Ab-Initio Computations of Electronic Structures of Methylammonium Lead Bromide/Iodide Perovskites as Wide Bandgap Active Materials in Solar Cells

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Abstract. Studies on the electronic structure of organo-lead halide perovskites have been much investigated in the last few years, as solar cells based on this novel materials exhibit high power conversion efficiency. In order to improve the chemical stability and vary the bandgap, for developing a solar cell with bulk heterojunction, the modification of this perovskite with hetero halide ions structure has also been investigated. We report here the electronic structure of Methylammonium lead bromide/iodide or MAPb(BrxI3-x)3 at different contents of bromide ions investigated by an ab-initio computation based on Density Functional Theory (DFT) using Quantum Espresso. The calculated results show the increment of bands gap with increasing bromide ion concentration. The obtained Densities of States show that the addition of bromide ions plays an important role in constructing their valence band, where it is predominated by the electrons at the outermost orbital of these halide (Br ˗ and I ˗) ions. On the other hand, the conduction band is still predominated by the 6p orbitals of the Pb 2+ ions, in agreement with some reports elsewhere. The organic molecule orbitals, however, seems to give insignificant influence to those valence and conduction bands.

1. Introduction
Development in perovskite solar cells has shown a rapid progress within the last few years after the reports by Snaith and Gratzel groups. [1,2] Inspired by more than 10 % efficiencies performed by the single layer architecture, some researchers are developing perovskite solar cell with tandem and heterostructure layer structure, by combining low and wide bandgap active materials, in order to obtain even higher power conversion efficiency [3,4]. One of the most promising wide bandgap active materials is methylammonium lead bromide/iodide (CH3NH3Pb(BrxI3-x)), or shortly MAPb(BrxI3-x)). To the best of authors’ knowledge, the highest achieved efficiency was just still about 13.7% for this perovskite solar cell [5]. However, it has also been reported that perovskite with such hetero halide ions shows better chemical stability. However, because the most effective method for preparing these materials is by the wet chemical process, there is still remaining a question on the produced crystal structure of this MAPb(BrxI3-x)). There are two possible products where the first possibility produces a blend of
nanocrystals of MAPbBr$_3$ and MAPbI$_3$ at a certain ratio, producing a bulk heterojunction layer. The second possibility is nanocrystals of MAPb(BrxI$_{3-x}$)$_3$ which are formed by interstitial replacements of I anions by Br anions. As we are more concern on the second possible structure, it is necessary to know whether such structure may also exhibit an electronic structure with semiconductor characteristics, that is composed of a conduction band and valence band separated by an energy gap. We may then suppose that the energy gap will be dependent on the ratio of the number of Br anions with respect to the numbers of I anion inside a unit cell. We hereby report our ab-initio computation results based on the density functional theory (DFT) method for this perovskite by varying the content ratio of Br anions.

2. Computational Details
The computations were performed by using Quantum Espresso software package which are built based on the DFT method. Generalized Gradients Approximations (GGA) and Ultrasoft Pseudopotentials (US PPs) were applied. Scalar relativistic exchange-correlation functionals constructed by Perdew-Burke-Ernzerhof (PBE) were applied to each constituent atom. Hence, the valence orbitals comprised of 2s and 2p of C, 1s of H, 2s, and 2p of N, 5d, 6s, and 6p of Pb, 4s and 4p Br, 5s and 5p of I are included. There are four different crystals of MAPb(BrxI$_{3-x}$)$_3$ that have been investigated, namely for $x=0, 0.33, 0.67$ and 1. The details are presented in Table 1.

The kinetic energy cut-offs for each wave-functions were limited to 40 Ry to attain precise yet plausible computation cost. For the same reason, the Brillouin zones were divided by Monckhorst Pack $k$-mesh with $4\times4\times3$ grid in the case of MAPbI$_3$ (or shortly MAPI). More details of this structure can be found in our previous report [6]. Other current investigated structures (see table 1) were reported to have cubic structures [7]. Thus, a homogenous Monchhorst Pack $k$-mesh grid of $3\times3\times3$ was chosen. The chosen grids were applied for both structure optimizations and electronic structure calculations.

Due to the presence of Pb atoms in the crystal structures, a smearing type of Methfessel-Paxton was employed [7]. The declared lattice constants were extracted from experimental results reported by other groups [8-10]. A pre-optimization of organic molecules’ position was performed by applying DFT method with B3LYP (Becke, three parameters, Lee-Yang-Parr) exchange-correlation functional [11]. The unit cell of each crystal structure is depicted in Figure 1 and their initial lattice parameters are shown in Table 1.

![Figure 1](image1.png)

Figure 1. Crystal structures of MAPb(BrxI$_{3-x}$)$_3$ crystals investigated here. The x-values represent the ratio content of Br/I atom in the MAPb(BrxI$_{3-x}$)$_3$ crystals.

3. Results and Discussion
The unit cell volume after relaxation and the total energy of each system is depicted in Table 2. From Table 2, one can see that the unit cell volume decreases by increasing the ratio of Br anion. The least total energy value was performed in the MAPI calculation. Although the choice of using MAPI as active materials for perovskite solar application is still facing the chemical stability issue,
this material shows the best crystal structure stability compared to the wider band gap methylammonium lead bromide/iodide alternatives [12-13].

Table 1. Crystal structures and lattice parameters of each computed unit crystal.

| Crystal Structure | Lattice Parameter (Å) |
|-------------------|-----------------------|
| MAPI [6]          | Pseudocubic           |
|                   | a=6.2621, c=6.3275    |
| MAPI2Br(x=0.33) [9]| Cubic                |
|                   | 6.18                  |
| MAPIBr2(x=0.67) [9]| Cubic                |
|                   | 6.07                  |
| MAPBr3 [10]       | Cubic                |
|                   | 5.90                  |

Table 2 shows the bandgaps values obtained in this work in comparison to the result by Noh et al., where the energy gap was formulated as $E_g(x) = 1.57 + 0.39x + 0.33x^2$, where $x$ is the ratio of Br anions compared to the I anions. Lower values obtained here are due to the application of generalized gradient approximation (GGA) as the exchange-correlation functional [8]. However, one can still see that the obtained bandgap increases as the Br anion numbers increases. As reported by Hao et al. in the case of CH3NH3Sn3-xI, the increase of bandgap was found also as the
consequence of Br anions addition in our results can be explained by the higher total energy computed [14].

Table 2. Computational results.

|                | Volume (Å³) | Total Energy (eV) | Obtained Bandgap (eV) | Theoretical Bandgap (eV) |
|----------------|-------------|-------------------|-----------------------|--------------------------|
| MAPI           | 248.126     | -363.087          | 1.232                 | 1.570                    |
| MAPI\textsubscript{1}Br(x=0.33) | 236.029 | -338.078          | 1.266                 | 1.734                    |
| MAPI\textsubscript{1}Br\textsubscript{2}(x=0.67) | 223.648 | -313.058          | 1.428                 | 1.980                    |
| MAPBr\textsubscript{3} | 205.379 | -288.049          | 1.636                 | 2.290                    |

Figure 3. PDOS of (a) MAPI, (b) MAPI\textsubscript{1}Br\textsubscript{2}, (c) MAPI\textsubscript{1}Br\textsubscript{2}, and (d) MAPBr\textsubscript{3}

As shown in Figure 2, MAPI configuration shows a direct bandgap at the A high symmetry point while the rests are at the R high symmetry point. Both the tops of valence and conduction bands of each configuration are quite broad, indicating that the electrons are non-localized. The broadness of valence and conduction bands have been reported as the origin of long exciton diffusion in these perovskites.
Accordingly, the combination of bromide/iodide can increase the exciton transport distance in comparison to that of MAPI due to the broader bands. Besides, the bottoms of conduction bands fluctuate significantly, with MAPI as the most fluctuate. This fact explains the experimental observation of fast photoelectrons transport, where MAPI exhibit the fastest transport speed [15].

The projected densities of states (PDOS) of each configuration are presented in Figure 3. The valence is predominantly constructed by the outermost orbitals of both halide ions (4p Br⁻ and 5p I⁻). On the other hand, the conduction band is predominantly constructed by the 6p orbital of the Pb²⁺ ions, as reported elsewhere. The contribution of organic molecule orbitals in both valence and conduction bands are very minor, as also shown in our previous report [6].

4. Conclusions

In summary, our computational results show that the bandgap energy of methylammonium lead bromide/iodide (MAPb(BrₓI₃₋ₓ)₃) enlarge with the increase of Br⁻ concentration as the results of the increase in total energy. However, the energy gap does not increase linearly with the content of Br⁻. All configurations exhibit non-localized electrons in both valence and conduction bands. Meanwhile, the PDOS graphs show that the outermost orbitals of halide (Br⁻ and I⁻) ions and Pb²⁺ 6p predominantly contribute to the valence and conduction bands, respectively. The organic molecule orbitals contributions to those bands are very minor.

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