased from Solaronix, Spiro-OMeTAD (99.99%) was purchased from Borun Chemicals, China.

2.2. Preparation of the precursor perovskite solutions

The MAPbI_{1.8}Cl_{1.2} solution was prepared by dissolving, MAI (159 mg), PbI₂ (184.40 mg), PbCl₂ (166.86 mg) in DMF: DMSO (8:1) mixture. The second perovskite solution MAPbI_{1.8}Br_{1.2} was prepared by dissolving, MAI (159 mg), PbI₂ (184.40 mg), PbBr₂ (220.21 mg) in DMF: DMSO (8:1) mixture. The solutions were left to stir for 24 hours at room temperature before deposition under nitrogen atmosphere.

2.3. Solar cell fabrication

The mesoscopic PSCs: FTO/TiO_{2c-m}/perovskite/Spiro-oMeTAD/Au was elaborated according to the following procedure:

First the FTO-coated glass slides were cleaned with a detergent solution and rinsed with plenty of distilled water, followed by sonication in acetone and then in isopropanol in an ultrasonic bath for 10 min for each solvent. Before the (c-TiO₂) compact layer deposition, the FTO/Glass substrates were exposed to O_2 plasma treatment for 10 min.

The compact TiO₂ (c-TiO₂) was then deposited by spray pyrolysis, using Ti(iProp)₂AcAc₂ in IPA (1:30 molar ratio), holding in the meantime the substrates on a hot plate at 450°C, followed by annealing treatment at 450°C for 30 min. Mesoporous TiO₂ films were deposited by spray coating a precursor colloidal solution consisting of commercial 20 nm-sized particles dispersed in anhydrous ethanol at 1:200 weight ratio, while the substrates were kept on a hot plate at 100°C during pulverization. After deposition, all final substrates were placed in a furnace for 1 h at 500°C.

The perovskite solutions with the different concentrations were spin coated at 2000 rpm for 25s. While spinning, after the first 15 s, ~150 μ L of CB was dropped to facilitate perovskite crystallization. Then, the perovskite films were annealed at 100 °C for 3 min.

A mixture of 80 mg spiro-OMeTAD, 28 μ L 4-tert-butylpyridine, and 18 μ L of bis(trifluoromethane) sulfonimide lithium salt in acetonitrile solution (520 mg.ml⁻¹), were dissolved in 1 mL chlorobenzene. This solution was spun at 3000 rpm for 30s over the perovskite surface.

Finally, the gold electrodes (80 nm thickness, 0.083 cm^2 surface area) were deposited on top of structures by *rf* magnetron sputtering in argon atmosphere at 3.10^{-3} mbar, through a shadow mask.

The schematic illustration of the mesoscopic standards perovskite solar cell is shown in Figure.1.



Figure 1. Schematic of device fabrication process and the structure of a complete "standard" mesoscopic solar cell.

2.4. Characterization

The X-ray diffraction (XRD) patterns of the thin films were measured by a Bruker-AXS Advance diffractometer using Cu anode (λ =1.54 Å). The UV–vis spectra were collected using a conventional spectroscopy mode using a V-Vase Woollam spectroscopic ellipsometer equipped with a high-pressure Xe discharge lamp incorporated in an HS-190 monochromator. Photoluminescence spectra have been recorded at room temperature using a FluoroMax 4Pspectrophotometer with excitation light having an oblique angle of incidence (selected wavelength λ_{exc} =450 nm). Scanning Electron Microscopy images were inspected by Zeiss GeminiSEM-500. Optical microscopy images were obtained with a Zeiss microscope. Surface morphologies were also investigated by atomic force microscopy (AFM) (NTMDT Aura Ntegra Prima Station, samples were scanned in non-contact mode). The current–voltage characteristics for the solar cells were measured under AM 1.5G, 100 mW cm2 simulated sunlight OrielLSH-7320, Class ABA LED Solar Simulator coupled with a Keithley 2601B Source Meter) in forward and reverse scan direction.

The current–voltage characteristics for the solar cells were measured under AM 1.5G, 100 mW/ cm² simulated sunlight OrielLSH-7320, Class ABA LED Solar Simulator coupled with a Keithley 2601B Source Meter) in forward and reverse scan direction. The solar simulator was calibrated with an NREL-certified KG5-filtered Si reference diode to an irradiation intensity of 100mW/cm². Electrical measurements were performed outside in ambient environment, at room temperature (<25°C), starting first in reverse direction, just above the Voc to Jsc, to avoid unintentional prepoling according to the procedure described elsewhere [59] of the samples and backward (towards positive voltage direction), at 20 mV/s. All devices were measured in ambient environment without encapsulation.

3. Results

3.1. X-ray diffraction

X-ray diffraction studies were conducted to investigate the microstructure of the perovskite layers and the resulted graphs are presented in figure 2. Multiple diffraction peaks indicate that the films are polycrystalline.



Figure 2. XRD patterns of the elaborated perovskite layers with different halogens composition a) $MAPbI_{1.8}Br_{1.2}$ and b) $MAPbI_{1.8}Cl_{1.2}$

The typical diffractogram of the perovskite films with chlorine, MAPbI_{1.8}Cl_{1.2}, presents a wellcrystallized primary phase with tetragonal structure, with the characteristic peaks of parent MAPI₃ at 14.15° (002/110), 20.08° (200), 23.55° (211), 24.55° (202), 28.52° (004/220), 31.90° (310), 35.07° (312), 40.79° (400) and 43.31° (330) according to ICDD 01-084-7607. In addition, the presence of two other minor secondary phases of unreacted lead iodide (PbI₂) at 12.7° (ICDD 00-007-0235) and segregated MAPbCl₃ perovskite at 15.7° (ICDD 01-085-5450) [60, 61], are observed.

The samples with bromine (MAPbI_{1.8}Br_{1.2}) have a cubic structure, similar to MAPbBr₃ - ICDD 00-069-1350 [62], inferred also from the symmetry of the 001 and 002 reflections. Since the largest instrumental errors are present at smaller 2θ angles, we focused our analysis of the

average crystallite size and lattice parameters on the peaks observed in the 28-30 angles range. The results are presented in table 1. Figure 3 presents the zoomed XRD patterns of the main peaks along with the fitted Lorentzian components.



Figure 3. Zoomed XRD patterns and component peaks /fits of each resulted from Lorentz function fitting routine of 001 and 002 for the MAPbI_{1.8}Br_{1.2} and 002/110 and 004/220 for the MAPbI_{1.8}Cl_{1.2}

As stated above, MAPbI_{1.8}Br_{1.2} characteristic peaks do not indicate any asymmetry. Contrary, MAPbI_{1.8}Cl_{1.2} peaks are asymmetric, the splitting being clear for 004/220 reflections, thus confirming the cubic structure for the Br samples, and the tetragonal structure for the Cl ones. The main difference between the two XRD spectra in Figure.3 is the considerable shift of the diffraction lines as well as the difference in the crystal structure [63].

Composition	Reflection hkl	2 θ(°)	w _{exp} (°)	$\mathbf{W}_{ins}(^{\circ})$	D(nm)
MAPbI _{1.8} Br _{1.2}	002	29.14	0.141	0.063	117
MAPbI _{1.8} Cl _{1.2}	004	28.27	0.101	0.063	237
	220	28.52	0.093	0.063	296

Table 1. Lattice parameters of the diffraction planes for the two different compositions.

The crystallite size of this different composition was determined by the Debye-Scherrer formula, and listed in Table 1:

$$D = \frac{K\lambda}{\mathrm{wcos}\Theta} \qquad \qquad \text{eq. 1}$$

where D is the crystallite size, λ is the X-ray wavelength in nanometers (nm), w is the peak width of the diffraction peak profile at half maximum height (calculated after subtracting the

full width at half maximum characteristic for the instrument w_{ins} from the experimental w_{exp}), K is a constant related to the crystallite shape taken as 0.94 and D_{ave} is the average crystallite size of the film [64]. The calculated average crystallite size of MAPbI_{1.8}Br_{1.2} and MAPbI_{1.8}Cl_{1.2} were 117 nm and 267 nm respectively.

The full width at half maximum (w) of the 002-characteristic peak in the XRD patterns from the MAPbI_{1.8}Br_{1.2} film appears sharper (w: 0.141°) than that from the 004/220 characteristic peak of MAPbI_{1.8}Cl_{1.2} (w: 0.101 and 0.093°), as shown in Table 1. A lower FWHM value is noted for the formulation with Cl⁻, which indicates larger crystallites [65].

However, the perovskite films with chlorine presents a detectable amount of PbI_2 secondary phase, by the presence of the diffraction line at 12.27°. No residual PbI_2 diffraction peaks were noted in the brominated-iodine perovskite film as shown in Figure 2, suggesting the complete conversion of the precursors to perovskite. Most likely, the incorporation of bromine has increased the speed of the crystallization process of perovskite thus stopping the formation of the PbI₂ salt.

This difference is not attributed to the higher ionic radius of Br (0.196 nm) relative to Cl (0.185 nm), which results in a very slight decrease of the Goldschmidt tolerance factor t, of the perovskite structure from 0.918 for the MAPbI_{1.8}Cl_{1.2} and to 0.915 for MAPbI_{1.8}Br_{1.2}, respectively, calculated by:

$$\mathbf{t} = \frac{(rA + rX)}{\sqrt{2} (rB + rX)} \qquad \text{eq.2},$$

where $r_A r_B$ and $r_{X are}$ the ionic radii for A, B and X. The other ionic radii taken for calculation are of MA⁺ (0.216 nm), Pb²⁺ (0.119 nm), and I⁻ (0.220 nm [66,67].

3.2. Optical microscopy

Surface topography and roughness of the prepared perovskite films were inspected by optical microscopy, AFM and SEM in Figure 4, Figure 5 and Figure 6.



Figure 4: Optical microscopy images of the perovskite films prepared with chlorine (a) and bromine (b).

Figure 4 shows the optical microscopy images of the perovskite films prepared of the two type of perovskite films. The surface coverage as well as the grain morphology are different for the two solutions. The effect of the chlorine and bromine halides can be observed. The

MAPbI_{1.8}Cl_{1.2} films (Figure (4ba)), show a structure with uneven, inhomogeneous surface. The crystals are agglomerated in different areas, and therefore, the perovskite film does not cover the entire substrate surface, since the TiO₂ under layer is visible. However, for the sample with bromine Figure (4b), the perovskite film looks homogeneous, providing uniform coverage of the TiO₂.

3.3. Atomic force microscopy

Atomic force microscopy was used to explore the surface morphology of the prepared films. Figure 4 shows the AFM images for the mixed halide perovskite films fabricated onto TiO_{2m} with chlorine and bromine.



Figure 5. AFM images of: a) mesoporous TiO₂ layer and perovskite layers: b) MAPbI_{1.8}Cl_{1.2} and c) MAPbI_{1.8}Br_{1.2}

MAPbI_{1.8}Cl_{1.2} films have a relatively ordered surface with needles-shaped features shown in Figure 5a). The root mean square (RMS) calculated for a $20x20 \,\mu\text{m}$ area is 112 nm. The image shows a dendritic structure with tightly packed needle-like shapes and the voids between them, evidence of an incomplete surface coverage, with a negative impact on the performance of the device.

Solution	Root mean square, RMS (nm)	Average roughness Sa (nm)
TiO ₂ mesoporous	136	98
MAPbI _{1.8} Cl _{1.2}	112	86
$MAPbI_{1.8}Br_{1.2}$	31	25

Table 2. Surface parameters extracted from AFM images analysis for the different samples

In comparison, the typical AFM topographical image of the MAPbI_{1.8}Br_{1.2} film (Figure 5c) shows a dense and smooth film, with an RMS roughness of only 31 nm, an order of magnitude smoother than the Cl perovskite film. At the same time, the TiO₂ rough shape is smoothened by the thick, compact brominated perovskite. This improvement of the surface coverage

supports the carrier mobility and transport, within the perovskite film but also at the interface with the mesoporous, which further leads to higher device efficiency [68, 69].

3.4. Scanning Electron Microscopy

The two different surface morphologies of the perovskite films were investigated by scanning electron microscopy (SEM) and shown in Figure 6.



Figure 6. Surface morphologies of perovskite films: a) MAPbI_{1.8}Cl_{1.2} and b) MAPbI_{1.8}Br_{1.2}.

The MAPbI_{1.8}Cl_{1.2} film shows a partially compact surface with large void-defects, as shown by the SEM images in Figure 6a. Moreover, the dendritic growth of the crystalline films based on iodine and chlorine mixture, shows an aggressive crystallization, with distinct areas containing tightly packed crystallites in the form of branches and in between them, micron-sized large gaps, thus resulting a discontinuous perovskite coverage. It is widely accepted that the formation of such films is sensitive to the thermal annealing conditions, such as time and temperature) [70,71]. This specific morphology can originate from the differences in grain nucleation and crystal growth between the Cl and Br containing films. This is in good agreement

with the XRD measurements in which the MAPbI_{1.8}Cl_{1.2} shows a larger crystallite size compared to that of the MAPbI_{1.8}Br_{1.2} [72]. Notably the needle-like crystalline PbI₂ vaguely appeared on the perovskite surfaces, which is likewise confirmed by the recorded XRD pattern shown in Figure.2.

In the case of the MAPbI_{1.8}Br_{1.2} perovskite (Figure 6b), the film morphology looks completely different regarding grain order and film coverage. The SEM image reveals a uniform film with dense nano-sized crystal domains. Additionally, reducing pinholes eliminates the possibility of direct contact between adjacent p- and n-type charge selective layers preventing device short-circuit.

3.5. Optical properties

To investigate the influence of halogens, the derivatives UV-visible absorption and photoluminescence spectra were reported for the perovskite films made from different solutions and elaborated on FTO/TiO₂-cm substrates. (Figure 7).



Figure 7: a,b) Optical band gap determined from linear fits of the Tauc plot; c,d) normalized Photoluminescence and Vis-NIR absorbance derivatives spectra of the MAPbI_{1.8}Cl_{1.2} and MAPbI_{1.8}Br_{1.2} respectively.

From the curves in Figure 7, the band gap was calculated for each of the two compositions. It is observed that when a halogen with higher electronegativity is chosen, the affinity with the

Pb ion increases, thus reducing the ionic character of the halogen-Pb bond in favor of the covalent character of the bond, leading to a redshift of the optical absorption curves.

The absorption spectra for halide perovskite has shifted to lower wavelength by changing the halide from Cl to Br. The E_g shift of of MAPbI_{1.8}Cl_{1.2} compared with MAPbI_{1.8}Br_{1.2} is due to the decrease in the covalent character of the halogen bonding with Pb, which means a decrease in the electron negativity of the halogen [73,74].

Analogously, the normalized PL emission peak show same behavior while Br doping leads to a detectable red shift, and the Pl emission peak shifted from 690 nm to 768 nm.

Meanwhile, this shift behavior of the photoluminescence peak can be explained by the formation of ordered crystals. The red-shift of the PL emission of the hybrid perovskite material has been reported to occur due to the crystallization of the perovskite [75] and observed by other groups as well [76].



Figure 8: Photoluminescence spectra of the two different samples

Furthermore, looking at the photoluminescence spectra in figure.8, a relatively lower photoluminescence intensity is observed for the perovskite film with iodine and bromine which suggests either a low level of defects inside the perovskite layer and/or a good quenching at the n-type layer interface. This is most likely due to the absence of the PbI_2 residues (previously indicated by the XRD analysis) in this sample and the good surface quality, as observed in the morphological characterization (AFM, SEM).

The band gap energy can be calculated from the Tauc plot (figure 6a,b). The calculated optical band gap has been shifted from 1.55eV to 1.80 eV, with the bromine content, due to its lower electronegativity. According to the literature [77-79], the band gap of the ABX₃ perovskite increases as the electronegativity of the X anion decreases. Therefore, the lower electronegativity of Br induces a larger energy gap.

3.6. Solar cells performance

The effect of the second halogen, Cl / Br incorporation in the perovskite matrix on the photovoltaic properties has been investigated by current–voltage (J–V) measurements performed on the solar cells (figure.9). The average photovoltaic values obtained for 16 cells of each composition are presented and the photovoltaic parameters of the champion devices are summarized in Table 4.



Figure 9. a) Schematic illustration of mesoscopic cells configuration, b) Forward and reserve J-V curves of champion cells with for the different composition.

Figure 9 shows the J-V characteristics of the PSCs based on MAPbI_{1.8}Cl_{1.2} and MAPbI_{1.8}Br_{1.2} perovskite thin films and their corresponding schematic illustration of mesoscopic cells configurations.

Perovskite		$V_{OC}(V)$	J _{SC} (mA/cm ²)	FF (%)	PCE (%)
	Champion device reverse values	0.84	9.02	71	5.77
MAPbI _{1.8} Cl _{1.2}	Average between forward and reverse of champion device	0.84	8.91	71	5.50
	Average of 16 devices	0.86	8.06	72	5.01
	Champion device reverse values	0.95	16.17	69	10.65
MAPbI _{1.8} Br _{1.2}	Average between forward and reverse of champion device	0.95	16.03	67	10.12
	Average of 16 devices	0.01	0.61	2.4	0.35

Table.4 photovoltaic parameters extracted from the champion and average solar cells elaborated from the different perovskite composition

The devices with MAPbI_{1.8}Cl_{1.2} present a V_{OC} of 0.84 V, a short-circuit current, J_{SC} of 9.02 mA/cm², a fill factor, FF of 71% corresponding to a power conversion efficiency (PCE) of 5.77%. MAPbI_{1.8}Br_{1.2} perovskite-based devices show a considerable higher power efficiency of, due to an improvement of all electrics parameters. Thus, an open circuit voltage (V_{OC}) of 0.95 V, a short-circuit current (J_{SC}) of 16.17 mA/cm², a fill factor (FF) of 74% were obtained, resulting a maximum PCE of 10.65%.

3.7. Stability evaluation

The long-term stability of the average PCE of the devices prepared from the different solutions was assessed. Figure 10 shows the evolution of the average PCE, shelf storage lifetime. The devices were stored inside the glovebox for 1200 hours and tested periodically outside, in conditions specified at the Experimental section, to investigate their long-term stability. The evolution of the average PCE during 1200 h is similar for the two compositions. Nevertheless, the degradation for the cells with MAPbI_{1.8}Br_{1.2} seems to reach a plateau at 3.84 % PCE after 1200 h of storage and a loss of approximately 64% of the initial PCE. This is not the case for the MAPbI_{1.8}Cl_{1.2} based device that seem to lose 92% of its initial efficiency after 1200 h and continues to degrade rapidly. This behavior of the device with bromine is owed to the compactness of the perovskite layer, with fewer defects and high structural stability.



Figure 10: Stability tests of the cells with different perovskite composition

4. Conclusions

In summary, we have elaborated standard mesoscopic mixed-halide perovskite-based devices by one step spin-coating deposition method. Only by changing the type of the second added halogen, Cl or Br, but keeping the same ratio, the structural, morphological and optical properties of the perovskite film suffer dramatic changes. We have shown that the morphology of the perovskite crystallites obtained under the given processing conditions is affected considerably by the choice of the second halogen, Cl or Br, during the formation of the MAPbI₃ dominated perovskite films.

The use of hybrid perovskite based on mixed iodine and bromine halide in solar cells has shown a photovoltaic performance of 10.65% PCE. Compared to the cells based on mixed iodine and chlorine halide, the improved photovoltaic performance produced from MAPbI_{1.8}Br_{1.2} results from the good quality of perovskite films, leading to an efficient separation of the generated charges and improved charge carrier transport.

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