



## Research article

## Structural changes and band gap tunability with incorporation of n-butylammonium iodide in perovskite thin film



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## ABSTRACT

The current work presents structural change and band gap tunability using hybrid organic-inorganic perovskite with the incorporation of long chain ammonium halide. Thin films of MAPbI<sub>3</sub> with different ratio of n-butylammonium iodide (BAI) have been successfully deposited on the substrate using a single step coating technique. X-ray diffraction scans revealed the transition of the 3D structure of MAPbI<sub>3</sub> to quasi-2D perovskite structure when BAI loading increase with a crystallite size range approximately 16 nm. This structural change reflected in the band gap as it increased from 1.59 eV for bulk crystal MAPbI<sub>3</sub> to 2.13 eV for BAI and MAPbI<sub>3</sub> ratio of 1:1. Correspondingly, photoluminescence measurement showed a blue shift in perovskite emission due to the transition of 3D to 2D layered structure perovskite. Raman spectra confirm that all fabricated films are of pristine quality and no corresponding degradation peaks of PbI<sub>2</sub> is observed. These characteristics are important to address the single step deposition method of hybrid perovskite for perovskite solar cells application.

## 1. Introduction

Hybrid organometal halide perovskite solar cells (PSCs) have been extensively studied due to their remarkable power conversion efficiency (PCE), low cost and facile fabrication process [1]. Methylammonium lead iodide (MAPbI<sub>3</sub>) is one of the intensely studied perovskite composition for application in photovoltaic but plague with issues such as moisture, UV and heat [2]. These affect the chemical stability of the PSCs and hinders the performance. Variety of approaches have been explored by implementing larger cation constituents to reduce the dimensionality of hybrid perovskite and maintaining better moisture stability [3, 4]. These types of constituents were able to create confinement within the perovskite structure and increase the band gap of the perovskite. Currently, large cation constituents such as butylammonium iodide (BAI) are employed to create low dimensionality perovskite [5]. BAI has longer organic chain compare to methylammonium iodide (MAI) which this organic chain acts as a spacer between crystal phases. However, the introduction of BAI produces low device performance defects due to charge transport. Therefore, systematic studies should be realized to explicate the structural and optical properties of the constituents

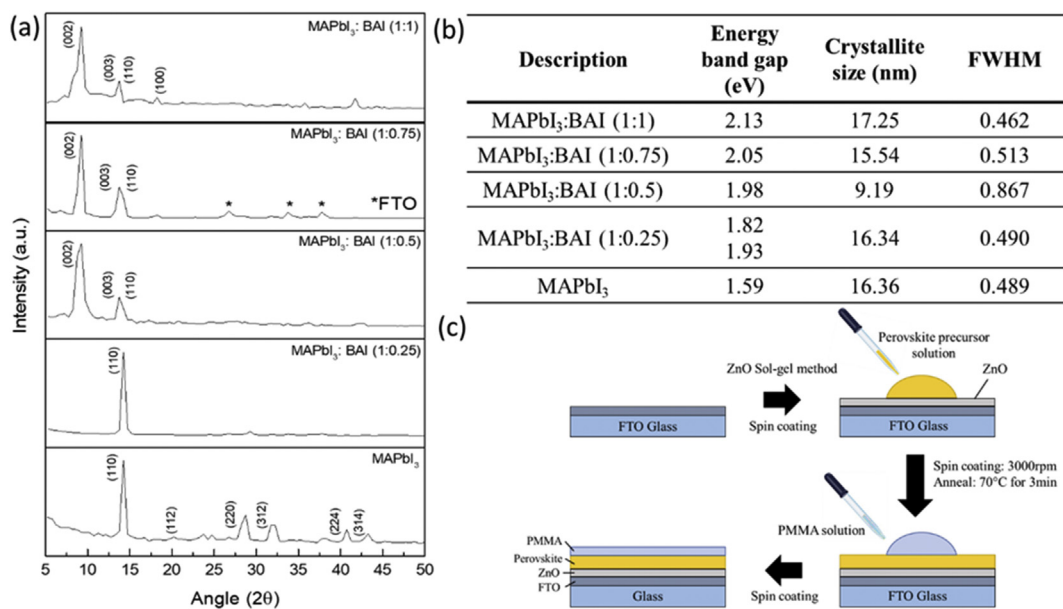
produced from the composition of MAPbI<sub>3</sub> and BAI. Herein, we report morphological and optical properties of MAPbI<sub>3</sub> perovskite film incorporated with BAI in the volumetric ratio through single step spin coating technique.

## 2. Experimental

ZnO coated substrate was prepared using pre-cleaned FTO substrates according to previous studies [6]. Lead iodide (PbI<sub>2</sub>), methyl ammonium iodide (MAI) and BAI were dissolved in N,N-Dimethyl formamide (DMF) at a concentration of 0.5M. The perovskite precursor solution is prepared through volumetric mixing of the stock solution in an inert environment with <1% relative humidity and <200ppm oxygen [7]. The solution was then spin coated at 3000 rpm on the substrate. Overall experimental setup is shown in Figure 1(c). The observed film thickness is approximately 700 nm, as determined through cross-sectional SEM. Poly(methyl methacrylate) PMMA is then mixed with chlorobenzene (10 mg/mL) and deposited on top of the perovskite. Zeiss Supra 55VP FESEM was used to collect images at an accelerating voltage of 15 kV. X-ray diffraction was measured using a Panalytical Empyrean X-ray diffractometer with a step

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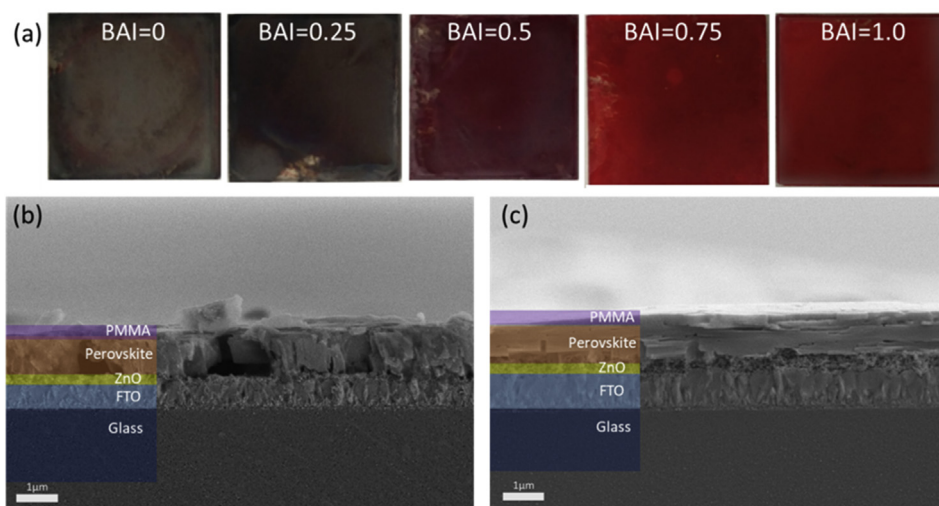
**Figure 1.** (a) XRD spectra and (b) Energy band gap, FWHM and corresponding crystallite size with various BAI loading ratios (c) Experimental setup of one-step spin coating technique.

size of 0.05°. The optical properties of the perovskite film were characterized using Agilent Cary UV-VIS spectrophotometer and Horiba LabRAM HR Evolution for photoluminescence and Raman spectroscopy. All perovskite films were characterized in ambient air.

### 3. Results and discussion

XRD peaks observed at 14.2°, 20.3°, 28.7°, 31.9°, 40.7° and 43.3° are assigned to (110), (112), (220), (312), (224) and (314) crystal planes of MAPbI<sub>3</sub> perovskite structure. The MAPbI<sub>3</sub> film shows tetragonal crystalline perovskite phase which in good agreement with a previous report [8]. There is no obvious peak at 12.7° which means no crystallization of PbI<sub>2</sub> phase (JCPDS No. 07-0235) is observed. Figure 1(a) shows diffraction peaks corresponding to layered perovskite grains for BAI molar ratio 1:0.25 which represented by diminished significant (220), (312), (224) and (314) crystal planes. As BAI ratio is increased to more than 1:0.25, a peak at 9.25° is observed while the intensity of MAPbI<sub>3</sub> characteristic (110) peak at 14.2° decrease indicating the structural

change from 3D to 2D layered perovskite structure. Subsequently, at a ratio of 1:1, XRD peaks show more periodicity and (110) peak diminished, attributed to the formation of layered 2D structure. This corresponds with the observed blue shift in excitonic absorption peak as shown in Figure 3(a). It should also be noted that the full width at half maximum (FWHM) of the diffraction peaks increases with the addition of BAI, signifying a decrease in crystallite size. The average crystallite size of MAPbI<sub>3</sub> is shown in Figure 1 (b) and in good agreement with reported literature [9]. The crystallite size increases with the increment of BAI loading more than 1:0.5. This shows that loadings beyond this threshold values, BAI does not act as a surfactant or impede crystal growth but rather assist in film crystallization thus grain size increase during transition. In addition, there is a competition between the larger BA cation and MA cation. The BA cation confines perovskite crystal to grow within the planar layer whereas MA cation expands the growth outside the planar layer [4]. Therefore, incorporation of BAI in precursor solution impedes the growth of 3D grains during film formation process thus result in smaller grain size of perovskite film as result in reduced in



**Figure 2.** (a) Physical images of perovskite thin film with different BAI loading ratio (b) Cross sectional image of MAPbI<sub>3</sub> (c) Cross sectional image of MAPbI<sub>3</sub>:BAI (1:1).

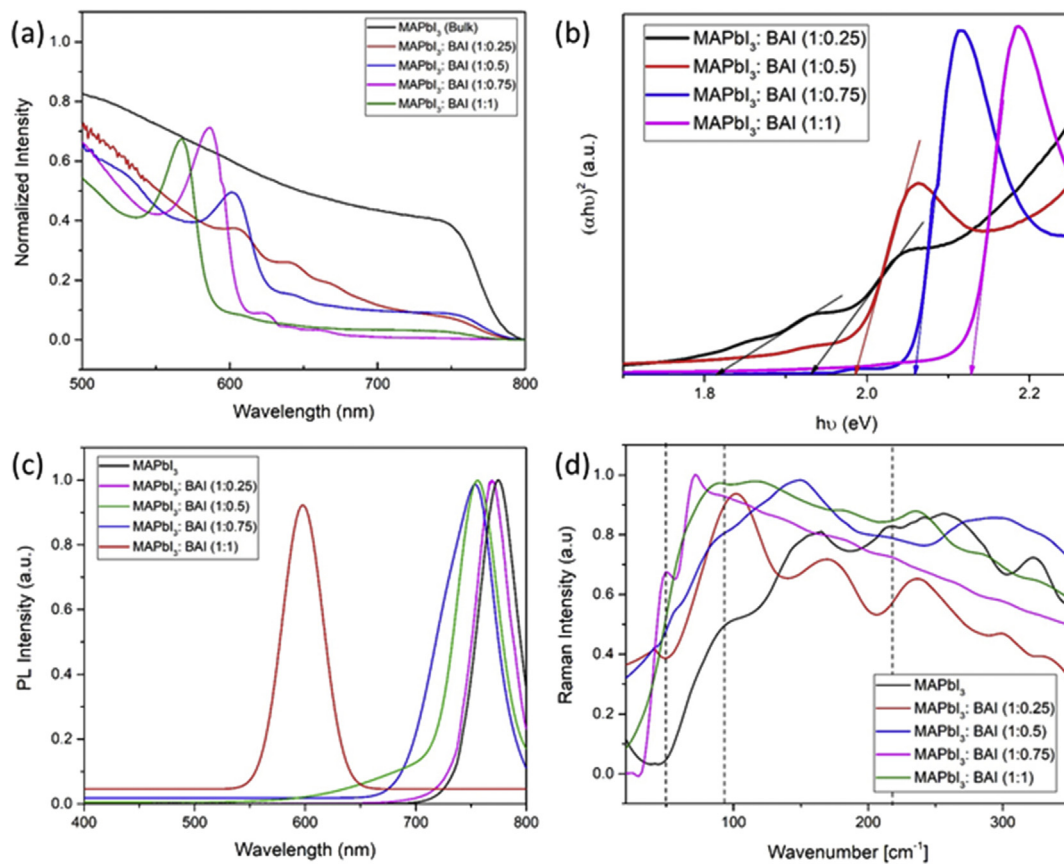


Figure 3. MAPbI<sub>3</sub> thin film with different BAI ratio (a) Absorbance spectra (b) Tauc plot (c) PL spectra (d) Raman spectra.

crystallite size at ratio 1:0.5. Bulk crystals characteristic of MAPbI<sub>3</sub> form voids in between grains can be observed from cross section FESEM image in Figure 2 (b) while compact structure is formed for the ratio 1:1. Interestingly, the structural changes from 3D to 2D can be seen with the change in thin film colors from black to reddish.

Figure 3 (a)–(b) shows the absorbance spectra and Tauc plot of increasing BAI in the precursor solution. Generally, the absorbance spectra show a blue shift with increment in BAI loading in the perovskite precursor solution. This is reflected in the steady increment in bandgap value from 1.59 to 2.13 eV. The blue shift of the absorption edge is due to the transition of the bulk 3D perovskite crystallite to the 2D layered structure. Larger cation size of BA present in the precursor induce a disordering effect towards the lattice periodicity of the material [5]. When BAI ratio increases further than 1:0.25, layered perovskite grains with excitonic absorption form, causing a significant blue shift. The onset absorption band decrease from 780 nm to 582 nm wavelength which corresponding to optical band gap at 1.59 eV and 2.13 eV respectively as BAI loading increase. Due to the transitional of bulk to layered perovskite structure present in ratio 1:0.25, Tauc plot thus present two bandgaps at 1.82 eV and 1.93 eV. Subsequently, Figure 3(c) shows the photoluminescence properties of different composition of BAI in MAPbI<sub>3</sub>. As BAI increase in the mixture of precursor solution, PL peak of BAI: MAPbI<sub>3</sub> films gradually blue-shifted from 0:1 to 0.75:1. Above ratio of 0.75:1, PL peak further blue-shift to lower wavelength of 598 nm. This also can be observed through the physical image of the fabricated perovskite thin film as shown in Figure 2(a). The perovskite thin film change from dark brown colour to light brick red colour as BAI loading increase in precursor solution. This is due to the reduced crystal dimensionality structure of bulk perovskite crystal of MAPbI<sub>3</sub> to layered perovskite grains which are corresponding to respective absorption spectra and XRD results. The introduction of BAI into MAPbI<sub>3</sub> Raman spectra is shown in

Figure 3(d). For ratio 1:0.25, the band peak observed are near to degradation peak represented by Pb-I stretching at 101 cm<sup>-1</sup> and 237 cm<sup>-1</sup> whereas for the ratio of 1:0.5 had a broad peak around 100 cm<sup>-1</sup> to 200 cm<sup>-1</sup> and around 280 cm<sup>-1</sup> which is assigned to librational modes and torsional mode of organic cations respectively. As BAI loading increased, significant sharp peak band around 62 cm<sup>-1</sup> is observed for BAI: MAPbI<sub>3</sub> (1:0.75) which is attributed to I-Pb-I bending and Pb-I stretching of the inorganic component in the crystal. Broad peaks located at 204 cm<sup>-1</sup> and 250 cm<sup>-1</sup> are weakly attributed to the vibrational modes of MAPbI<sub>3</sub> due to the torsional mode of the organic cation present in the crystal. These results are in good agreement with Quarti et al. [10] and Pistor et al. [11] which investigated theoretical and experimental analysis on MAPbI<sub>3</sub> based on Raman spectroscopy. Therefore, Raman analysis showed there are no significant sharp and broad peaks at 94 cm<sup>-1</sup> and 250 cm<sup>-1</sup> which represent PbI<sub>2</sub> produced in the thin film.

#### 4. Conclusion

Overall, incorporation of n-butylammonium iodide (BAI) into bulk crystal MAPbI<sub>3</sub> through volumetric ratio mixing prepared using one-step spin coating technique had been successfully investigated. The constituent of MAPbI<sub>3</sub>: BAI has colour tunability wavelength between 600 till 750 nm as the ratio of BAI increased. This is due to the smaller crystallite size present in the thin film with the introduction of long chain ammonium halide cation, BAI. Thus, BAI is the cause of MAPbI<sub>3</sub> bulk crystal growth towards lower dimensional perovskite structure acting as a surfactant layering perovskite sheets. Therefore, the reported method is promising for low cost thin film solar cells due to its tunable one step spin-coating synthesis method for bandgap between 1.59–2.13 eV.

## Declarations

### Author contribution statement

Leong Wei Xian Rebecca: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Zainal Arif Burhanudin, Mundzir Abdullah: Analyzed and interpreted the data.

Mohamed Shuaib Mohamed Saheed: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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